

VII. REFERENCES

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VIII. APPENDIX I
METHOD FOR SAMPLING METHYL ALCOHOL IN AIR

General Requirements

- (a) Collect air samples from within the employee's breathing zone.
- (b) Record the following on all sampling data sheets:
 - (1) Date and time of sample collection.
 - (2) Sampling duration.
 - (3) Volumetric flowrate of sampling.
 - (4) Description of sampling location.
 - (5) Serial number of pump.
 - (6) Name of person performing the calibration or sampling.
 - (7) Other pertinent information (temperature, pressure, and information listed in paragraph (i) of Calibration of Equipment).

Recommended Method

The sampling train consists of a silica gel tube and a vacuum pump.

(a) Collect breathing zone samples in a silica gel tube as near as practicable to the employee's face without interfering with his or her freedom of movement. The shirt collar is convenient for this purpose.

(b) Collect the samples with a portable, battery-operated personal sampling pump whose flow can be accurately controlled to within $\pm 5\%$ at 0.05 l/min and a silica gel tube.

(c) Operate the sampler at a flowrate of 0.05 l/min or less. Some pumps are designed for high flowrates and some for low; consequently care

should be taken to use a pump with the proper flowrate, eg, up to 0.20 l/min.

(d) Collect sufficient breathing zone samples to permit calculation of a ceiling exposure for every operation involving exposure to methyl alcohol.

(e) Provide to the analytical laboratory at least one unused silica gel tube from the same batch to correct for the blank.

Air Sampling Equipment

(a) Use silica gel tubes having an inside diameter of 8 mm and two sections of 45/60 or 42/60 mesh silica gel. The adsorbing section should contain 700 mg of silica gel while the backup section should contain 150 mg of silica gel. These two sections must be separated by a 7-mm section plug (one 100-mesh, stainless steel disc between two Teflon cylinder supports), a 12-mm airspace, and another 7-mm section plug.

(b) Use a battery-operated personal sampling pump and a clip for attachment to the employee's clothing. Calibrate all pumps and flowmeters using a calibrated test meter, or other reference as described in the section of this Appendix under Calibration of Equipment.

Calibration of Equipment

Since the accuracy of an analysis can be no greater than the accuracy with which the volume of air is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicated. The frequency of calibration is dependent upon the use, care,

and handling to which the pump is subjected. Pumps should also be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary. Regardless of use, maintenance and calibration should be performed on a regular schedule and records of these kept.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, standards such as a spirometer or soapbubble meter are recommended, although other standard calibration instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

The calibration setup for personal sampling pumps with a silica gel tube is as shown in Figure XIII-1. If another calibration device is selected, equivalent procedures should be used. Since the flowrate given by a pump is dependent on the pressure drop of the sampling device, in this case a silica gel tube, the pump must be calibrated while operating with a representative silica gel tube. Instructions for calibration with the soapbubble meter are as follows:

(a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration; charge the battery as needed.

(b) Break the tips of a silica gel tube to produce openings of at least 4-mm in diameter.

- (c) Assemble the sampling train as shown in Figure XIII-1.
- (d) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret into the soap solution and drawing bubbles up the inside until they travel the entire buret length without bursting.
- (e) Adjust the pump flow controller to the desired flowrate.
- (f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 2.0 inches of water at 0.05 l/min.
- (g) Start a soapbubble up the buret and with a stopwatch determine the time it takes the bubble to move from one calibration mark to another.
- (h) Repeat the procedure in (g) at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between the two preselected marks divided by the number of strokes.
- (i) Record the following calibration data: volume measured, elapsed time or number of strokes, pressure drop, air temperature, and atmospheric pressure.
- (j) Also record the serial number of the pump, the date, and the name of the person performing the calibration.

Collection of Samples

- (a) Break both ends of the silica gel tube to provide openings of at least half of the internal diameter of the tube, ie, 4 mm. A smaller

opening causes a limiting orifice effect which reduces the flow through the tube. The smaller section of silica gel in the tube is used as a backup section and should therefore be placed nearest the sampling pump. Tubing may be used to connect the back of the tube to the pump, but no tubing must ever be put in front of the silica gel tube. Support the tube in a vertical position for sampling to prevent channeling.

