DICHLOROMETHANE

Prepared at the 51st JECFA (1998), published in FNP 52 Add 6 (1998) superseding specifications prepared at the 39th JECFA (1992), published in FNP 52 Add 1 (1992). ADI "should be limited to current uses", established at the 39th JECFA in 1992.

SYNONYMS Methylene chloride, methylene dichloride

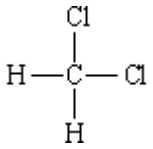
DEFINITION Dichloromethane (DCM) is derived from the chlorination of methane during which other chlorinated methane derivatives may be formed. Propylene oxide, cyclohexane, and/or 2-methyl-2-butene are added as stabilizers. Purity depends on the amount of C_2 and higher hydrocarbons in the methane and the extent of chlorination. Small amounts of several other chlorinated compounds may be present. Dichloromethane is commonly recovered from extraction processes and several grades are commonly found in commerce. Dichloromethane is stable when dry but hydrolyzes in the presence of water.

Chemical names Dichloromethane

C.A.S. number 75-09-2

Chemical formula CH_2Cl_2

Structural formula



Formula weight 84.93

Assay Not less than 99.0%

DESCRIPTION Clear colourless non-flammable liquid

FUNCTIONAL USES Extraction solvent

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4) Sparingly soluble in water; miscible with ethanol and ether

Refractive index (Vol. 4) n^{20}_{D}: 1.423 - 1.425

Specific gravity (Vol. 4) d^{25}_{25}: 1.323 - 1.327

PURITY

Water (Vol. 4) Not more than 0.02% (Karl Fischer Method)

Distillation range (Vol. 4) 39 - 41°

Non-volatile residue (Vol. 4)

Not more than 2 mg/100 ml

Free chlorine

Shake 10 ml of the sample vigorously for 2 min with 10 ml of 10% potassium iodide solution and 1 ml of starch TS. A blue colour does not appear in the water layer.

Acidity

Not more than 0.002% w/w (as HCl)
Place 100 ml of freshly boiled and cooled distilled water (neutralized to phenolphthalein TS) in a 500-ml glass-stoppered conical flask. Add 100 ml of the sample and shake vigorously. Allow the layers to separate, transfer the aqueous phase into an Erlenmeyer flask, add 0.5 ml of phenolphthalein TS and titrate with 0.1 N sodium hydroxide to a red endpoint using a microburette. Calculate any acidity thus found as hydrochloric acid, HCl, per cent by weight of sample. 1 ml 0.1 N NaOH = 0.00365 g HCl

Alkalinity

Not more than 0.01% w/w (as NaOH)
Place 100 ml of freshly boiled and cooled distilled water (neutralized to phenolphthalein TS) in a 500-ml glass-stoppered conical flask. Add 100 ml of the sample and shake vigorously. Allow the layers to separate, transfer the aqueous phase into an Erlenmeyer flask, add 0.5 ml of phenolphthalein TS and titrate with 0.1 N hydrochloric acid using a microburette. Calculate any alkalinity thus found as sodium hydroxide, NaOH, per cent by weight of sample. 1 ml 0.1 N HCl = 0.0040 g NaOH.

Lead (Volume 4)

Not more than 1 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

Lead

Principle
The sample is treated with bromine, heated on a steam bath to decompose the alkyl lead and alkyl lead salts, and then extracted with dilute nitric acid. The pH of the aqueous extract is adjusted by means of a buffer and the lead is extracted with a chloroform solution of dithizone. The absorbance of the chloroform extract is measured and the lead content is determined from a previously prepared calibration curve.

Apparatus
- The glassware should be borosilicate and confirmed to be lead-free.
- Spectrophotometer, fitted with covered absorption cells having a 1-cm light path.
- Shaking machine (optional), capable of approximately 250 rpm.
- Separatory funnels, Squibb-type, 125-ml volume.

Reagents

- Purity of reagents: Reagent grade chemicals shall be used in all tests.
- Purity of water: Unless otherwise indicated, references to water shall be understood to mean distilled water or other water of equivalent purity.
- Bromine Solution: Dilute 300 ml of bromine to 1000 ml with chloroform. Filter through a sintered-glass filter before using. (Do in fume hood).
-Buffer solution: Dissolve 20 g of potassium cyanide (KCN) (Caution), 6 g of ammonium citrate, and 6 g of sodium sulfite (Na_2SO_3), separately in water. Mix the solutions, add 150 ml of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90), and dilute to 1,000 with water. This solution is stable for 3 months (in refrigerator).
- Dithizone solution: Dissolve 30 mg of dithizone in 1000 ml of chloroform. This solution is stable for only 4 weeks.
- Lead standard solution: Dissolve l.5985 g of lead nitrate ($Pb(NO_3)_2$) in 250 ml of water contained in a liter volumetric flask. Add 8 ml of concentrated HNO_3 (sp gr l.42), dilute to volume with water, and mix thoroughly. For calibration purposes, pipet 5.0 ml of this solution into a 1-liter volumetric flask, add 8 ml of concentrated HNO_3 (sp gr 1.42), and dilute to volume with water (1 ml = 0.005 mg Pb).
- Nitric acid (sp gr 1.42): Concentrated nitric acid (HNO_3).
- Nitric acid (8:992): Mix 8 ml of concentrated HNO_3 (sp gr 1.42) with 992 ml of water.

