



A Honeywell Company

Trace Hydrocarbons in Udex Solvent by GC

UOP Method 919-11

Scope

This method is for determining low concentrations of hydrocarbons in lean UOP Udex™ process solvent. Benzene, toluene, C₈ aromatics composite, and C₉+ aromatics composite are determined. Light non-aromatics through C₉ paraffins, if present, are reported as a composite. Higher non-aromatics, i.e., greater than C₉, may interfere with the determination of benzene. The lower limit of quantitation for each aromatic component is 3 mg/kg (mass-ppm).

References

- ASTM Practice D4307, "Preparation of Liquid Blends for Use as Analytical Standards,"
www.astm.org
- Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, **23**, 333-340 (1985)
- UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is injected into a gas chromatograph that is equipped with a fused silica capillary column internally coated with poly(ethylene glycol), an autosampler, and a flame ionization detector. The concentrations of individual or group impurities are determined by the external standard method of quantitation, wherein peak areas of the sample components are compared to the peak areas of a calibration blend analyzed under identical conditions and injection volumes.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.0001 g

Chromatographic column, 60 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.50 µm with cross-linked poly(ethylene glycol), Restek, Cat. No. 10642

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 3 mg/kg of toluene when operated at the recommended conditions, Agilent Technologies, Model 7890

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).
--

© COPYRIGHT 1992, 2011 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured. Agilent Technologies, ChemStation.

Leak detector, gas, Grace Davison, Cat. No. 60229

Refrigerator, flammable-materials storage, Fisher Scientific, Cat. No. 97-938-1

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Sample injector, any syringe or injector capable of injecting a repeatable 1.0- μ L volume of sample. The use of an automatic injection device is required to achieve necessary repeatable injection volumes. Agilent Technologies, Model 7693.

Vortex mixer, VWR, Cat. No. 58816-121

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Benzene, 99.9% minimum purity, Sigma-Aldrich, Cat. No. 270709

Cumene, 98.0% minimum purity, Sigma-Aldrich, Cat. No. 28230

Ethylbenzene, 99.8% minimum purity, Sigma-Aldrich, Cat. No. 296848

Gas purifier, for hydrogen, to remove oxygen and moisture from carrier gas, VICI Mat/Sen, Cat. No. P200-1, and (optional) indicating oxygen trap, Restek, Cat. No. 22010, see *Procedure, Chromatographic Technique*, Step 1

Hydrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Pipets, disposable, Pasteur, VWR, Cat. No. 14673-043

Pipet bulbs, VWR, Cat. No. 15001-362

Propylene glycol (1,2-propanediol), 99.5% minimum purity, Sigma-Aldrich, Cat. No. 398039

Syringe, replacement, for recommended sample injector, 10- μ L, Agilent Technologies, Cat. No. 5181-1267

Tetraethylene glycol, 99% minimum purity, Sigma-Aldrich, Cat. No. 110175

Toluene, 99.9% minimum purity, Sigma-Aldrich, Cat. No. 650579

Vials, autosampler, for recommended sample injector, with caps, Agilent Technologies, Cat. No. 5182-0864

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used. Replace the gas purifier at intervals determined by good laboratory practice. An indicating oxygen trap may be placed downstream of the gas purifier. When the indicator shows one-half used, replace both the gas purifier and the indicating trap.
2. Install the fused silica capillary column in the gas chromatograph according to the column and gas chromatograph manufacturer's instructions.
 - CAUTION: Hydrogen leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.
 - Different conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figures 1 and 2).

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Mode	constant flow
Flow rate	2.5 mL/min
Head pressure @ 50°C	74 kPa gauge (10.7 psig)
Linear velocity @ 50°C	41 cm/sec
Split flow	250 mL/min
Injection port	
Temperature	280°C
Autoinjector viscosity delay	5 sec
Column temperature program	
Initial temperature	50°C
Initial hold time	0 min
Programming rate	10°C/min
Final hold temperature	250°C
Final Time	20 min
Detector	flame ionization
Detector temperature	280°C
Hydrogen flow rate^a	28 mL/min
Air flow rate^a	400 mL/min
Makeup gas	nitrogen
Makeup gas flow rate^a	30 mL/min
Sample size	1.0 µL, repeatable

^aConsult the manufacturer's instrument manual for suggested flow rates.

