Designation: D 5075 – 96ε1

An American National Standard

Standard Test Method for Nicotine and 3-Ethenylpyridine in Indoor Air[1]

This standard is issued under the fixed designation D 5075; 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.

ε[1] NOTE—The Keywords section was added editorially in November 1996.

1. Scope

1.1 This test method covers the sampling/analysis of nicotine and 3-ethenylpyridine (3-EP) in indoor air. This test method is based upon the collection of nicotine and 3-EP by adsorption on a sorbent resin, extraction of nicotine and 3-EP from the sorbent resin, and determination by gas chromatography (GC) with nitrogen selective detection. **(1)**[2]

1.2 The active samplers consist of an XAD-4 sorbent tube attached to a sampling pump. This test method is applicable to personal or area sampling.

1.3 This test method is limited in sample duration by the capacity of the XAD-4 tube for nicotine (about 300 µg). This test method has been evaluated up to 24-h sample duration; however, samples are typically acquired for *at least* 1 h (sometimes *only* 1 h). **(2)**

1.4 For this test method, limits of detection (LOD) and quantitation (LOQ) for nicotine at a sampling rate of 1.5 L/min are, respectively, 0.11 µg/m^3 and 0.37 µg/m^3 for 1-h sample duration and 0.01 µg/m^3 and 0.05 µg/m^3 for 8-h sample duration. The LOD and LOQ for 3-EP at a sampling rate of 1.5 L/min are, respectively, 0.06 µg/m^3 and 0.19 µg/m^3 for 1-h sample duration and 0.01 µg/m^3 and 0.02 µg/m^3 for 8-h sample duration **(2)**. Both LOD and LOQ can be reduced by increasing the sensitivity of the thermionicspecific detector.

1.5 The values stated in SI units are to be regarded as standard.

1.6 *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.* Specific precautionary information is given in 13.6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[3]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[3]

D 3631 Test Methods for Measuring Surface Atmospheric Pressure[3]

D 5337 Practice for Flow Rate for Calibration of Personal Sampling Pumps[3]

E 260 Practice for Packed Column Gas Chromatography[4]

E 355 Practice for Gas Chromatography Terms and Relationships[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1356 and Practice E 355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *environmental tobacco smoke (ETS)*—an aged, dilute composite of exhaled tobacco smoke and smoke from tobacco products.

3.2.2 *nitrogen-phosphorus detector (NPD)*—a highly sensitive device selective for detection of nitrogen- and phosphorus-containing organic compounds.

3.2.3 *XAD-4 resin*—macroreticular polystyrene-divinylbenzene copolymer beads.

4. Summary of Test Method

4.1 A known volume of air is drawn through a sorbent sampling tube containing XAD-4 resin to absorb the nicotine and 3-EP present.

4.2 The XAD-4 sorbent tube contents are transferred to a 2-mL autosampler vial, and the nicotine and 3-EP are desorbed with ethyl acetate containing 0.01 % triethylamine and a known quantity of quinoline, the internal standard.

4.3 An aliquot of the desorbed sample is injected into a gas chromatograph equipped with a thermionic-specific (nitrogen-phosphorus) detector.

4.4 The areas of the resulting nicotine and 3-EP peaks are each divided by the area of the internal standard peak and compared with area ratios obtained from the injection of standards.

[1] This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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[2] The boldface numbers in parentheses refer to a list of references at the end of the text.