Calibration

Prepare a calibration curve using the lead solution (1 ml = 0.005 mg Pb) as follows: Pipet 0.0, 2.0, 5.0, 10.0, and 15.0 ml of the solution respectively into each of five separatory funnels and dilute each solution to 50 ml with HNO_3 (8:992). Treat these solutions as described in paragraphs 3 and 4, under Procedure, using the one not containing lead as the reagent blank. Construct a calibration curve by plotting the absorbance of the solutions against the mg of lead per 25 ml of dithizone solution.

Procedure

Pipet 50 g of the sample into a 250 ml-beaker. Add bromine solution until the bromine colour persists for at least 2 min, then allow the beaker to stand for an additional 5 min. At the same time prepare a reagent blank by adding the same amount of bromine solution to 25.0 ml of HNO_3 (8:992) in a 250 ml-beaker. Place the beakers on a steam bath and heat until the bromine colour disappears. Place the beakers on a hot plate and bring the solutions to a vigorous boil. Cool to room temperature and transfer each solution quantitatively into separatory funnels using 25.0 ml of HNO_3 (8:992). Shake the test sample for 2 min.

Drain the aqueous extract of the test sample into another separatory funnel. Repeat the extraction of the tests sample using 25.0 ml of HNO_3 (8:992). Drain the aqueous layer into the separatory funnel containing the initial extract. Transfer the reagent blank solution quantitatively to a 50 ml volumetric flask using 25.0 ml of HNO_3 (8:992). Dilute to the mark with water and drain the contents of the flask into a separatory funnel.
Add 120 ml of the buffer solution to both separatory funnels to adjust the pH to a point between 9.5 and 11.0. Pipet 25 ml of dithizone solution and shake for 2 min.

Drain and discard a small portion of the chloroform layer from the funnel to

remove any water or lead that may have accumulated in the stem. Transfer a portion of each chloroform layer into separate absorption cells. Adjust the spectrophotometer to read zero absorbance for the reagent blank and then measure the absorbance of the sample with respect to the blank at a wavelength of 510 nm.

Convert the absorbance measurement to concentration of lead in milligrams of lead per 25 ml of dithizone solution by means of the previously prepared calibration curve.
Calculate the lead content in milligrams per kilogram as follows:

$$\text{Lead, mg/kg} = \frac{1000A}{50} = 20A$$

where A is the lead concentration, in mg per 25 ml of dithizone solution corresponding to the measured absorbance.

METHOD OF ASSAY

Principle
Test material is injected into a suitable gas chromatograph equipped with two capillary gas chromatographic columns connected in series and a flame ionization detector. Quantification of contaminants and added stabilizers is made by comparing peak areas against external standards.

Apparatus
A gas chromatograph equipped with a flame ionization detector and capable of split and splitless capillary column injection. Peak areas of unknowns are compared to external standard solutions by electronic integration. A 25 m by 0.53 mm i.d. fused silica capillary column coated with a 2.0 µm film of 5% phenyl/95% methylsilicone liquid phase (or equivalent) and a 30 m by 0.32 mm i.d. fused silica capillary column coated with 1.8 µm film of (6% cyanopropyl-phenyl)-methylpolysiloxane liquid phase or equivalent are connected in series with the 0.32 mm i.d. column placed ahead of the 0.53 mm i.d. column.

Instrumental conditions:
Temperatures:
Injector: 150^{o}
Detector: 250^{o}
Oven: 40^{o} isothermal
Carrier gas: He 4.4 ml/min
Split flow: 98 ml/min

Standard
A standard solution containing appropriate concentrations of methyl chloride, chloroform, methylene chloride, vinyl chloride, ethyl chloride, vinylidene chloride, 2-methyl-2-butene, trans-1,2-dichloroethylene, cyclohexane, and propylene oxide is prepared in high purity DCM by adding each reagent to DCM in a glass bottle fitted with a silicone rubber septum. Sufficient amounts of each standard analyte are added to the make the approximate concentrations as given below:

Methyl chloride: 0.014% (w/w)
Vinyl chloride: 0.007

Ethyl chloride: 0.0084
Propylene oxide: 2.4
Vinylidene chloride: 0.0098
trans-1,2-Dichloroethylene: 0.017
Chloroform: 0.012
Cyclohexane: 0.047
2-Metyl-2-butene: 0.009

Addition of the analytes to the high purity DCM is made by accurately weighing an appropriate syringe containing the analyte, injecting the analyte into the standard DCM through the septum and re-weighing the syringe to determine the amount of analyte added. The DCM used to make standards must be assayed without added analytes to determine the possible presence of the analytes.

Procedure

The standard solution prepared above is diluted to a series of standards in the range of approximately 10 to 300 ppm (mg/kg) except for propylene oxide which is made in the range of 0.06 to 2.4 (w/w%). Standards and unknowns are injected into the gas chromatograph in the range of 1 to 5 µl (using split injection mode) and the peak areas determined by electronic integration. A standard curve is constructed from these dilutions by plotting peak area against concentration for each analyte. The concentration of additives and by-products are determined by comparison to the standard curve. The sum of the concentrations of the impurities and stabilizers must be less than 1.0%. The order of elution and approximate retention times (min) are:

Methyl chloride: 2.8
Vinyl chloride: 3.0
Ethyl chloride: 3.5
Propylene oxide: 4.1
2-Methyl-2-butene: 4.5
Vinylene chloride: 4.6
Dichloromethane: 5.3
trans-1,2-Dichloroethylene: 5.9
Chloroform: 8.7
Cyclohexane: 10.5
Carbon tetrachloride: 12.0