4. Program the column oven to 250°C (see Table 1) and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 50°C.

6. Mix the sample by shaking. Fill an autosampler vial with an aliquot of the sample and place in the autosampler (or autoinjector) tray.
 - Multiple samples may be prepared in advance for unattended operation.
7. Inject nominally 1.0 μL (repeatable) of sample into the gas chromatograph and start the data system and the column oven programming sequence.
 - The use of an autoinjector or autosampler automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.
 - To remove residual tetraethylene glycol from the injection port, column, etc., an injection of water is to be made between each sample or blend. Also use water in the syringe wash vial, and replace it after every series of injections.
8. Identify the components in the resultant chromatogram and determine the areas of the impurity peaks.
 - A typical chromatogram is shown in Figure 1. An expanded region is shown in Figure 2.
 - Non-aromatics are determined as a composite group that includes all unidentified components eluting before o-xylene. Typically, all non-aromatics elute before benzene.
 - C_8 aromatics are defined as a composite group that includes ethylbenzene, p-, m-, and o-xylene. The C_8 aromatics may be reported individually or as a composite.
 - C_9+ aromatics are defined as a composite group that includes cumene and all peaks eluting after o-xylene and before propylene glycol. To identify the propylene glycol site, it may be necessary to spike a sample with a small amount of propylene glycol.

Calibration

Quantitative results are based on the injection of repeatable volumes of both the calibration blend and the sample. Absolute response factors, derived from the calibration blend, are used to relate the peak areas of each known component to mg/kg.

1. Prepare 10 g or more of a stock solution as described in ASTM Practice D4307, "Preparation of Liquid Blends for use as Analytical Standards," to contain approximately 1.0 mass-% each of benzene, toluene, ethylbenzene and cumene in tetraethylene glycol, by weight. Thoroughly mix the solution using a vortex mixer. Record all weights to the nearest 0.0001 g.
 - Tetraethylene glycol is used in the blend to represent the Udex solvent, which is usually composed of tetraethylene glycol, triethylene glycol, or mixtures.
 - Obtain the purest tetraethylene glycol possible to prepare the blend. Analyze it, looking for impurities that elute at the benzene, toluene, ethylbenzene and cumene sites. If an impurity in the tetraethylene glycol is present, obtain tetraethylene glycol from a different vendor and check for the impurity. If no tetraethylene glycol can be found without an impurity at the benzene, toluene, ethylbenzene and cumene sites, correct for the impurity as described in ASTM Practice D4307.
2. From the recorded weights, calculate the concentrations of each of the analytes in the stock solution to three significant figures using Equation 1 or the procedure described in ASTM Practice D4307:

$$A = 100 \frac{B}{C} \quad (1)$$

where:

- A** = concentration of each analyte in the stock solution, mass-%
- B** = mass of each analyte in the stock solution, g
- C** = total mass of the stock solution prepared, g
- 100** = factor to convert to mass-%

3. Prepare 10 g or more of a calibration blend containing approximately 1.0 mass-% of stock solution in tetraethylene glycol. Thoroughly mix the calibration blend using a vortex mixer. Record all weights to the nearest 0.0001 g.
 - If refrigerated, the stock solution and calibration blend should remain stable for six months.
4. Calculate the concentration of benzene, toluene, ethylbenzene and cumene in the calibration blend to the nearest mg/kg using Equation 2 or the procedure described in ASTM Method D4307. Using the above dilutions, the resulting calibration blend should contain approximately 100 mg/kg of each added component.

$$M = 10^4 \frac{AD}{E} + F \quad (2)$$

where:

- A** = concentration of each analyte in the stock solution, from Equation 1, mass-%
- D** = mass of stock solution in the calibration blend, g
- E** = total mass of the stock solution prepared, g
- F** = concentration of benzene, toluene, ethylbenzene, or cumene, if any, in the tetraethylene glycol, mg/kg
- M** = concentration of benzene, toluene, ethylbenzene, or cumene in the calibration blend, mg/kg
- 10⁴** = factor to convert mass-% to mg/kg

