Method number:	PV2295
Control number:	T-PV2295-01-9112-CH
Matrix:	Air
Target concentration:	5 ppm (15 mg/m^3)
OSHA PEL:	5 ppm (15 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through two XAD-7 tubes connected in series. Samples are desorbed with methanol and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Air volume and sampling rate:	100 min at 0.1 L/min (10 L)
Status of method:	Partially validated method. This method has been partially evaluated and is presented for information and trial use only.

December 1991

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA laboratory periodically receives samples collected on charcoal with requested analysis for pyridine (NIOSH 1613). The NIOSH method recommends a maximum of 150 liters of air be sampled at 1.0 L/min. However, the samples the laboratory receives usually have only 10 liters of air sampled. This is a problem because at low loadings of pyridine the desorption efficiency from charcoal is low and not constant. The goal of this evaluation was to develop a sampling and analytical procedure for pyridine which has high and constant desorption efficiency at low loadings which would permit 10 liters of air to be sampled.

1.1.2 Toxic effects (This section is for information purposes only and should not be taken as the basis for OSHA policy.)

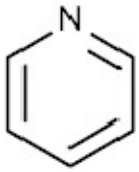
Vapor from pyridine is irritating to mucous surfaces, causing eye and nasal irritations. Exposures at levels from 15 - 330 ppm cause nausea, headache, insomnia, and nervousness. (Ref. 5.1). Small oral doses (2 to 3-mL) in humans produce mild anorexia, nausea, fatigue, and mental depression. Ingestion of several ounces causes severe vomiting, diarrhea, hyperpyrexia, delirium, and death (Ref. 5.2).

1.1.3 Potential workplace exposure

No potential workplace exposure data could be found. However, the major use of pyridine is in the synthesis of vitamins and drugs, solvent waterproofing, rubber chemicals, denaturant for alcohol and anti-freeze mixtures, dyeing assistant in textiles, and fungicides (Ref. 5.3).

1.1.4 Physical properties:

CAS:	110-86-1
RTECS:	UR 8400000; 70423
IMIS:	2220
Compound:	Pyridine
Molecular weight:	79.10
Density:	0.9780 (25/4 ºC)
Boiling point:	115.5 ºC
Freezing point:	- 42.0 ºC
Odor:	Nauseating odor
Color:	Slightly yellow or colorless liquid
Solubility:	Soluble in water, alcohol, ether, benzene, ligroin, and fatty oils.
Molecular formula:	C_5H_5N
Flash point:	68 ºF (20 ºC) (closed cup)
Structure:	



1.2 Limit defining parameters

The detection limit of the analytical procedure is 0.87 pg per injection (1.0 µL injection). This is the smallest amount of analyte which will produce a peak 5 times the baseline noise (See Figure 1).

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of GC column and parameters.

2 Sampling procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated to within ±5% at the recommended flow rate with the sampling tubes in-line.

2.1.2 Samples are collected with two solid sorbent sampling tubes containing XAD-7 connected in series. Each tube consists of two sections of adsorbent separated by a glass wool plug. The front section contains 100 mg of adsorbent and the back section 50 mg. The sections are held in place with glass wool plugs in a glass tube 110-mm × 6-mm o.d. For this evaluation, SKC XAD-7 tubes (catalog no. 226-95) were used.

2.2 Technique

2.2.1 Immediately before sampling, break off the ends off the adsorbent tube. All tubes should be from the same lot. Connect both tubes with a small piece of flexible tubing.

2.2.2 Connect the sampling tubes in series to the sampling pump with flexible tubing. Position the tubes so that sampled air passes through the 100-mg section first.

2.2.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.2.4 Place the sampling tubes vertically (to avoid channeling) in the employee's breathing zone.

2.2.5 After sampling, separate the tubes and seal them with plastic end caps. Wrap samples lengthwise with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sampling tube with each sample set. Blanks should be handled in the same manner as samples (break ends, seal, and transport), except no air is drawn through them.