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

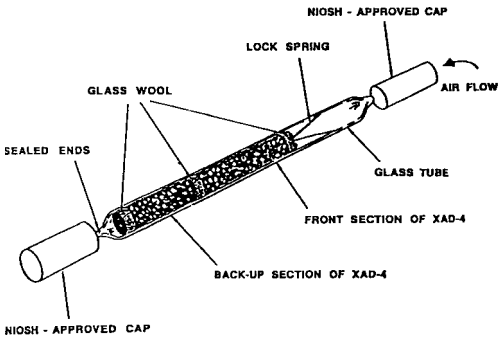

FIG. 1 1 XAD-4 Sorbent Tube

5. Significance and Use

5.1 In order to estimate ETS concentrations, there needs to be a marker or tracer for ETS that is unique or highly specific to tobacco smoke, in sufficient concentrations in air to be measured easily at realistic smoking rates, and in constant proportion to the other components of ETS for a variety of tobacco blends and environmental conditions. Nicotine and 3-Ethenylpyridine have been used as tracers of the vapor phase of ETS. Nicotine is the major alkaloid of tobacco and a major constituent of ETS. The determination of nicotine concentration has often been used to estimate the concentration of ETS; however, due to its unpredictable decay kinetics, nicotine may not be an ideal tracer. Because nicotine readily adsorbs to building materials and room furnishings and is depleted from ETS at a rate faster than most other components, some have suggested that nicotine concentrations underestimate ETS concentrations. Although this is true in many environments during the generation of smoke, the converse is true in environments with a recent past history of smoking. The adsorbed nicotine slowly desorbs over time, resulting in an overestimation of ETS concentrations. Thus, measured concentrations of nicotine precisely assess only airborne nicotine and indicate only that smoking has taken place; they do not necessarily indicate the presence, and certainly not the concentrations, of other ETS constituents. 3-Ethenylpyridine, on the other hand, has been shown to track exactly the vapor phase of ETS as measured by CO and FID response **(3)**. It is for these reasons that 3-ethenylpyridine may be a better tracer of ETS **(1,4,5)**. The ETS at high concentrations is known to be annoying and irritating to individuals, and concerns over potential health effects have also been expressed. There is a definite need to have reliable methods for the estimation of ETS levels in order to evaluate its effect. The NIOSH has previously set a threshold limit value (TLV) for nicotine in the workplace of 0.5 mg/m^3.

5.2 Studies show that more than 90 % of nicotine in indoor air is found in the vapor phase **(6,7)**. The described test method collects vapor-phase nicotine quantitatively. Early studies on freshly generated ETS indicated that some but not all of the particulate phase was trapped on the XAD-4 resin **(7).** A more recent investigation of the trapping of particulate materials by sorbent beds suggests that the trapping of the particles from indoor air may be nearly quantitative **(8)**. 3-Ethenylpyridine is found exclusively in the vapor phase.

5.3 Nicotine concentrations typically range from ND (not detected) to 70 µg/m^3 in various indoor environments with values usually at the lower end of this range **(9)**. Because such low concentrations of nicotine are often encountered, sophisticated analytical procedures and equipment are required for quantifying nicotine in indoor air. Other methods for the determination of nicotine in indoor air have also been reported **(6,10,11,12)**. 3-Ethenylpyridine concentrations typically are about one third the concentrations of nicotine in real-world environments **(13)**.

6. Interferences

6.1 Use of packed GC columns may result in readings lower than expected because nicotine can adsorb onto undeactivated glass, metal, and solid support particles. Fused silica capillary columns and the modified extraction solvent prescribed here can circumvent this problem.

6.2 Quinoline (internal standard) is present in ETS at a concentration approximately 1 % of that for nicotine and is collected by the XAD-4 resin. If >10 µg nicotine is collected on the resin, there will be sufficient quinoline present to cause a detectable bias in results (approximately 1 %). (For example, this quantity of nicotine would be collected if a nicotine concentration of 167 µg/m^3 was sampled at 1 L/min for 1 h.) In these cases, one of the following alternative procedures should be followed:

6.2.1 Quantitatively dilute the sample with the same modified solvent containing internal standard (described in 11.2) used to extract the original sample; that is, decrease the amount of quinoline (and also nicotine) present in the sample while keeping the quinoline concentration in the solvent constant. To prevent significant interference, the nicotine concentration in the most concentrated sample should be less than or equal to the quinoline concentration in the solvent.

6.2.2 Use an alternate internal standard [N′-ethylnornicotine is recommended **(14)**].

7. Apparatus

7.1 *Sample Collection*:

7.1.1 *XAD-4 Sorbent Tube*, see Fig. 1.

7.1.2 *XAD-4 Sorbent Tube*[5]—Glass tube with both ends flame-sealed, approximately 7 cm long with 6-mm outside diameter and 4-mm inside diameter, containing two sections of 20/40 mesh XAD-4 resin. The front section contains 80 mg of resin, the backup section contains 40 mg of resin. A glass wool plug is located at each end of the tube and between the front and backup sections. The front plug is held in place with a metal lockspring (see Fig. 1).

7.1.3 *Tube Holder*,[6] with clip attachment for attaching tube to clothing or objects.

7.1.4 *Tube Breaker*,[7] to break sealed ends from sample tubes.

7.1.5 *NIOSH-approved Plastic Caps*, for capping tubes after sampling.