5. Analyze the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*.
 - The peak areas from each of the triplicate runs should not deviate from the average by more than 2% (relative) of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make additional runs until the required repeatability is obtained on three consecutive runs.
 - Confirm the stability of the chromatographic system by analyzing the calibration blend again at the end of a series of analyses. If the results differ by more than 5% from the average of the triplicate runs, a problem has developed with the chromatographic system, and the series of samples must be rerun after the problem is resolved. Typical problems to look for include a leaky septum and a dirty or partially plugged syringe.
6. Use the average peak areas to calculate the absolute response factor for benzene, toluene, ethylbenzene, or cumene, to three significant figures, using Equation 3.

$$L = \frac{M}{P} \quad (3)$$

where:

- L** = absolute response factor for benzene, toluene, ethylbenzene, or cumene
- M** = concentration of benzene, toluene, ethylbenzene, or cumene in the calibration blend, from Equation 2, mg/kg
- P** = average peak area for benzene, toluene, ethylbenzene, or cumene in the calibration blend

7. Multiply the absolute response factor determined for benzene by 1.10 to obtain the absolute response factor for non-aromatics.
 - Non-aromatics are not easily soluble in tetraethylene glycol, therefore no non-aromatic component is included when preparing the calibration blend. The 1.10 factor relative to benzene is determined using the effective carbon number (ECN) concept as described by Scanlon and Willis.
8. Use the absolute response factor for ethylbenzene to calculate the concentration of the C₈ aromatics, and the absolute response factor for cumene to calculate the concentration of the C₉+ aromatics.

Calculations

Obtain peak areas for each individual component or group of components and calculate the composition of the sample to the nearest mg/kg using Equation 4. Use the absolute response factor for ethylbenzene to calculate the concentration of each of the C₈ aromatics, and the absolute response factor for cumene to calculate the concentration of the C₉+ aromatics.

$$\text{Component, mg/kg} = LS \quad (4)$$

where:

L = absolute response factor, previously defined, Equation 3

S = peak area of individual component or group of components

Report each measured component or group of components to the nearest mg/kg.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from precision data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining impurities in two Udex solvent samples by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence.

Table 2
Repeatability and Site Precision, mg/kg

<u>Component</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Non-aromatics	11	0.7	2	0.6	2
Benzene	47	0.1	0	0.6	4
Benzene	256	1.1	4	2.4	14
Toluene	25	0.1	0	0.3	2
Toluene	186	0.8	3	1.2	5
C₈ Aromatics	63	0.3	1	0.3	1
C₈ Aromatics	373	1.7	5	2.4	11
C₉+ Aromatics	10	0.3	1	0.4	1
C₉+ Aromatics	117	1.2	4	1.1	4

The data in Table 2 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis is 0.9 hour. The labor requirement is 0.3 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610, USA (302-633-8000)
www.agilent.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300)
www.fishersci.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600)
www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936, USA (215-641-2700)
www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA (814-353-1300) www.restek.com

Sigma-Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233, USA (414-273-3850)
www.sigma-aldrich.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055, USA (713-688-9345) www.vicimatsen.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA (610-431-1700)
www.vwr.com