2.2.7 Record sample air volumes (in liters of air) for each sample, along with any potential interference.

2.2.8 Ship bulk sample(s) in a container separate from the air samples.

2.3 Desorption Efficiency

Three sets of six tubes each were liquid spiked at three separate loadings. The average desorption efficiency for pyridine from XAD-7 is 99.8% over the range of 0.1 to 1 times the target concentration. (Table 2.3)

Table 2.3
Desorption Efficiency

	% desorption		
sample #	0.1 × 16.3 µg	0.5 × 81.5 µg	1 × 163.0 µg
1	99.0	98.9	101.4
2	96.4	99.4	101.8
3	95.0	99.0	100.6
4	96.4	98.9	102.4
5	99.0	100.3	104.4
6	99.6	100.0	103.6
average	97.6	99.4	102.4
standard deviation	±1.89	±0.636	±1.41

overall average = 99.8%

2.4 Retention Efficiency

The front glass wool plug for six sets of two XAD-7 tubes connected in series was spiked at the target concentration with pyridine. Ten liters of humid air (78% RH) were drawn through the tubes at 0.1 L/min. The XAD-7 tubes were stored for several hours and then desorbed with 1 mL of methanol containing 1.0 µL/mL *N,N*-dimethylformamide (DMF) as the internal standard. The samples were analyzed by gas chromatography (GC) with a flame ionization detector (FID). The average retention efficiency was 100% (Table 2.4).

Table 2.4
Retention Efficiency

tube #	air volume	µg spiked	% recovered
1	10 L	163.0	100.3
2	10 L	163.0	100.7
3	10 L	163.0	99.1
4	10 L	163.0	98.7
5	10 L	163.0	101.2
6	10 L	163.0	99.7

average = 100%

2.5 Storage

Storage samples were generated by spiking twelve XAD-7 adsorbent tubes with pyridine at the target concentration. Half of the tubes were stored at ambient temperature (about 23 ºC) and the other half were stored in a freezer (-12 ºC). Three samples from each set were analyzed approximately every three days. The average recovery for ambient storage was 97.9%; for freezer storage, it was 99.9% (Table 2.5).

Table 2.5
Storage Study

days stored	% recovered (ambient)			% recovered (freezer)		
0	101.4	101.8	100.6	102.4	104.4	103.6
5	98.8	96.9	98.1	99.0	97.0	101.0
11	94.6	94.8	94.2	97.3	97.2	97.3

2.6 Precision

Precision is measured by the pooled coefficient of variation (CV) from repeated injections of three standards prepared at levels from 0.5 × to 2 × the PEL. The pooled CV is 0.002569 (Table 2.6).

Table 2.6
Precision Study

injection number	0.5 × 81.5 µg	1 × 163.0 µg	2 × 326.1 µg
1	80.774	164.055	325.927
2	80.185	163.650	325.887
3	80.469	163.513	326.564
4	80.866	163.759	325.057
5	80.218	163.793	326.314
6	80.396	164.157	327.311
average	80.485	163.821	326.177
standard deviation	±0.282	±0.243	±0.752
CV	0.00351	0.00149	0.00230

pooled CV = 0.002569

Where:

$$CV\left(Coefficient\ of\ Variation\right) = \frac{\left(standard\ deviation\right)}{\left(average\right)}$$

$$Pooled\ CV = \sqrt{\frac{A1\left(CV1\right)^2 + A2\left(CV2\right)^2 + A3\left(CV3\right)^2}{A1 + A2 + A3}}$$

A1, A2, A3 = number of injections at each level
CV1, CV2, CV3 = Coefficients of variation at each level

2.7 Air volume and sampling rate studies

2.7.1 The air volume studied was 10 liters.

2.7.2 The sampling rate studied was 0.1 L/min.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on the employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph (GC) equipped with a flame ionization detector (FID) and an automatic sample injector.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. A 60-m x 0.32-mm i.d. (with 1.0 µm d_f Stabilwax-DB) fused silica capillary column was used in this evaluation.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas. A Hewlett-Packard 3396A integrator was used in this evaluation.