[5] XAD-4 sorbent tubes for nicotine and 3-EP, Cat. No. 226-93, available from SKC, Inc., 863 Valley View Rd., Eighty Four, PA 15330-9614, or equivalent, have been found suitable for this purpose.

[6] Tube holders available from SKC, Inc., Cat. No. 222-3-1, or equivalent, have been found suitable for this purpose.

[7] Tube breaker, Cat. No. 2-0596, available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, or equivalent, has been found suitable for this purpose.

7.1.6 *Barometer and Thermometer*, for taking pressure and temperature readings at the sampling site (optional).

7.1.7 *Bubble Flowmeter*,[8] for sample pump calibration.

7.1.8 *Personal Sampling Pump*,[9] portable constant-flow sampling pump calibrated for the flow rate desired (up to 1.5 L/min).

7.2 *Analytical System*:

7.2.1 *Gas Chromatograph*, with a nitrogen-phosphorus (thermionic) detector[10] and autosampler.[11]

7.2.2 *GC Column*[12]—A 30-m by 0.32-mm inside diameter fused silica capillary column, coated with a 1.0-µm film of 5 % phenyl methylpolysiloxane (DB-5).

7.2.3 *Chromatography Data Acquisition System*,[13] for measuring peak areas electronically.

7.2.4 *Sample Containers*, borosilicate glass autosampler vials, 2-mL capacity, with PTFE-lined septum closures.

7.2.5 *Dispensing Pipets*, 1.25-mL.

7.2.6 *Triangular File*, for scoring and breaking open sample tubes.

7.2.7 *Forceps*, for assisting transfer of sorbent tube contents from tube to autosampler vial.

7.2.8 *Glass Wool Removal Tool*,[14] for assisting transfer of sorbent tube contents from tube to autosampler vial.

7.2.9 *Wrist-action Shaking Device*, for solvent extraction.

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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[15] 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 *Ethyl Acetate*, chromatographic quality.

8.3 *Quinoline (internal standard)*, 99+ %.

8.4 *Triethylamine*, 99+ %.

8.5 *Nicotine*, 99+ %.

8.6 *4-Ethenylpyridine (4-EP)*, 95 %, commercially available isomer of 3-ethenylpyridine.

8.7 *Helium Cylinders*, for carrier or detector makeup gas, or both, 99.995 % grade.

8.8 *Hydrogen Cylinders*, for detector gas, 99.995 % grade.

8.9 *Air*, for detector gas (<0.1 ppm hydrocarbon).

9. Sampling

9.1 *General*—For planning sampling programs, refer to Practice D 1357.

9.2 *Procedure*:

9.2.1 Prepare XAD-4 sampling tubes immediately before sampling. Break both ends of the sealed sorbent tube using a tube breaker tool. The opening should measure at least 2 mm in diameter.

9.2.2 Connect the sorbent tube to the personal sampling pump with tubing. Position the sorbent tube so that the air being sampled will pass first through the front section of resin and then through the backup section. The inlet end of the tube is exposed directly to the atmosphere, and the outlet end is inserted in the tubing; or the tube itself is put into a safety casing in the personal sampling setup and attached accordingly. Adjust the potentiometer on the sampling pump until the desired flow rate (≤1.5 L/min) is obtained. With the bubble flowmeter connected to the inlet end of the sorbent tube, measure and record the rate of airflow through the sorbent tube in litres per minute. Refer to Practice D 5337 for standard practice in calibrating personal sampling pumps.

9.2.3 After the XAD-4 sorbent tube is correctly inserted and positioned, turn on the power switch for the pump to begin sampling. Record the start time.

NOTE 1—Most pumps have microprocessing capabilities for preset sampling periods.

9.2.4 Record the barometric pressure and ambient temperature (optional).

9.2.5 Turn off the pump at the end of the desired sampling period, and record the elapsed time in minutes.

9.2.6 Measure and record the flow rate after sampling so that an average of initial and final flow rates can be used in subsequent calculations.

9.2.7 Remove the sorbent tube from the sampling system and place plastic caps over both ends of the tube.

9.2.8 Treat a minimum of two sorbent tubes in the same manner as the sample tubes (break, measure flows, cap, and transport). Label and process these tubes as flow blanks.

9.2.9 Transport capped sorbent tubes to the laboratory for analysis.

NOTE 2—If the samples are not prepared and analyzed immediately, they should be stored at 0°C or less. All sorbent tube samples should be analyzed within eight weeks after sample collection. It has been established that samples are stable for at least eight weeks at −10°C.

