

AROMATICS IN MOLEX™ PROCESS *n*-PARAFFIN PRODUCTS BY ULTRAVIOLET SPECTROPHOTOMETRY

UOP™ Method 495-03

SCOPE

This method is for estimating total aromatics in Molex process *n*-paraffin products. The method determines an average amount of naphthalenes and alkylbenzenes that may be present, provided the concentration of the alkylbenzenes is at least ten times greater than the naphthalenes. In practice, this condition is satisfied for the specified applications. Other samples with similar compositions may also be suitable for this analysis. The lower limit of detection is 0.0003 mass-%.

REFERENCES

- API Project 44, American Petroleum Institute, 1220 L Street, N.W., Washington, DC 20005 (202-682-8000) www.api.org
ASTM™ Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org
UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

OUTLINE OF METHOD

The ultraviolet absorbance spectrum of the sample is measured. Average absorptivities from published spectral data are used to compute the concentrations of the naphthalenes and alkylbenzenes. Sample complexity does not permit experimental calibration.

APPARATUS

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

Absorption cells, matched pairs, silica, 10-, 5- and 1-cm, Fisher Scientific, Cat. Nos. 14-385-930F, -930E, and -904C, respectively

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).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19442-2959, United States. The 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.

Balance, readability 0.1-mg

Flasks, volumetric, Class A, 25-mL, Fisher Scientific, Cat. No. 10-210-5A, several required

Spectrophotometer, capable of scanning and operation in the 360-220-nm region with a spectral bandwidth of 1 nm and capable of 0.5% precision in absorbance measurements at the 1.0 level at this resolution

Vacuum source, a water aspirator, Fisher Scientific, Cat. No. 09-960-2, is sufficient

REAGENTS AND MATERIALS

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

Isooctane, spectroscopic grade, Fisher Scientific, Cat. No. 0300-4

CALIBRATION

Instead of directly calibrating the spectrophotometer with known naphthalenes, the average absorptivities of the C₁₀ through C₁₃ naphthalenes at 285 nm, 33.7 L/g-cm, and, near 270 nm, 30.0 L/g-cm, are used in this method (see Table 1). Similarly, the average absorptivity of available C₁₀ to C₂₀ alkylbenzenes near 270 nm, 3.01 L/g-cm, is used (see Table 2).

Absorptivities of individual naphthalene and alkylbenzene hydrocarbons at their respective wavelengths are derived from data in the API catalog of ultraviolet spectral data issued by Research Project 44, and are listed in Tables 1 and 2.

Table 1
Naphthalene Absorptivities, L/g-cm

Compound	API Serial Number	285 nm	Near 270 nm
Naphthalene	605	28.5	32.6
1-Methylnaphthalene	539	32.0	32.0
2-Methylnaphthalene	572	22.9	31.8
1,2-Dimethylnaphthalene	215	37.3	26.5
1,3-Dimethylnaphthalene	216	36.4	26.5
1,4-Dimethylnaphthalene	217	43.5	26.0
1,5-Dimethylnaphthalene	218	54.0	29.0
1,6-Dimethylnaphthalene	219	36.4	35.0
1,7-Dimethylnaphthalene	220	36.0	32.5
1,8-Dimethylnaphthalene	221	46.0	30.0
2,3-Dimethylnaphthalene	222	22.0	30.0
2,6-Dimethylnaphthalene	226	21.3	27.5
2,7-Dimethylnaphthalene	224	23.5	29.5
1-Isopropylnaphthalene	203	31.7	31.7
Average		33.7	30.0

Table 2
Alkylbenzene Absorptivities, L/g-cm

Compound	API Serial Number	Near 270 nm
Tetralin	133	4.45
2-Methyltetralin	398	3.83
5-Methyltetralin	134	1.89
6-Methyltetralin	135	5.41
6-<i>n</i>-heptyltetralin	287	4.96
<i>n</i>-Butylbenzene	176	1.82
1,4-Diethylbenzene	188	3.05
<i>n</i>-Hexylbenzene	143	1.40
1,4-Diisopropylbenzene	191	2.19
<i>n</i>-Octylbenzene	144	1.40
<i>n</i>-Undecylbenzene	146	2.50
<i>n</i>-Tetradecylbenzene	394	2.39
1,1-Diphenylethane	199	2.65
1,1-Diphenylbutane	200	2.72
1,4-Diphenylbutane	283	4.50
Average		3.01

PROCEDURE

The size of the cells to be used (10-, 5- or 1-cm) is determined by the concentration expected in the samples. If an estimate is not available, use the 1-cm pair first, and switch to the 5- or 10-cm pair only if greater sensitivity is required. The detection limit for this method is based upon the use of a 10-cm cell for alkylbenzenes.