3.1.4 Two-milliliter vials with PTFE-lined caps.

3.1.5 A 10 µL syringe and other convenient sizes for standard preparations.

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this evaluation.

3.1.7 Volumetric flasks - 5 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Methanol, Reagent grade.

3.2.3 *N,N*-Dimethylformamide, Reagent grade.

3.2.4 Internal standard solution; 1.0 µL/mL *N,N*-dimethylformamide in methanol.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1 mL of internal standard solution.

3.3.3 The vials are immediately sealed with PTFE-lined caps and allowed to desorb for 60 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of pyridine with the internal standard solution.

3.4.2 At least two separate standards should be made.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min)**	**Temperature**	**(°C)**
Nitrogen (make-up):	30	Injector:	200
Hydrogen (carrier):	3.0	Detector:	250
Hydrogen (detector):	30	Column:	60 -160
Air:	350		

Injection size: 1.0 µL (with a 5:1 split)
Elution time: 13.5 minutes
Chromatogram: (See Figure 2)

Column: 60-m x 0.32-mm i.d. (with 1.0 µm d_f Stabilwax-DB) fused silica capillary.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is an interference. GC parameters may be adjusted to eliminate interferences.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Pyridine in samples containing greater than the OSHA PEL should be confirmed by GC/Mass Spectrometry or other suitable means.

3.7 Calculations

3.7.1 The mass of pyridine found on each section of the sampling train is added together for reporting purposes. If the backup section of tube "B" contains a mass of pyridine equal to or greater than 25% of the mass in the front section of that tube, the sample should be labeled as possibly saturated.

3.7.2 The analyte concentration for samples is obtained from the following formula. If any analyte is found on the backup sections, the concentration of each section is calculated separately and then added to the amount found on the front section.

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)(desorption\ volume,\ mL)}{(air\ volume,\ L)(desorption\ efficiency,\ decimal)}$$

$$ppm = \frac{(mg/m^3)(24.46)}{(MW)}$$

where 24.46 = molar volume (liters/mole) at 760 mmHg and 25 °C.
MW = molecular weight = 79.10 for pyridine.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all chemicals.

3.8.3 Wear safety glasses, disposable gloves and a lab coat at all times in lab areas.

4 Recommendations for further study

Further work should be done to fully validate the method.

5 References

5.1 “Documentation of the Threshold Limit Values and Biological Exposure Indices.” 5th ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 1986.

5.2 Gosselin, R.E., R.P. Smith, H.C. Hodge. “Clinical Toxicology of Commercial Products”. 5th ed. Baltimore: Williams and Wilkins, 1984.

5.3 "Hawley's Condensed Chemical Dictionary", 11th edition; Sax, N.I., Lewis, R.J., ed.; Van Norstrand Reinhold Company, New York, 1987; p. 982.