10. Analysis

10.1 *System Description*:

10.1.1 Analysis is performed using a GC fitted with a nitrogen-phosphorus detector and an autosampler equipped for split/splitless injection.

10.1.2 The GC column is as listed in 7.2.2.

[8] The Gilibrator primary standard airflow calibrator manufactured by Gilian Instrument Corp., 35 Fairfield Place, W. Caldwell, NJ 07006-6206, or equivalent, has been found suitable for this purpose.

[9] Personal sampling pump available from SKC, Inc., Model No. 224-50, or equivalent, has been found suitable for this purpose.

[10] GC system, Model 5890, available from Hewlett-Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610, or equivalent, has been found suitable for this purpose.

[11] Autosampler available from Hewlett-Packard Co., Model 7673A, or equivalent, has been found suitable for this purpose.

[12] GC column, Cat. No. 123-5033, available from J and W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630-4714, or equivalent, has been found suitable for this purpose.

[13] Chromatography data acquisition system, MULTICHROM Version 2, available from VG Instruments, 32 Commerce Ctr., Cherry Hill Dr., Danvers, MA 01923-9896, or equivalent, has been found suitable for this purpose.

[14] Puller/Inserter tool available from Supelco, Inc., Cat. No. 2-2406, or equivalent, has been found suitable for this purpose.

[15] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, 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 and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

10.1.3 The GC conditions are as listed in Table 1.

10.1.4 The autosampler uses default settings for the injection sequence, and 1 or 2 µL of sample is injected with a 30-s splitless period.

10.1.5 Peak areas are measured electronically with a chromatography data acquisition system.

10.2 *Systems Performance Criteria*:

10.2.1 Approximate retention times for 3-EP, 4-EP, quinoline, and nicotine are listed in Table 1.

10.2.2 Desorption efficiency should be determined for each new lot of sorbent tubes. Failure to determine the desorption efficiency and adjust results may impair the accuracy of the test.

10.2.3 Breakthrough (>5 % of tube contents found in backup resin section) can occur after collecting approximately 300 µg nicotine in a single XAD-4 tube. A shorter sampling time is necessary if sample concentration and duration of sampling suggest a breakthrough occurrence.

11. Procedure

11.1 *XAD-4 Sorbent Tube Analysis*—The analytical procedure for nicotine and 3-EP is performed by extracting the XAD-4 resin with modified ethyl acetate solvent followed by GC/NPD analysis. Ethyl acetate extracts nicotine and 3-EP from the XAD-4 resin beads, but the solvent is modified with 0.01 % *v/v* triethylamine to prevent any adsorption of nicotine on the glass walls of the vials **(14)**. The solvent also contains the internal standard quinoline, at a concentration of approximately 7.5 µg/mL. Solvent henceforth will refer to this modified ethyl acetate solvent.

11.2 *Preparation of Modified Ethyl Acetate Solvent*:

11.2.1 To a previously unopened 4-L bottle of ethyl acetate, add 0.5 mL triethylamine and 30 µL quinoline. Shake vigorously to mix.

11.2.1.1 To a separate freshly opened 4-L bottle of ethyl acetate, add 0.5 mL triethylamine; shake vigorously to mix. Use modified solvent containing no internal standard only when specifically called for in the procedure.

TABLE 1 Summary of Gas Chromatograph Conditions

Temperatures	
Injector	225°C
Oven	
Initial temperature	50°C
Hold time	1 min
Program Step 1	
Rate	10°C/min
Final temperature	215°C
Hold time	0 min
Program Step 2	
Rate	20°C/min
Final temperature	275°C
Hold time	2 min
Detector	300°C
Gas flows	
He, carrier	4 mL/min (15 psig)
H_2, detector	3 mL/min
Air, detector	75 mL/min
He, makeup	15 mL/min
Retention times	
3-EP, 4-EP	8.5 min
Quinoline	13.5 min
Nicotine	15 min

11.2.2 Store the modified ethyl acetate solvent containing quinoline at 4°C or less when not in use. Allow the solvent to reach room temperature before using it to prepare standard solutions or samples.

11.2.3 Prepare fresh modified solvent as needed. Deterioration of the modified solvent has not been observed, and no definitive time interval has been established for its replacement; however, storage and use for more than 12 months is not recommended.