1. Fill a matched pair of absorption cells with isooctane and place them in their respective beam paths. Perform a background correction by scanning in the region from 360 to 220 nm.
2. Empty the sample cell and dry it using the vacuum.
3. Transfer the sample, as received, into the cell and return it to the spectrophotometer.
4. Obtain the spectrum from 360 to 220 nm. Typical examples are shown in Figures 1 and 2.
5. If the absorbance maximum near 270 nm exceeds 1.0, sample dilution is required. (Some instrument manufacturers may recommend a different maximum; follow the manufacturer's recommendations.) Proceed to Step 7 if the sample requires dilution.
6. If the sample does not require dilution, obtain the density of the as received sample using ASTM Method D 4052, Density and Relative Density of Liquids by Digital Density Meter (or equivalent), see *NOTE 1*. If the absorbance maximum near 270 nm is less than 0.1, proceed to Step 11, otherwise, proceed to Step 12.
7. Dilute sequentially with isooctane until the absorbance is within the recommended range (0.1 to 1.0). Weigh a portion of the sample to the nearest 0.1-mg, into a 25-mL volumetric flask. Dilute to volume, cap, and invert several times to thoroughly mix the contents.
8. Empty the sample cell, clean with isooctane, and dry.

9. Fill the sample cell with the diluted sample and return the cell to the instrument sample beam.
10. Obtain the spectrum of the diluted sample from 360 to 220 nm. Go to Step 12.
11. If greater sensitivity is required, use the 5- or 10-cm matched pairs of cells. Perform Steps 1 through 4 with the longer path length cells. Then go to Step 12.
 - Use 10-cm cells if the absorbance using the 1-cm cell is well below 0.1. Use 5-cm cells if the absorbance using the 1-cm cell is near 0.1 or the supply of sample is limited. Do not use 5- or 10-cm cells for diluted samples.
12. Calculate the naphthalene and alkylbenzene concentrations in the sample.

CALCULATIONS

Significant Figures

When using the equations that follow, carry a minimum of three significant figures through all calculations. When reporting final alkylbenzenes and naphthalenes, report a single significant figure for data below 0.1 mass-% and two significant figures at or above 0.1 mass-%.

Baseline Correction

The procedure below describes the determination and use of baseline correction by mathematical means. If it is desired to perform the baseline correction manually, see *NOTE 2*.

Calculate the baseline corrected absorbances (Figures 1 and 2) by the following equations:

$$A_b^{270} = A^{270} - A^{320} - 1.25(A^{320} - A^{360}) \quad (1)$$

$$A_b^{285} = A^{285} - A^{320} - 0.88(A^{320} - A^{360}) \quad (2)$$

where:

A^{270} = maximum absorbance measured near 270 nm

A^{285} = absorbance measured at 285 nm

A^{320} = absorbance measured at 320 nm

A^{360} = absorbance measured at 360 nm

A_b^{270} = baseline corrected absorbance near 270 nm (at A^{270} maximum)

A_b^{285} = baseline corrected absorbance at 285 nm

1.25 = constant = $(320 - 270)/(360 - 320)$

0.88 = constant = $(320 - 285)/(360 - 320)$

Calculations for as received samples, and for samples requiring dilution, are different. Naphthalenes interfere with the alkylbenzenes determination and a correction is made for their effect.

As Received Samples

Spectra of samples run as received may be obtained using 1-, 5- or 10-cm cells; the longer path lengths are used to maximize sensitivity

$$\text{Naphthalenes, mass-\%} = 100 \frac{A_b^{285}}{33.7BD} \quad (3)$$

where:

- A_b^{285} = previously defined, Equation 2
 B = cell path length, cm
 D = density of as received sample, g/L (see *NOTE 1*)
 33.7 = average absorptivity, or calibration coefficient, of naphthalenes listed in Table 1, L/g-cm
 100 = conversion factor, g/g to mass-%

$$\text{Alkylbenzenes, mass-\%} = 100 \frac{A_b^{270} - 0.89A_b^{285}}{3.01BD} \quad (4)$$

where:

