HEXANES

Prepared at the 51st JECFA (1998), published in FNP 52 Add 6 (1998) superseding specifications prepared at the 14th JECFA (1970), published in NMRS 48B (1971) and in FNP 52 (1992). ADI "limited by GMP" established at the 14th JECFA in 1970.

DEFINITION The product "hexanes" refers to the hexane petroleum hydrocarbon distillation fraction that contains a high proportion of n-hexane. Typically hexanes contain mainly n-hexane, 2-methylpentane, 3-methylpentane or mixtures of these with smaller amounts of n-pentane, isopentane, cyclohexane, n-heptane, dimethylbutanes and methylcyclopentane.

Chemical names: Hexanes

Chemical formula: C_6H_{14}

Formula weight: 86.18

DESCRIPTION Clear colourless highly flammable liquid with a characteristic petroleum-like odour; free from sediment and suspended matter

FUNCTIONAL USES Extraction solvent

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4): Insoluble in water, soluble in ether, alcohol, and acetone

Specific gravity (Vol. 4): d^{20}_{20}: 0.665 - 0.687 (pure n-hexane: about 0.660)

Refractive index (Vol. 4): n^{20}_{D}: 1.381 - 1.384 (pure n-hexane: about 1.375)

PURITY

Distillation range (Vol. 4): 95% v/v distils between 64 to 70°

pH (Vol. 4): Neutral to methyl orange (pH indicator)

Non-volatile residue (Vol. 4): Not more than 0.0005% w/v

Sulfur (Vol. 4): Not more than 5 mg/kg

Benzene: Not more than 0.05% v/v
See description under TESTS

Lead (Vol. 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.”

Polycyclic aromatic hydrocarbon	Passes test See description under TESTS

TESTS

PURITY TESTS

Polycyclic aromatic hydrocarbon	Transfer 25.0 ml of sample to a 125 ml separator and add 25 ml of hexane. Mix and add 5.0 ml of dimethyl sulfoxide. Shake vigorously for 1 min and allow to stand until two clear layers are formed. Transfer the lower layer to a second separating funnel, add 2 ml of hexane and shake the mixture vigorously. Allow to stand until two clear layers are formed. Separate the lower layer and measure its absorbance over the range 260 nm to 420 nm using as reference liquid the clear lower layer obtained by vigorously shaking 5.0 ml of dimethyl sulfoxide with 25 ml of hexane for 1 min. Prepare a reference solution in trimethyl pentane containing 7.0 mg of naphthalene per liter and measure the absorbance of that solution at 275 nm using trimethylpentane as a blank. At no wavelength in the range 260 nm to 420 nm does the absorbance of the test solution exceed one-third that of the reference solution at 275 nm. Use hexane, dimethyl sulfoxide and trimethylpentane in quality specified for ultraviolet spectrophotometry.
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.

Benzene

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Principle

An internal standard, methyl ethyl ketone (MEK) is added to the test hexane which is then introduced into a gas chromatograph equipped with two columns connected by a flow diversion valve (Figure 1). The specimen passes first through a column packed with a non-polar phase, methyl silicone, which separates the non-polar hydrocarbons (column A). After octane has eluted, the flow through the nonpolar column (column A) is reversed and diverted to a second column (column B) containing a highly polar phase. Components which have not eluted column A are thus diverted to column B which separates the aromatic and non-aromatic compounds. The eluted components are detected by a flame ionization detector and recorded on a strip chart. The peak areas are measured and the concentration of each component is calculated by reference to the internal standard.

Apparatus

Chromatograph - Any gas chromatographic that has a backflush system, a flame ionization detector, and suitable electronic recorder.
Columns - one 0.8 m long by 3.2 mm outside diameter stainless steel column packed with 10% methyl silicone coated on 60-80 mesh acid washed diatomaceous earth and one 4.6 m long by 3.2 mm outside diameter stainless steel column packed with 25% 1,2,3-Tris(2-cyanoethoxy) propane (TCEP) coated on 80-100 mesh acid washed diatomaceous earth. Join Columns A and B as shown in Figure 1 using an appropriate flow diverting valve. Adjust the helium gas flow through both columns to approximately 40 ml/min with the flow valve in the forward flow position (Figure 2a). Set the valve in the backflush position and set the flow rate for column B to 40 ml/min (Figure 2b).