NOTE 3—In order to keep the amount of internal standard constant for both standards and samples, the same batch of modified solvent that is used to prepare standard solutions must be used to extract samples. Therefore, whenever a new batch of modified solvent is prepared, a new batch of standard solutions must also be prepared. Otherwise, if standards and samples contain different amounts of internal standard, the exact amounts in both solutions must be known precisely, and the regression and equations in 11.6.1 and 12.1 must be modified to reflect the different internal standard concentrations.

11.3 *Preparation of Standard Solutions*:

11.3.1 Clean all volumetric flasks and screw-cap jars used for the preparation and storage of standard solutions with detergent,[16] thoroughly rinse with tap water followed by distilled water followed by ethyl acetate containing only 0.01 % triethylamine with no quinoline, and allow to air dry.

11.3.2 Prepare a primary standard of nicotine containing 400 µg/mL by weighing 100 mg of nicotine directly into a 250-mL volumetric flask, diluting to volume with solvent, and shaking to mix. Prepare a primary standard of 4-EP containing 500 µg/mL by weighing 100 mg of 4-EP into a 200-mL volumetric flask, diluting to volume with solvent, and shaking to mix. Prepare a secondary standard containing 4.8 µg/mL nicotine and 2.0 µg/mL 4-EP by transferring 3.0 mL of the primary nicotine standard and 1.0 mL of the primary 4-EP standard to a 250-mL volumetric flask, diluting to volume with solvent, and shaking to mix. Use the secondary standard as one of five calibration standards, and prepare the remaining four calibration standards from the secondary standard by transferring 30.0, 15.0, 6.0, and 2.0 mL of the secondary standard to each of four 100-mL volumetric flasks, diluting each to volume with solvent, and shaking each standard to mix. This provides a calibration range with the following concentrations of nicotine: 6.0, 1.80, 0.90, 0.36, and 0.12 µg/1.25 mL. The corresponding range for 4-EP is: 2.5, 0.75, 0.375, 0.15, and 0.05 µg/1.25 mL. These ranges typically cover the expected ranges of nicotine and 3-EP concentrations in the samples.

11.3.2.1 For the determination of desorption efficiency, prepare primary spiking standards of nicotine and 4-EP as described in 11.3.2, except dilute them in the ethyl acetate that contains only 0.01 % triethylamine and no quinoline. Then prepare a secondary spiking standard containing 9.6 µg/mL nicotine and 4.0 µg/mL 4-EP by transferring 6.0 mL and 2.0 mL of the primary nicotine and 4-EP spiking standards, respectively, to a 250-mL volumetric flask, also diluting with ethyl acetate containing only 0.01 % triethylamine and no quinoline, and shaking to mix. Use this secondary spiking standard in 11.7.2 for desorption efficiency determination.

[16] Micro, or equivalent, has been found suitable for this purpose.

11.3.3 Store all standards in borosilicate glass screw-cap jars at −10°C or less when not in use. Allow standards to reach room temperature and transfer approximately 1 mL of each of the five calibration standards to two 2-mL autosampler vials each day for instrument calibration. Cap and tightly seal the vials.

11.3.4 Prepare fresh secondary and calibration standards as needed. Prepare fresh primary standards from neat nicotine and 4-EP once every 6 months.

11.4 *Extraction/Desorption of XAD-4 Resin*:

11.4.1 In preparation for analysis, the analyst thoroughly washes his or her hands with soap and water immediately prior to handling the samples and refrains from smoking or otherwise contacting a known nicotine-containing environment until all samples and standards have been prepared and loaded in the autosampler tray.

11.4.2 Extraction/desorption of the XAD-4 requires transferring the contents of each sorbent tube to an autosampler vial for extraction. Prepare and analyze two previously unopened XAD-4 sorbent tubes as laboratory blanks. If sorbent tube samples have been stored frozen, allow them to equilibrate to room temperature before beginning the extraction procedure. Remove the plastic caps from the ends of each sorbent tube. To facilitate the transfer of the sorbent tube contents, widen the front and back openings of the tube by scoring the glass with a file and breaking. Use forceps and a glass wool removal tool to help transfer the entire contents of the tube (front and backup sections of resin; front, middle, and back plugs of glass wool; metal lockspring) to the autosampler vial.

NOTE 4—If the resin beads cling to the glass walls of the tube, push them out using the glass wool. If this does not work, flush them out of the tube with a stream of air.