- A_b^{270} = previously defined, Equation 1
 A_b^{285} = previously defined, Equation 2
 B = previously defined, Equation 3
 D = previously defined, Equation 3
 0.89 = constant, ratio of average naphthalene absorptivities at 270 nm over 285 nm (30.0/33.7), from Table 1
 3.01 = average absorptivity, or calibration coefficient, of alkylbenzenes listed in Table 1, L/g-cm
 100 = factor to convert g/g to mass-%

Diluted Samples

Spectra of diluted samples are obtained using 1-cm cells.

$$\text{Naphthalenes, mass-\%} = 100 \frac{A_b^{285}}{33.7BF} \quad (5)$$

where:

- A_b^{285} = previously defined, Equation 2
 B = previously defined, Equation 3
 F = concentration of sample in dilution, g/L (see *NOTE 1*)
 33.7 = average absorptivity, or calibration coefficient, of naphthalenes listed in Table 1, L/g-cm
 100 = conversion factor, g/g to mass-%

$$\text{Alkylbenzenes, mass-\%} = 100 \frac{A_b^{270} - 0.89A_b^{285}}{3.01BF} \quad (6)$$

where:

- A_b^{270} = previously defined, Equation 1
 A_b^{285} = previously defined, Equation 2
 B = previously defined, Equation 3
 F = previously defined, Equation 4

0.89 = constant, ratio of average naphthalene absorptivities at 270 nm over 285 nm (30.0/33.7), from Table 1

3.01 = previously defined, Equation 3

100 = factor to convert g/g to mass-%

NOTE

1. The units of density used in this method are g/L, not the common g/mL. Multiply the values obtained from ASTM Method D 4052 by 1000 to obtain g/L.
2. For Manual Baseline Correction, draw a straight baseline from approximately 360 nm to 320 nm, extrapolating beyond 270 nm, see Figures 1 and 2. Determine the baseline corrected absorbances, in absorbance units, of the sample at 285 nm and at the maximum absorbance near 270 nm. Define the absorbance at 285 nm, above the background baseline, as A_b^{285} . Define the maximum absorbance near 270 nm, above the background baseline, as A_b^{270} . Proceed with the calculations under *As Received Samples* or *Diluted Samples*.

PRECISION

The precision statements were determined using UOP Method 999.

ASTM and UOP Repeatability

A nested design was carried out for determining alkylbenzene and naphthalene in *n*-paraffins with two analysts in one laboratory. Each analyst carried out four tests at each of two concentrations on two separate days. The total number of tests at each concentration was 16. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated for each concentration and is listed in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 3 with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference shown in Table 3 with 95% confidence.

Table 3
ASTM and UOP Repeatability

<u>Mean Concentration</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
	<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Sample 1				
Alkylbenzene, 11 mass-%	0.015	0.05	0.038	0.2
Naphthalene, 0.2 mass-%	0.00057	0.002	0.00112	0.004
Sample 2				
Alkylbenzene, 0.01 mass-%	0.000038	0.0001	0.0001	0.0005
Naphthalene, 0.003 mass-%	0.000004	0.00001	0.00001	0.00006

The data in Table 3 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time and labor requirement for a single analysis are identical, 0.7 hours.