(b) The recommended sampling flowrate is 0.05 l/min or less. A 3-liter sample is normally adequate. Using the manufacturer's directions, set the calibrated flowrate as accurately as possible. Record the temperature, pressure, and humidity of the sampled atmosphere.

(c) Record the initial and final counter readings. The sample volume can be obtained by multiplying the number of counter strokes times the volume/stroke factor.

(d) Immediately after sampling, cap the silica gel tubes with the plastic caps supplied by the manufacturer. Masking tape is the only suitable substitute for sealing the tubes. Rubber caps should never be used.

(e) Treat one silica gel tube in the same manner as the sample tubes (break, seal, ship), but draw no air through it. Label this tube as the blank.

Special Considerations

(a) When two or more compounds are known or suspected to be present in the air, convey such information, including their suspected identities, with the sample.

(b) Because of the high resistance of the silica gel tube, the

sampling pump should not be operated for more than 8 hours without recharging the battery.

(c) With the use of the large size silica gel tubes, the problem of nonquantitative trapping of methyl alcohol in the presence of high humidity or water mist is minimized to a great extent.

(d) Since the desorption efficiency of silica gel varies from batch to batch, all the tubes used to collect a set of samples must contain silica gel from the same batch. Several unused silica gel tubes and information on the batch number should accompany the samples.

Shipping Samples

Capped silica gel tubes should be padded and packed tightly to minimize breakage during transportation. Bulk samples and silica gel tubes must be shipped in separate containers.

IX. APPENDIX II
ANALYTICAL METHOD FOR METHYL ALCOHOL

The following analytical method for methyl alcohol is adapted from that described by Baker et al. [69]

Principle of the Method

(a) A known volume of air is drawn through a silica gel tube; organic vapors are adsorbed on the silica gel. The sample is then desorbed with distilled water.

(b) An aliquot of the aqueous sample is injected directly into a gas chromatograph.

(c) The area under the resulting peak is determined and compared with areas obtained from standards.

Range and Sensitivity

The sampling method is intended to provide a measure of airborne methyl alcohol in the range of 100-1,000 ppm. This method has been validated at methyl alcohol concentrations of 100, 200, and 400 ppm and a sampling time of 60 minutes, and at 1,000 ppm for at least a 15-minute sampling period. [60]

The gas chromatographic method can measure from 1 to 40 $\mu\text{g}/\text{ml}$ of methyl alcohol in aqueous solutions. [69] When used in combination, it is estimated that the sampling and analytic methods will determine as little

as 0.8 ppm methyl alcohol in a 3-liter air sample. For aqueous solutions, the working range for methyl alcohol is linear up to concentrations of 40 $\mu\text{g/ml}$. [69] However, the gas chromatographic method can easily be applied to higher concentrations by appropriate serial dilution of the desorbing solution with distilled water.

Interferences

Any compound which has the same retention time as methyl alcohol at the operating conditions described in this method will interfere with the analysis. The retention time of any substance suspected of being present in the sample should be determined to evaluate the likelihood of its interfering with the procedure.

Precision and Accuracy

The coefficient of variation (Cv) for 10 replicate determinations of methyl alcohol in aqueous samples performed in the same laboratory was 0.025. This value corresponds to a standard deviation of 0.25 $\mu\text{g/ml}$ with a mean of 10.0 $\mu\text{g/ml}$. [69] The efficiency of the combined sampling and analytic method has not yet been established.

Apparatus

- (a) Gas chromatograph equipped with a flame ionization detector.
- (b) Column (183 cm x 5 mm ID) with 60/80 mesh Porapak Q, preconditioned for 18 hours at 225 C.
- (c) A mechanical or electronic integrator or some other method for

determining areas under peaks.

(d) Glass-stoppered test tubes.

(e) Microsyringes: 10 μ l and other convenient sizes for making standards and sample injections.

(f) Volumetric flasks: convenient sizes for making standards.

(g) Pipets.

Reagents

(a) Distilled and deionized water.

(b) Methyl alcohol, chromatographic grade.

(c) Anhydrous acetonitrile, chromatographic grade.

(d) Purified nitrogen.

(e) Purified hydrogen.

(f) Purified air.

(g) Industrial grade compressed air (as per instrument requirements).

Procedure

(a) Cleaning of Equipment

All glassware used for laboratory analyses should be washed in detergent followed by tap and distilled water rinses.