NOTE 5—An alternate means of preparing the XAD-4 sorbent tubes is to transfer the front and backup sections of a tube to two separate autosampler vials. The front section is comprised of the front section of resin, the front plug of glass wool, and the metal lockspring; the backup section consists of the backup section of resin and the middle and back plugs of glass wool. This procedure should be used to confirm that there is no sample breakthrough from the front to the back section of the tube; that is, that no more than 5 % of sample is in the backup section. Once this is confirmed, it is not necessary to perform the dual analysis of the sorbent tube sample.

11.4.2.1 Label each vial. Add exactly 1.25 mL of solvent to each sample vial. Cap and tightly seal the vials and place them in a holding tray. After all samples have been prepared, transfer the tray to a wrist-action shaking device and extract under agitation for 30 min.

11.5 *Loading the Autosampler*:

11.5.1 Load one set of the five calibration standards at the beginning of the autosampler queue. Next, load all samples, flow blanks, and laboratory blanks. Load the second set of five calibration standards at the end of the autosampler queue.

NOTE 6—In the event that more than 40 sample vials are loaded after the first five standards, additional sets of standards should be loaded within the tray so that no more than 40 samples are analyzed between standards. Place the same number of samples before and after the middle set of calibration standards.

11.5.1.1 Load the autosampler with wash and waste vials. The wash vials should contain ethyl acetate with 0.01 % triethylamine and no quinoline. The operating conditions for the GC are listed in Table 1. Make one trial injection of the first calibration standard in the queue in order to verify correct operation of the GC in terms of peak location and detector sensitivity.

11.5.2 Obtain integrated peak areas and peak area ratios of analyte to quinoline for all standards, samples, and blanks by way of the chromatography data acquisition system. The peak area ratios of the samples and standards are compared, and concentrations of nicotine and 3-EP are calculated using the nicotine and 4-EP calibration curves. Fig. 2 shows a typical chromatogram from an ETS sample.

NOTE 7—Response factors for 3-EP and 4-EP have been determined to be equivalent **(15)**, and the two isomers have the same retention time and peak shape under the chromatographic conditions listed.

11.6 *Constructing the Calibration Curve*:

11.6.1 For the internal standard method of quantitation, two calibration curves are constructed: (*1*) a plot of the mean peak area ratio of nicotine to quinoline (*y*-axis) versus the concentration of nicotine (in µg/1.25 mL on the *x*-axis) in the calibration standards, and (*2*) a plot of the mean peak area ratio of 4-EP to quinoline (*y*-axis) versus the concentration of 4-EP (in µg/1.25 mL on the *x*-axis) in the standards. The data from each plot are then fit to a second-order polynomial regression model with $1/x$ weighting.

NOTE 8—Other regression models may be deemed more appropriate and, if so, may be used instead of the second-order regression. If other models are used, the appropriate regression equations must be substituted in the calculations in 12.1.

11.6.2 The correlation coefficients of the fitted lines are expected to be at least 0.990 for this test method. A significantly lower value indicates unusual scatter in the data points defining the calibration curve, and preparation and analysis of additional standards should be carried out.

11.7 *Determination of Desorption Efficiency*:

11.7.1 Determine the decimal fraction of nicotine and 4-EP recovered in the desorption process for every batch of XAD-4 sorbent tubes that are received.