SUGGESTED SUPPLIER

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

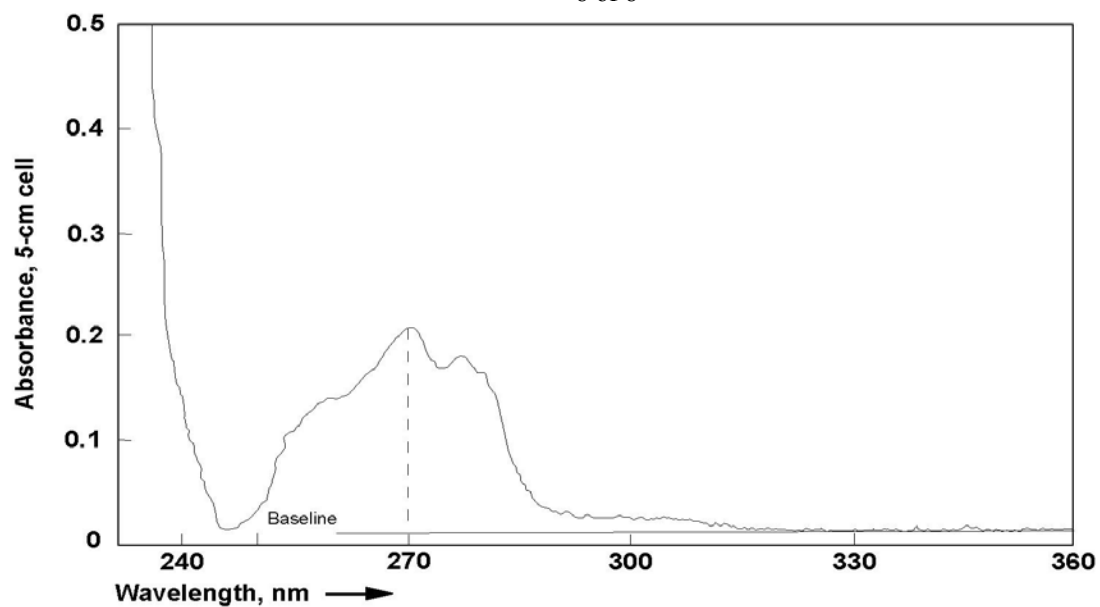


Figure 1
Ultraviolet Spectrum of 18 ppm Alkylbenzenes in Molex *n*-Paraffins

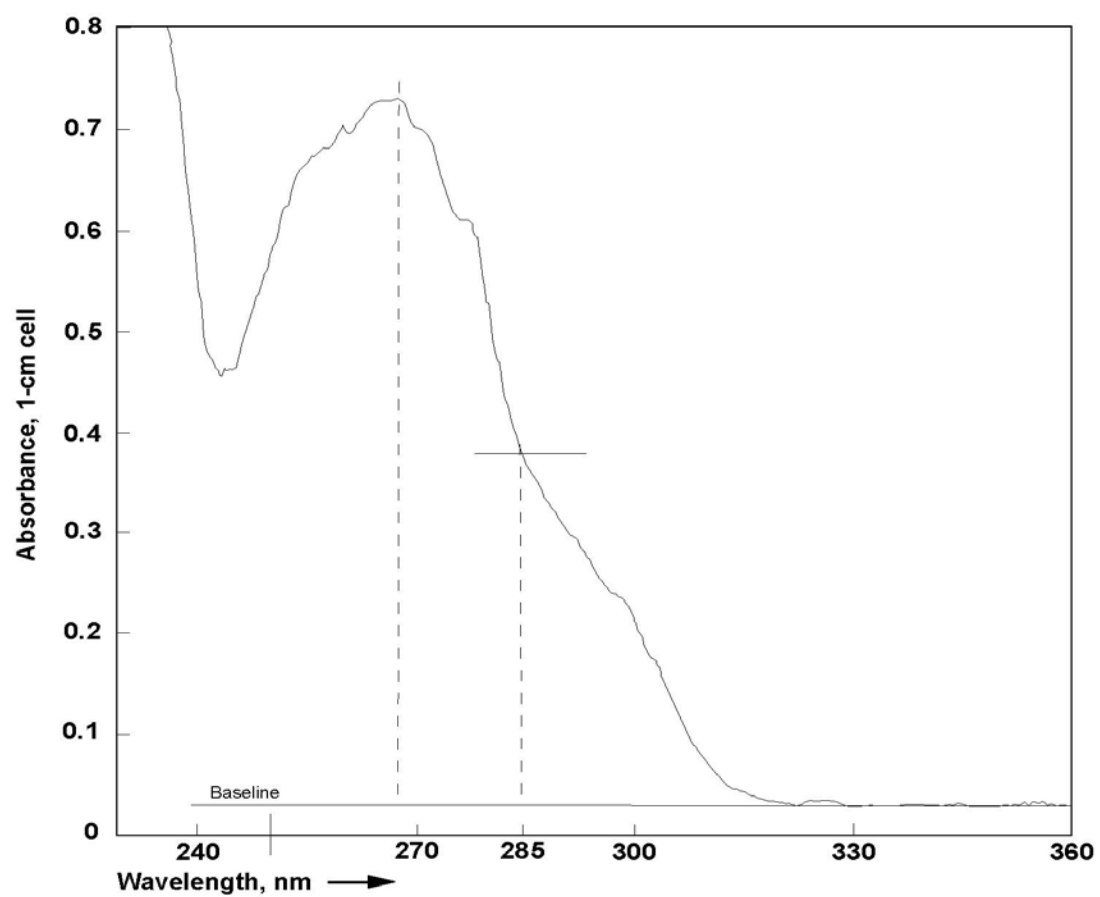


Figure 2
Ultraviolet Spectrum of ca. 1% Aromatics in Molex *n*-Paraffins