

CARBONYL COMPOUNDS IN LIGHT HYDROCARBON GASES

UOP Method 496-63T

SCOPE

This method is for the determination of carbonyl compounds in light hydrocarbon gases, such as ethylene, propane and butane.

OUTLINE

The gas sample is scrubbed through two scrubbers containing dilute sodium bisulfite solution. An aliquot of the scrubber solution is reacted with 2,4-dinitrophenylhydrazine at 50 C for 1 hour and the resulting complex is taken up in hexane. After several washings of the hexane phase, the absorbance of the product is measured at 340 mμ.

APPARATUS

Bucket, for water

Cylinder, graduated, 50-ml

Flasks, volumetric, 50-, 100- and 200-ml

Funnels, separatory, 250-ml

Pipets, 5-, 10- and 20-ml

Scrubbers, 125-ml, with sintered-glass dispersion tube

Spectrophotometer, capable of light absorbance measurement at 340 mμ

Support, for test tubes

Test tubes, borosilicate glass, 25 × 50 mm

Water bath, maintained at 50 C

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water. Unqualified references to solutions mean aqueous solutions.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

n-Butyl alcohol

2,4-Dinitrophenylhydrazine solution. Dissolve 0.2 g of recrystallized, 2,4-dinitrophenylhydrazine in 200 ml of carbonyl-free ethanol.

Ethanol, carbonyl-free

Hexane. Purify by percolation through silica gel.

Hydrochloric acid, concentrated

Sodium bisulfite solution, 0.2%

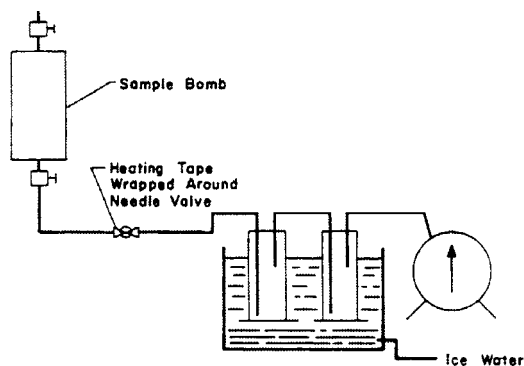
CALIBRATION FACTOR

The curves of absorbance vs. concentration for aldehydes and ketones studied by Lohman (see Ref.) were all straight lines passing through the origin. Therefore, an average molar extinction coefficient, E_{340} , was selected to be 20,000. This gives a calibration factor of 0.05 micromoles per ml – absorbance unit for a 1-cm cell using hexane as reference.

PROCEDURE

Sampling

Measure 50 ml of 0.2% sodium bisulfite solution into each of the 2 scrubbers. Connect the scrubbers in series by a small piece of tygon tubing. Place them in a bucket of ice water. Flush out the metal sampling lines with gas for a few minutes before sampling. Connect a needle valve to the main outlet. See diagram below.



Wrap the needle valve with heating tape and maintain the temperature at that valve at approximately 150–160 F, to ensure that no condensation of heavier materials occurs there. Connect the scrubbers and a wet test meter to the closed needle valve. Keep all tygon and metal lines as short as possible.

Open the main valve, then slowly open the needle valve. Pass the gas at a rate of 1 cu ft/hr or less. See the table below for the proper amount of sample.

	Carbonyl Expected, ppm	Sample Needed, cu ft
Butane	20	1.0
Ethylene	20	2.2
Propane	20	1.5

If more than 20 ppm of carbonyl compounds are expected, take less sample. If less than 20 ppm, take more sample.

Color Development

Analyze each scrubber solution separately as follows: Transfer the solution quantitatively into a 100-ml volumetric flask. Rinse out the scrubber and the dispersion tube with water a few times and combine the rinsings in the 100-ml volumetric flask. Dilute to volume and mix. Pipet a 10-ml aliquot into a test tube and add by pipet 20-ml of 2,4-dinitrophenylhydrazine reagent. Add 3 drops of concentrated hydrochloric acid and mix. Stopper the test tube loosely and heat it at 50 C in a water bath for 1 hour. Cool, pour the contents into a 250-ml separatory funnel, add 50-ml of water and 40-ml of hexane. Stopper and shake for 3 minutes, allow the phases to separate and discard the aqueous phase. Add 5-ml of *n*-butyl alcohol and wash with 20-ml portions of water acidified with a few drops of concentrated hydrochloric acid. Wash several times until the aqueous phase is colorless, discarding this phase each time.

Pour the upper phase into a 50-ml volumetric flask, dilute to the mark with hexane and mix. Pipet a 10-ml aliquot into another 50-ml flask and dilute to volume with hexane. Mix and measure the absorbance at 340 mμ in a 1-cm cuvette against hexane reference solution.

Repeat this procedure for the solution from Scrubber No. 2.

Always run a blank with the samples, prepared exactly like the samples. Subtract the absorbance of the blank from the respective absorbances of the scrubber solutions to obtain net absorbances.

CALCULATIONS

Carbonyl compounds,

$$\text{calculated as wt ppm acetone} = \frac{(A_1 + A_2) 6140}{B \times M}$$

where:

A₁ = net absorbance of Scrubber No. 1

A₂ = net absorbance of Scrubber No. 2

B = volume of gas at lab conditions

M = molecular weight of gas

PRECAUTIONS

To avoid contamination use no acetone or other carbonyl solvent for washing glassware. Also avoid working in an area where acetone is being used.

REFERENCES

Lohman, F. H., *Anal. Chem.* **30**, 972 (1958)