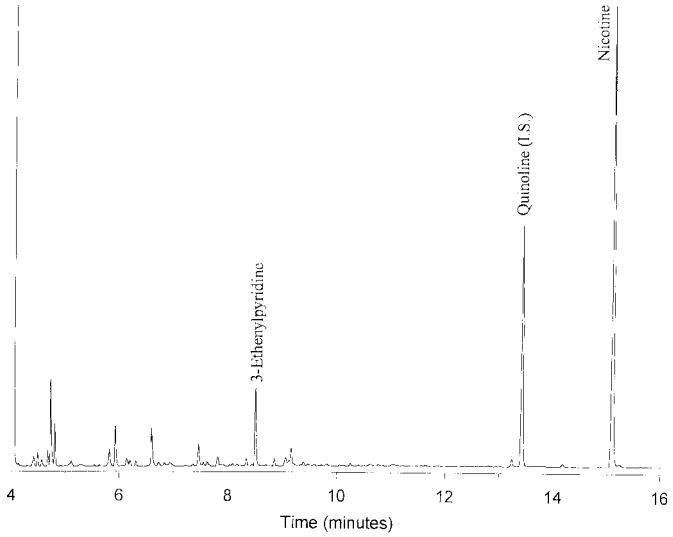

FIG. 2 Chromatogram of an Environmental Tobacco Smoke (ETS) Sample

11.7.2 Break open 20 XAD-4 sorbent tubes and transfer the XAD-4 resin constituting the front section of each tube together with the inlet glass wool plug and the metal lockspring to a 2-mL autosampler vial. Spike three sets of five vials by adding the secondary spiking standard prepared in 11.3.2.1 directly to the bed of resin in each vial. Add 10µ L (0.096 µg nicotine; 0.04 µg 4-EP) of the secondary spiking standard to each vial in the first set, 20 µL (0.192 µg nicotine; 0.08 µg 4-EP) to each vial in the second set, and 50 µL (0.48 µg nicotine; 0.20 µg 4-EP) to each vial in the third set. The remaining set of vials will be blanks.

NOTE 9—For determination of desorption efficiency, it is important that the standard solutions prepared in 11.3.2 are not used to spike the vials of resin because these standards already contain quinoline, the internal standard.

11.7.3 Cap, tightly seal, and store all vials under the same storage conditions of the samples. Since the desorption efficiency may be dependent on the length of time the sample tubes are stored, choose the storage time of the vials as the average time required to analyze field samples.

11.7.4 Aliquot ten calibration standards as described in 11.3.3.

11.7.5 If the vials have been stored frozen, allow them to equilibrate to room temperature before beginning the desorption procedure. Uncap each of the 20 vials. Then desorb and analyze as described in 11.4 and 11.5.

11.7.6 The desorption efficiency is defined as the average weight of analyte recovered from the tube divided by the weight of analyte added to the tube:

$$\text{desorption efficiency} = \frac{\text{average weight (µg) recovered}}{\text{weight (µg) added}} \quad (1)$$

11.7.7 The desorption efficiency may be dependent on the amount of analyte collected on the XAD-4 resin. If so, construct a plot of desorption efficiency versus weight of analyte found experimentally (not the amount added).

11.7.8 In most cases, the desorption efficiency is 1.00 over the calibration ranges suggested in 11.3.2 **(2, 14)**.

12. Calculation

12.1 When fitting data to a second-order polynomial regression model, the coefficients *A*, *B*, and *C* of the polynomial $y = A + Bx + Cx^2$ are found where *y* is equal to peak area ratio (analyte:quinoline), and *x* is equal to analyte concentration.

12.2 Calculate the concentration of analyte in µg/1.25 mL or, in other words, µg/sample (total volume of each sample is equal to 1.25 mL) corresponding to each peak area ratio of analyte to quinoline from the equations in 12.1.

12.3 Make corrections for the laboratory blanks for each sample with the following equation:

$$\text{µg analyte} = \text{µg sample} - \text{average µg blank} \quad (2)$$

where:
µg sample = µg analyte found in sample tube, and
average µg blank = average µg analyte found in blank tubes.

NOTE 10—Either the laboratory blanks (see 11.4.2) or the flow blanks (see 9.2.8) may be used, whichever are deemed more appropriate.

12.4 If desorption efficiency is less than 1.00, read the desorption efficiency from the curves generated in 11.7.7 (or, if no curves were generated, use the simple arithmetic means). Correct the weight of analyte by dividing the weight of analyte by desorption efficiency:

$$\text{corrected µg/sample} = \frac{\text{total analyte weight}}{\text{desorption efficiency}} \quad (3)$$

.

12.5 Convert µg of analyte found in each sample to µg of analyte per cubic metre of air by the following equation:

$$\text{µg/m}^3 = \frac{\text{corrected µg} \times 1000}{\text{time} \times \text{flow rate}} \quad (4)$$

where:
1000 = conversion factor, L/m^3,
time = elapsed sampling time, min, and
flow rate = average of initial and final flow rates of sampling pump, L/min.

12.6 Adjust the analyte concentration found in the sampled air to standard conditions of temperature and pressure by the following equation (optional):

$$\text{corrected µg/m}^3 = \text{µg/m}^3 \times \frac{101.325}{P} \times \frac{(T + 273)}{298} \quad (5)$$

where:
P = barometric pressure of air sampled, kPa,
T = temperature of air sampled,° C,
101.325 = standard pressure, kPa, and
298 = standard temperature, K.