Reagents and materials

Reagent grade chemicals shall be used in all tests
Methyl Ethyl Ketone (MEK), >99.9 %
Benzene, >99%
Isooctane, >99%; n-Nonane, >99%

Calibration

Determine time required for before changing the valve (i.e., backflushing), which varies for each column system and must be determined experimentally as follows: Prepare a mixture of 5 volume % isooctane in n-nonane. With the system in the forward flow mode (Figure 2a) inject 1 µl of the isooctane n-nonane mixture and allow both compounds to elute.

Measure the time in seconds from the injection until all the isooctane but none of the n-nonane has eluted. One half of the measured time approximates the time to switch the backflush valve. Repeat the run, including the injection, but switching the system to the backflush mode at the determined backflush time. This should result in a chromatogram of isooctane with little or no n-nonane evident. If necessary, make additional runs, adjusting the time to backflush until a chromatogram of all the isooctane and little or none of the n-nonane is obtained. This established backflush time, including the actual valve operations, must be used in all subsequent calibrations and analyses.

Calibration and standardization

Standard Solutions - Prepare seven standard solutions covering the range of 0 to 1 volume % benzene as follows: For each standard, measure the volume of benzene listed below into a 100 ml volumetric flask. Dilute to volume with isooctane, with all components and glassware at normal room temperature, and mix thoroughly.

Volume %	ml
1	1
0.5	0.5
0.25	0.25
0.10	0.10
0.05	0.05
0.01	0.01
0.005	0.005

Calibration Solutions - Accurately measure 0.5 ml of MEK into a 100-ml volumetric flask, fill to the mark with the first standard solution and mix thoroughly. Repeat with each of the other standard solutions.
Chromatographic Analysis - Using the conditions established above, chromatograph each of the calibration solutions after injecting approximately 3 µl.

Calibration - Measure the areas of the benzene and of MEK peaks. Calculate the ratio of the benzene peak area to the MEK peak area. Plot the concentration of benzene versus the ratio. The calibration must be done to ensure that the chromatographic system is operating properly and that the concentration of any one component has not exceeded the linear response range of any part of the system. The calibration plot should be linear. Determine the retention times for each component for future identification.

Procedure

Test solution - Accurately measure 0.5 ml of MEK into a 100 ml volumetric flask. Fill to the mark with the material under test and mix well. Chromatograph a specimen from the test solution. Identify on the chromatogram the benzene and the internal standard MEK peaks from the retention times of the standards. The order of elution is non-aromatic hydrocarbons, benzene, MEK, and toluene when using the specified columns. Measure the areas under the benzene peak and under the MEK peak.

Calculation

Calculate the ratio of peak area of benzene to the peak area of MEK. Read from the calibration curve the volume % of benzene corresponding to the calculated peak ratio. If the results are desired on a weight basis, convert to weight % as follows:

Benzene, weight % = (V/D) x 0.8844
where
V = benzene, volume %, and D = relative density of sample at 15.6/15.6ºC
Report the benzene content in volume or weight % to the nearest 0.005 %.

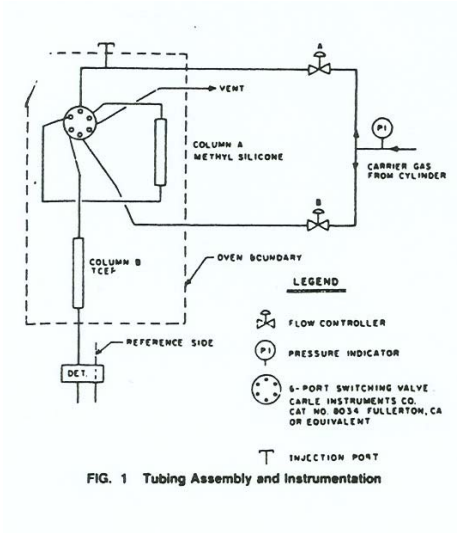

Fig.1 Tubing Assembly and Instrumentation

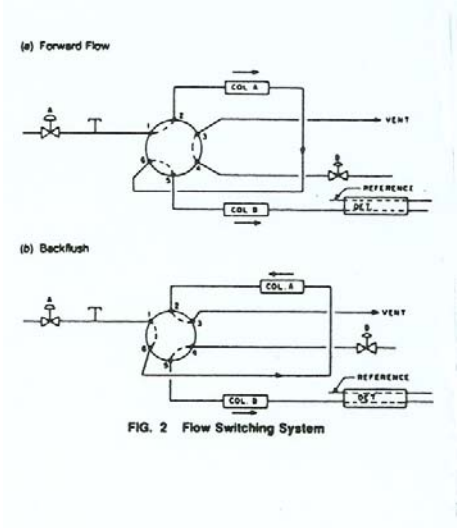

Fig.2 Flow Switching System