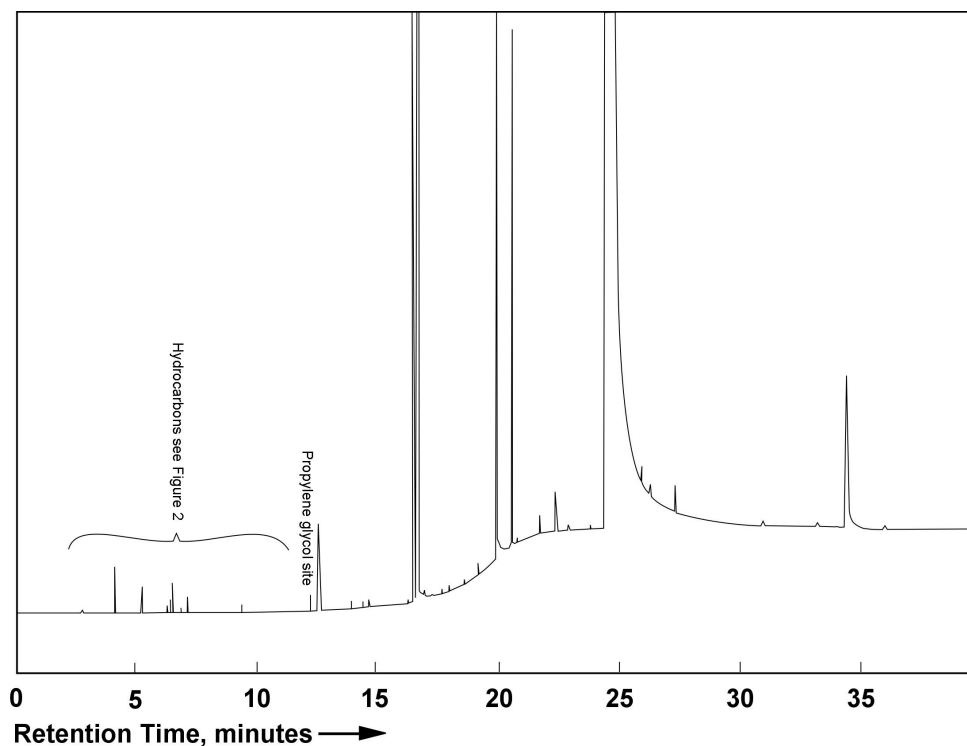


Figure 1
Typical Chromatogram

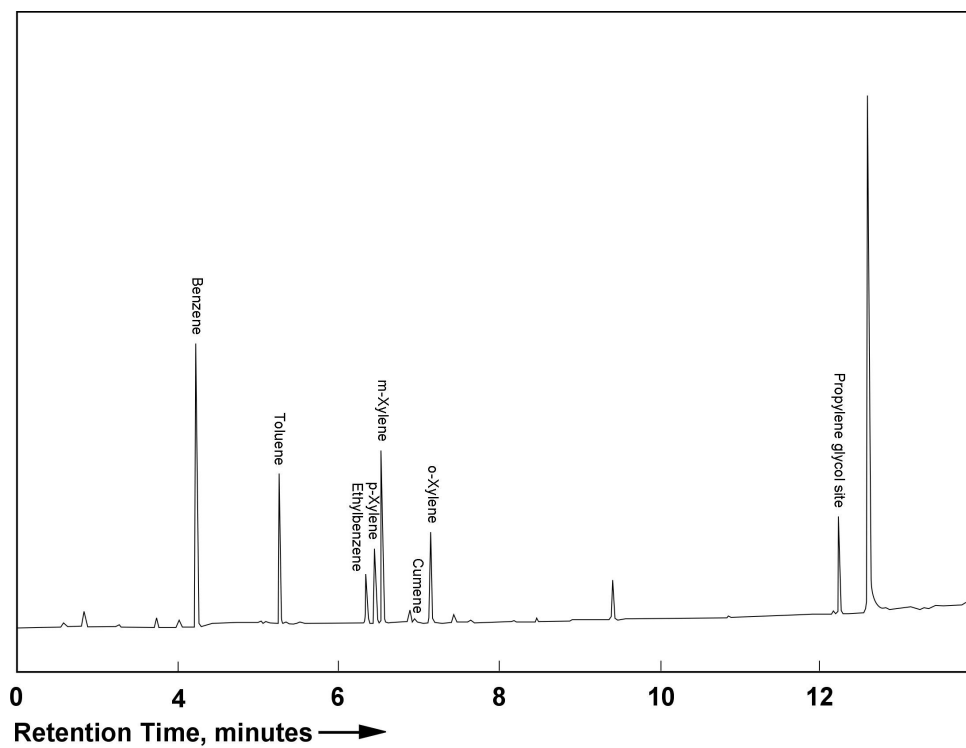


Figure 2
Typical Chromatogram, Expanded