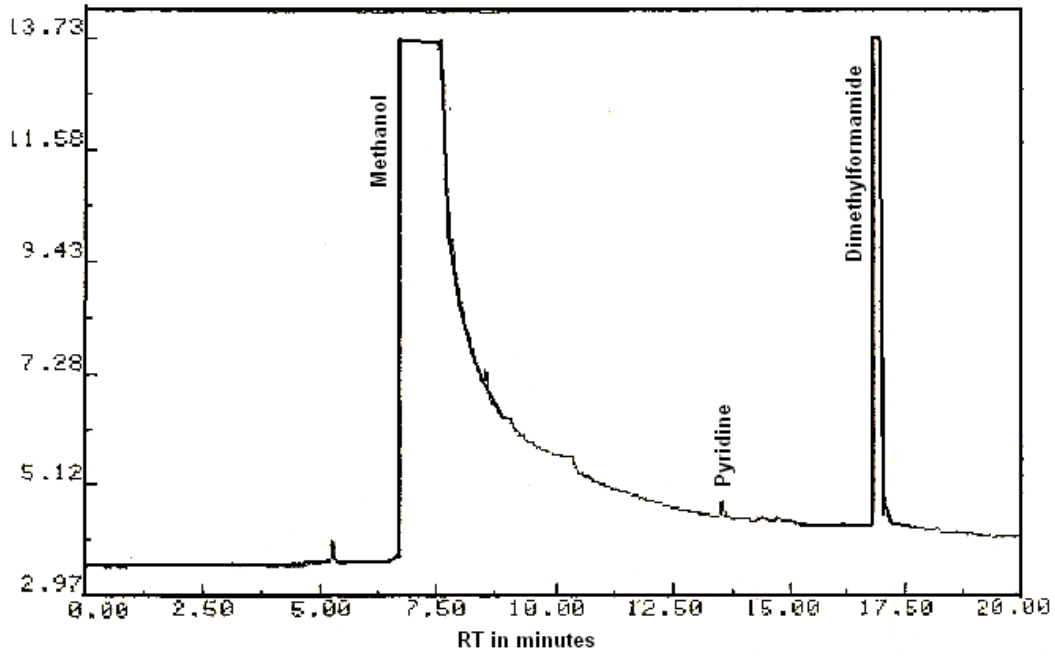


Figure 1. Chromatogram of Detection Limit of Pyridine

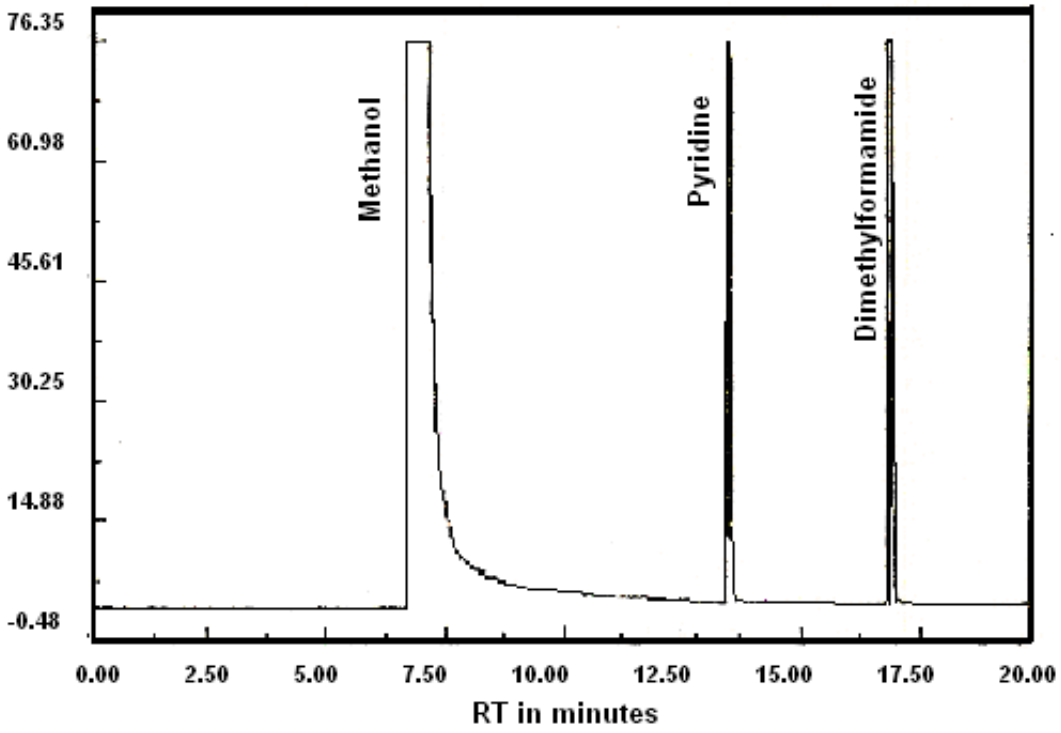


Figure 2. Chromatogram of Pyridine Standard