13. Performance Criteria and Quality Assurance

13.1 This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.2 *Standard Operating Procedures (SOPs)*:

13.2.1 Users should generate SOPs describing and documenting the following activities in their laboratory:

13.2.1.1 Assembly, calibration, leak-check, and operation of the specific sampling system and equipment used,

13.2.1.2 Preparation, storage, shipment, and handling of samples,

13.2.1.3 Assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used,

13.2.1.4 Sampler storage and transport, and

13.2.1.5 All aspects of data recording and processing, including lists of computer hardware and software used.

13.2.2 The SOPs should provide specific, step-by-step instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

13.2.3 Flow blanks should contain less than 0.05 µg nicotine and less than 0.01 µg 3-EP. Larger quantities would be evidence of contamination during sampling or analysis.

13.3 *Calibration of Personal Sampling Pumps*:

13.3.1 Sampling pumps are calibrated at the beginning and at the conclusion of each sampling period.

13.3.2 The pump flow controller is set using a bubble flowmeter at a sampling rate ≤1.5 L/min with the XAD-4 sorbent sampling tube in line according to Practice D 5337.

Alternatively, a commercial mass flowmeter[17] which gives comparable results may be used.

13.3.3 For conversion of measured flows to standard flows, record barometric pressure and ambient temperature during both pump calibration and sampling (see Test Methods D 3631).

13.4 *Test Method Sensitivity, Precision, and Linearity*:

13.4.1 The sensitivity of this test method is illustrated by the detection limits of 0.11 µg/m^3 for nicotine and 0.06 µg/m^3 for 3-EP for a 1-h sample duration.

13.4.2 Determining desorption efficiency, repeatability, and reproducibility ensures method precision.

13.4.3 Nonlinearity in the calibration curve or desorption efficiency curve may occur at concentrations near the limits of quantitation for the test method or at high concentrations near the breakthrough limit of 300 µg nicotine per tube.

13.5 *Test Method Modification*:

13.5.1 The sampling time described in this test method (up to 1 h) may be increased up to 24-h periods.

13.5.2 To perform 24-h sampling, modifications in the analysis may involve diluting the sample with additional solvent or adjusting the calibration standards and constructing a calibration curve with a higher range of nicotine or 4-EP concentrations, or both, if necessary.

13.5.3 The flow rate of air through the XAD-4 sorbent tube may be decreased from 1.5 L/min to any lower flow rate which can be reliably maintained by the sampling pump.

13.6 *Safety*:

13.6.1 If spilling of solvent or any of the reagents occurs, take quick and appropriate cleanup action. (See Material Safety Data Sheets that are provided by the seller of the chemicals as prescribed by law).

13.6.2 When preparing standards, as with handling any chemicals, avoid contact with skin and eyes. Particular caution should be taken with nicotine because it is readily absorbed through the skin.

13.6.3 *Breaking XAD-4 Sorbent Tube*—Use an efficient tube breaking tool when opening the sealed ends of the XAD-4 tube and when breaking the tube open to transfer contents for analysis. This should prevent injury from raw glass edges of the tube.

14. Precision and Bias

14.1 For this test method, precision coefficients of varia-tion of repeatability and reproducibility have been calculated for nicotine in two collaborative studies **(16,17)**. Combining the spiked sample and ETS sample results showed acceptable margins of variation by a two-way analysis of variance (ANOVA) **(18)**. The coefficient of variation of repeatability was found to be in the range from 1.1 to 10.9 % **(17)**, and the coefficient of variation of reproducibility was found to be in the range from 3.3 to 12.1 % **(17)**. No collaborative testing has been performed for 3-ethenylpyridine; however, the variation range is expected to be comparable.

14.2 Recovery of nicotine from the XAD-4 resin was found to average 100.1 % with an average standard deviation of 2.2 % over a range from 0.05 to 0.5 µg **(14)**. Recovery of 4-ethenylpyridine from the XAD-4 resin was found to average 100.8 % with a standard deviation of 0.8 % at 2.4 µg **(2)**.

14.3 No systematic bias of this test method was evident in either of two collaborative studies **(16, 17)**. The bias of this test method with nicotine-spiked XAD-4 sorbent tubes is typically less than 5 % **(17)**. Similar results are expected for ethenylpyridine.

15. Keywords

15.1 environmental tobacco smoke (ETS); 3-Ethenylpyridine; indoor air quality; nicotine

[17] The Top-Trak mass flowmeter, Model No. 821-1-(Air, 2SLPM), available from Sierra Instruments, Inc., 5 Harris Ct., Monterey, CA 93940, or equivalent, has been found suitable for this purpose.

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