Ketene

Analyte:	Ketene	Method No.:	S92
Matrix:	Air	Range:	0.40 - 1.74 mg/cu m
OSHA Standard:	0.9 mg/cu m	Precision $(\overline{CV}_T)$:	0.064
Procedure:	Bubbler Collection, Complexation, Colorimetric	Validation Date:	3/14/75

1. Principle of the Method

1.1 Ketene is collected in alkaline hydroxylammonium chloride absorbing solution where it is hydrolyzed to acetohydroxamic acid.

1.2 The resulting product is subsequently reacted with ferric chloride to form the purple complex.

1.3 The absorbance of the resulting solution is determined at 540 nm and is used as a measure of the amount of ketene present.

1.4 Ethyl acetate, which is less toxic and more stable than ketene, also reacts with alkaline hydroxylammonium chloride and ferric chloride in a similar manner and is used in place of ketene for standards. One mole of ethyl acetate is equivalent to one mole of ketene.

2. Range and Sensitivity

2.1 This method has been validated over the range of 0.40 - 1.74 mg/cu m at an atmospheric temperature and pressure of 23°C and 757 mm Hg, using a 50-liter sample. The probable range of the method is 0.20 to 2.2 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where absorbance is greater than the limits of the standard curve, the samples can be diluted with a mixture of equal amounts of the absorbing solution and the ferric chloride solution after the color development to extend the upper limit of the range.

2.2 A concentration of 0.20 mg/cu m of ketene can be determined in a 50-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 5-cm cell.

3. Interferences

3.1 Any material containing an RCO group will interfere with this determination. Among such materials are esters, acid chlorides and acid anhydrides.

3.2 The substance most likely to coexist with ketene in air is acetic anhydride. Interferences due to acetic anhydride can be minimized by initially passing the air through an absorber containing toluene before the air is collected in the alkaline hydroxylammonium chloride absorbing solution. The method is described in References 11.1 and 11.2.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.40 - 1.74 mg/cu m was 0.064. This value corresponds to a standard deviation of 0.058 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 0.944 ± 0.041 was determined for the collection medium. The collection efficiency was used as a correction factor to determine the concentration of the air sampled to compensate for any bias in the sampling method. There was no apparent bias in the analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The method is simple and requires approximately 1.5 hours to complete.

5.2 The alkaline hydroxylammonium chloride solution can produce dermatitis if it comes in contact with the skin.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

6.6.1 A glass standard midget bubbler with a fritted glass inlet. The fritted end should have porosity approximately equal to that of Corning EC (170 - 220 microns maximum pore diameter). The bubbler bottom holds the absorbing solution (Section 7.4).

6.1.2 A pump suitable for sampling for 1 liter per minute for at least 50 minutes. The sampling pump is protected from splashover or water condensation by a 2-inch glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Scintillation vials, linear polyethylene 20-ml Fisher-brand with screw caps.

6.3 Scintillation vial support.

6.4 Spectrophotometer. This instrument should be capable of measuring the developed color at 540 nm.

6.5 Matched glass cells or curvettes, 5 cm path length.

6.6 Assorted laboratory glassware: pipets, volumetric flasks, graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Distilled water.

7.2 Hydroxylammonium chloride solution. Prepare a 10% (W/V) solution in water. Store the solution in a refrigerator and reject any solution when it is 2 weeks old.

7.3 Sodium hydroxide, 2.5M solution. Dissolve 100 grams of sodium hydroxide in water in a 1-liter volumetric flask. Cool the solution to room temperature and dilute to volume.

7.4 Absorbing solution. Mix equal volumes of the hydroxylammonium chloride solution and the sodium hydroxide solution. This mixture is stable for only about 2 hours and should be freshly prepared for use.

7.5 Ferric chloride solution. Prepare a 5% (W/V) solution of the hydrated salt ($FeC\ell_3 . 6H_2O$) in a mixture of equal volumes of water and concentrated hydrochloric acid.

