

METHANOL

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SYNONYMS Carbinol

DEFINITION

Chemical names Methanol, methyl alcohol

C.A.S. number 67-56-1

Chemical formula CH_3OH

Structural formula $\text{H}_3\text{C}-\text{OH}$

Formula weight 32.04

Assay Not less than 99.5%

DESCRIPTION Clear colourless, mobile liquid with a characteristic odour

FUNCTIONAL USES Extraction solvent

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4) Miscible with water, ether and ethanol

Specific gravity (Vol. 4) 0.792 - 0.795

Refractive index (Vol. 4) $n(20, D): 1.328 - 1.330$

Boiling point (Vol. 4) About 65°

PURITY

Water (Vol. 4) Not more than 0.1% (Karl Fischer Method)

Distillation range (Vol. 4) $64.5 - 65.5^\circ$

Non-volatile residue (Vol. 4) Not more than 3 mg/100 ml

Acidity Not more than 15 mg/kg as formic acid
To a mixture of 10 ml of ethanol and 25 ml of water add 0.5 ml of phenolphthalein TS, and titrate with 0.02 N sodium hydroxide to the first pink colour that persists for at least 30 sec. Add 19 ml (about 15 g) of the sample, mix and titrate with 0.02 N sodium hydroxide until the pink colour is

restored. Not more than 0.25 ml is required.

Alkalinity

Not more than 3 mg/kg as ammonia

Add 1 drop of methyl red TS to 25 ml of water, add 0.02 N sulfuric acid until a red colour just appears, then add 29 ml (about 22.5 g) of the sample, and mix. Not more than 0.2 ml of 0.02 N sulfuric acid is required to restore the red colour.

Aldehydes and ketones

Not more than 0.015% w/v as acetone

See description under TESTS

Lead (Vol. 4)

Not more than 2 mg/kg

Determine using an atomic absorption technique appropriate to the specified level. The selection of sample size and method of sample preparation may be based on the principles of the method described in Volume 4, "Instrumental Methods."

TESTS

PURITY TESTS

Aldehydes and ketones

Principle

The aldehydes and ketones present are converted with 2,4-dinitrophenylhydrazine into the corresponding 2,4-dinitrophenylhydrazones. In alkaline medium these have a red colour, which is determined spectrophotometrically or visually.

Apparatus

- Photoelectric absorptionmeter or spectrophotometer, with 0.5-cm cells. Alternatively flat bottom tubes, capacity about 20 ml
- Water bath, controlled at $60 \pm 1^\circ$

Reagents

The reagents used shall be of a recognized analytical reagent quality.

Distilled water or water of at least equal purity shall be used throughout

- Carbonyl-free methanol: Reflux 1000 ml of methanol with 5 g of 2,4-dinitrophenylhydrazine and 5 drops of concentrated hydrochloric acid ($d = 1.18$) for 2-3 h. Distil off the methanol using a 300 mm by 25 mm diameter Widmer or other suitable distillation column. Reject the first 100 ml and collect the next 800 ml, rejecting the remainder. If, in spite of the precautions taken, the distillate is found to be coloured, then it should be re-distilled.

- 2,4-Dinitrophenylhydrazine solution: Dissolve 0.03 g of 2,4-dinitrophenylhydrazine in 40 ml of the carbonyl-free methanol containing 0.3 ml of concentrated hydrochloric acid ($d = 1.18$) and dilute to the mark in a 50-ml one-mark volumetric flask with the carbonyl-free methanol. Prepare this solution fresh each day.

- Potassium hydroxide solution: Dissolve 10 g of potassium hydroxide in 10 ml of water, cool and dilute to the mark in a 50-ml one-mark volumetric flask with carbonyl-free methanol. Prepare this solution fresh each day.

- Standard acetone solution: Weigh 1.00 g of acetone and dilute to the mark in a one-mark 100 ml volumetric flask with carbonyl-free methanol. Dilute 1.0 ml of this solution to 100 ml with the carbonyl-free methanol. 1 ml of the

diluted solution contains 0.1 mg of acetone.

Procedure

Prepare five solutions by diluting 1.0, 2.0, 4.0, 8.0 and 10.0 ml portions of the standard acetone solution to 25.0 ml with carbonyl-free methanol. To 1.0 ml of each of the solutions thus obtained (containing 0.004 - 0.04 mg of acetone/ml), contained in a test tube fitted with a ground glass stopper, add 1.0 ml of the 2,4-dinitrophenylhydrazine solution. Stopper the tube and heat for 50 min in the water bath at 60°, cool, add 8.0 ml of the potassium hydroxide solution and after 5 to 15 min measure the optical density of each solution at a wavelength of 430 nm using as a blank 1.0 ml of the carbonyl-free methanol treated in the same way. Prepare a calibration chart by plotting weights (in mg) of acetone against corresponding values of optical density.

Dilute 5.0 ml of the sample to 25.0 ml with the carbonyl-free methanol. Transfer 1.0 ml of this solution to a test tube fitted with a ground glass stopper and add 1.0 ml of the 2,4-dinitrophenylhydrazine solution. Stopper the tube and heat for 50 min in the water bath at 60°, cool, add 8.0 ml of the potassium hydroxide solution and after 5 to 15 min measure the optical density of the solution at the wavelength of 430 nm using as a blank 1.0 ml of the carbonyl-free methanol treated in the same way. By reference to the calibration chart prepared as described above, read the acetone content (in mg) of the solution.

The content is not more than 0.03 mg.

METHOD OF ASSAY

Using the procedures for *Gas chromatography* (see Volume 4), establish the following conditions:

Column

- length: 1.8 m
- diameter: 4 mm
- packing: 120-150 mesh Porapak R, or equivalent

Carrier gas: Nitrogen

Flow rate: 25 ml/min

Detector: FID

Temperatures

- injection port: 200°
- column: 160°
- detector: 210°

Prepare a standard solution of 0.4% (v/v) methanol in dioxane. Adjust column temperature and/or gas flow rate so that methanol retention time is about 5-7 min. Adjust detector so that 8 µl of standard solution provides at least one-half scale deflection. Inject 5-10 µl sample, obtain chromatogram and determine methanol content by the method of area normalization.