(b) Analysis of Samples

(1) Use a suitable aliquot of the aqueous methyl alcohol solution obtained in the sampling procedure (Appendix I). No further preparations of the sample are necessary.

(2) Typical operating conditions for the gas chromatograph are:

(A) 35 ml/min nitrogen carrier gas flow. [69]

(B) Hydrogen gas flow to detector as required by instrument specifications.

(C) Air flowrate to the detector as required by instrument specifications.

(D) 125 C injection port temperature. [69]

(E) 125 C detector temperature. [69]

(F) 100 C isothermal column temperature. [69]

(3) To eliminate difficulties arising from blowback or distillation within the needle, the solvent flush injection technique is used. A 10- μ l syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 μ l to separate the solvent from the sample by a pocket of air. The needle is then immersed in the sample and an aliquot (2-7 μ l) is withdrawn. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 μ l to minimize evaporation of the sample from the tip of the needle. If, for example, a 5- μ l aliquot were used the sample would measure 5.7-5.8 μ l because of the needle volume. Duplicate injections of each sample and standard should be made at a constant injection volume throughout the procedure.

(4) The area under the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and

the $\mu\text{g}/\text{ml}$ of methyl alcohol are read from a standard curve.

Determination of Desorption Efficiency

The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of methyl alcohol recovered in the desorption process. This procedure should be repeated for each new batch of silica gel tubes used.

Silica gel, equivalent to the amount in the first section of the sampling tube (700 mg), is measured into a 5-cm, 4-mm ID glass tube, flame-sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples. The open end is sealed with a plastic cap. A measured amount of pure methyl alcohol is injected directly into the silica gel with a microliter syringe, and the tube is capped with plastic. The amount of methyl alcohol used is usually equivalent to that expected in a 3-liter sample of air at the environmental limit.

At least six tubes are prepared in this manner and allowed to stand overnight or longer; this should assure complete adsorption of the methyl alcohol onto the silica gel. These six tubes are referred to as the samples. A tube referred to as the blank should be treated like the sample tubes except that no methyl alcohol is added to it. The blank and sample tubes are desorbed and analyzed in the same manner described above for unknown air samples.

Two or three standards are prepared by injecting identical volumes of methyl alcohol into 1.0 ml of distilled water with the same syringe used in the preparation of the sample. These are analyzed with the samples. The

desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube.

$$DE = \frac{\text{average weight recovered (mg)}}{\text{weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. The desorption efficiency versus the weight of analyte found should be plotted.

Standard Curve

Prepare a series of standards in the range of 1-40 $\mu\text{g/ml}$ methyl alcohol in distilled water containing 0.1% acetonitrile as an internal standard. Incorporation of the internal standard will adjust for day-to-day variations and variations during the same day due to changes in instrument sensitivity and column performance.

The internal standard is also added in the same concentration to the unknown samples. Standard curves are established by plotting the concentration of methyl alcohol ($\mu\text{g/ml}$) versus the ratio obtained by comparison of the area under the methyl alcohol peak with that under the internal standard peak. The concentration of methyl alcohol in the unknown sample is then calculated by comparison with the standard curve.

Calculations

(a) The concentration, in $\mu\text{g/ml}$, corresponding to each ratio is read from the standard curves for methyl alcohol.

(b) Corrections for the known desorption efficiency of the sampling method must be made for each unknown sample analyzed.

$$\text{corrected } \mu\text{g/ml} = \frac{\mu\text{g/ml from standard curve}}{\text{desorption efficiency}}$$

Convert $\mu\text{g/ml}$ to mg/ml ($1 \mu\text{g} = 0.001 \text{ mg}$).

(c) The concentration of methyl alcohol in the air sampled can be expressed in mg/cu m or in ppm.

$$\text{mg/cu m} = \frac{\text{corrected concentration (mg/ml)} \times \text{volume of desorbant (ml)}}{\text{air volume sampled (cu m)}}$$

$$\text{ppm} = \frac{\text{mg/cu m} \times 24.45 \times 760 \times (T + 273)}{\text{MW} \times P \times 298}$$

where:

P = Pressure (mmHg) of air sampled

T = Temperature (C) of air sampled

24.45 = Molar volume (liter/mole) at 25 C and 760 mmHg

MW = Molecular weight (g/mole) of methyl alcohol

760 = Standard pressure (mmHg)

298 = Reference temperature of 25 C in degree, Kelvin