7.6 Ethyl acetate standard solution. Dissolve 200 microliters of ethyl acetate in 1 liter of water.

1 ml of this solution = 0.180 mg ethyl acetate = 0.086 mg ketene

8. Procedure

8.1 Cleaning of Equipment. No specialized cleaning of glassware is required. However, since known interferences occur with esters and aldehydes, cleaning techniques should insure the absence of all organic materials.

8.2 Calibration of Personal Pump. Personal sampling pump should be calibrated using integrating volume meter (6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 10.0 ml of the alkaline hydroxylammonium chloride absorbing solution (Section 7.4) into each midget bubbler.

8.3.2 Connect the midget bubbler in series with the sampling pumps using a short piece of flexible tubing containing a glass wool plug to protect the pump. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1 liter per minute. Sample for 50 minutes making the final volume 50 liters.

8.3.4 After sampling, the bubbler stem can be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1.0 ml of unused absorbing solution and add the washing to the bubbler. Make up the solution volume in the bubbler to 10.0 ml using unused absorbing solution or distilled water. (Note: All subsequent dilutions and measurements are based on this sample volume of 10.0 ml)

8.3.5 Quantitatively transfer (avoiding any loss of sample solution) the total contents of the bubbler into a 20-ml polyethylene scintillation vial with screw cap. Close cap tightly and secure with plastic tape around edges to avoid sample loss during transit.

8.3.6 Care should be taken to minimize spillage or loss by evaporation at all times.

8.3.7 Whenever possible, hand delivery of the samples is recommended. Otherwise, special shipping cases should be used to ship the samples.

8.3.8 A "blank" bubbler should be handled as the other samples (fill, transfer, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

8.4.1 The sample in each vial is analyzed separately.

8.4.2 Pipet 2.5 ml of the 5% ferric chloride solution and 2.5 ml of distilled water into the bubbler. The purple complex is formed readily.

8.4.3 Mix thoroughly and let stand a few minutes to allow the gas bubbles formed to dissipate.

8.4.4 The aliquots of reagents added (2.5 ml of ferric chloride and distilled water respectively) are such that the final solution volume is 15.0 ml. If it is suspected that the level of the solution in the vial is less than 15.0 ml, the total volume of the resulting solution should be measured before absorbance readings are carried out and the appropriate volume correction factor must be used. Note that all calibration standards are based on a 15.0 ml solution volume.

8.4.5 Read the absorbance in a spectrophotometer at 540 nm against a blank prepared from the alkaline hydroxylammonium chloride and ferric chloride solution in the same fashion as the samples.

9. Calibration and Standards

9.1 Pipet into a series of tubes 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 1.5, and 2.0 ml of the ethyl acetate standard solution containing the equivalent of 0.086 mg ketene per ml.

9.2 Pipet 10.0 ml of freshly prepared absorbing solution (Section 7.4) into each tube, followed by 2.5 ml of the 5% ferric chloride solution and sufficient distilled water to make up total volume to 15.0 ml.

9.3 Proceed as directed in Section 8.4.3 and Section 8.4.5.

9.4 Construct a calibration curve by plotting absorbance against the equivalent mg of ketene in the color developed solution.

10. Calculations

10.1 Determine from the calibration curve (Section 9.3) the mg concentration of ketene present in each sample.

10.2 Corrections for the "blank" sample, if any, must be made for each sample.

$$\text{Total mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

10.3 Divide the total weight by the collection efficiency in the single bubbler. (Note: the collection efficiency when sampling an atmosphere containing 1.74 mg/cu m at 1.0-lpm for 50 minutes was determined to be 94%.)

$$\text{Corrected mg} = \frac{\text{Total Weight}}{\text{Collection Efficiency}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Hanson, N.W., D.A. Reilly, H.E. Stagg, eds., The Determination of Toxic Substances in Air, Heffer & Sons Ltd., Cambridge, England, pp. 152-156, 1965.

11.2 Diggle, W.M., and J.C. Gage, Analyst 78, 473 (1953).

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract No.CDC-99-74-45.