

Trace p-DEB or Indan in C₈ Aromatics and Trace C₈ Aromatics in p-DEB by GC

UOP Method 798-13

Scope

This gas chromatographic method is for determining trace amounts of p-diethylbenzene (p-DEB) or trace amounts of indan as impurities in C₈ and lower boiling aromatic streams. High levels of other C₉ or C₁₀ aromatics may interfere with the determination of trace p-DEB and indan in C₈ aromatics. The method can also be used for determining trace amounts of C₈ aromatics in p-DEB. The C₈ aromatic isomers are resolved and determined individually. The lower limit of quantitation for p-DEB or indane is 0.5 mass-ppm and for each xylene isomer it is 2 mass-ppm.

References

ASTM Practice D4307, "Preparation of Liquid Blends for Use as Analytical Standards,"
www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

Two gas chromatographic analyses are required. One set of conditions is used to determine trace p-DEB and indan in C₈ aromatics (Analysis A). Different conditions are required to determine trace C₈ aromatics in p-DEB (Analysis B). In both analyses, a repeatable volume of sample is injected into a gas chromatograph equipped with a fused silica capillary column internally coated with 1,2,3-tris (2-cyanoethoxy) propane (TCEP), and a flame ionization detector. The concentrations of individual 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, readable to 0.0001 g

Chromatographic column, 60 m of 0.25-mm ID fused silica capillary, internally coated to a film thickness of 0.4-μm with TCEP, Restek, Cat. No. 10999

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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 one mass-ppm of p-DEB when operated at the recommended conditions, Agilent Technologies, Model 7890A, with autosampler capable of injecting both a repeatable 0.5- μ L and 1.0- μ L volume of sample, Agilent Technologies, Model 7693A

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

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

Decane, 99% minimum purity, Sigma-Aldrich, Cat. No. D901

p-Diethylbenzene (1,4-diethylbenzene or p-DEB), 96% minimum purity, Sigma-Aldrich, Cat. No. D91004

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

Indan, 95% minimum purity, Sigma-Aldrich, Cat. No. I1804

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

Syringe, replacement, for recommended autosampler, 5- μ L, Agilent Technologies, Cat. No. 5181-1273

Vials, 22- and 30-mL, with polyseal-lined caps, VWR, Cat. Nos. 16087-068 and -058, respectively

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

m-Xylene (1,3-dimethylbenzene), 99% minimum purity, Sigma-Aldrich, Cat. No. 296325

o-Xylene (1,2-dimethylbenzene), 99.0% minimum purity, Sigma-Aldrich, Cat. No. 95662

p-Xylene (1,4-dimethylbenzene), 99.0% minimum purity, Sigma-Aldrich, Cat. No. 95682

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

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 Chromatograms (see Figures 1 - 4).

Table 1
Recommended Operating Conditions

	Analysis A Trace p-DEB/Indan	Analysis B Trace C₈ Aromatics
Carrier gas	hydrogen	hydrogen
Mode	constant flow	constant flow
Flow rate	1.6 mL/min	1.8 mL/min
Head pressure	139 kPa (20.2 psig) @ 120°C	121 kPa (17.5 psig) @ 50°C
Linear velocity	40 cm/sec @ 120°C	40 cm/sec @ 50°C
Split flow	50 mL/min	90 mL/min
Injection port temperature	200°C	200°C
Column temperature program		
Initial temperature	120°C	50°C
Initial time	6 min	20 min
Programming rate	10°C/min	10°C/min
Final temperature	130°C	130°C
Final time	15 min	15 min
Detector		
Temperature	250°C	250°C
Hydrogen flow rate^a	30 mL/min	30 mL/min
Air flow rate^a	400 mL/min	400 mL/min
Makeup gas	nitrogen	nitrogen
Makeup gas flow rate^a	30 mL/min	30 mL/min
Sample size	1.0 µL, repeatable	0.5 µL, repeatable

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

4. Program the column oven to 130°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 initial temperature according to the analysis being performed.
6. Mix the sample by shaking. Fill an autosampler vial with an aliquot of the sample and place it in the autosampler tray.
 - Multiple samples may be prepared in advance for unattended operation.
7. Inject nominally 0.5-μL or 1.0-μL (repeatable) of sample into the gas chromatograph, according to the analysis being performed (see Table 1), and start the data system and the column oven programming sequence.
 - The use of an autosampler automates the injection of the sample into the GC, starts the data system, and the GC oven program simultaneously.
8. Identify the components in the resultant chromatogram and determine the areas of the impurity peaks.
 - Typical chromatograms are shown in Figures 1 and 3 with expanded regions shown in Figures 2 and 4.

Calibration – Analysis A

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 the Analysis 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 p-DEB and indan in p-xylene, by weight. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.0001 g.
 - Obtain the purest p-xylene possible to prepare the blend. Analyze it, looking for impurities that elute at the p-DEB and indan sites. If an impurity in the p-xylene is present, obtain p-xylene from a different vendor and check for the impurity. If no p-xylene can be found without an impurity at the p-DEB and indan 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 Analysis A 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 Analysis A stock solution, mass-%
- B** = mass of each analyte in the Analysis A stock solution, g
- C** = total mass of the Analysis A stock solution prepared, g
- 100** = factor to convert to mass-%

3. Prepare 10 g or more of the Analysis A intermediate blend solution containing approximately 1.0 mass-% of the Analysis A stock solution in p-xylene. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.0001 g.
4. From the recorded weights, calculate the concentrations of each of the analytes in the Analysis A intermediate blend solution to three significant figures using Equation 2 or the procedure described in ASTM Practice D4307. The intermediate blend solution should contain approximately 0.01 mass-% each of p-DEB and indan in p-xylene.

$$D = A \frac{E}{F} \quad (2)$$

where:

A = concentration of each analyte in the Analysis A stock solution, from Equation 1, mass-%

D = concentration of each analyte in the Analysis A intermediate blend solution, mass-%

E = mass of the Analysis A stock solution, g

F = total mass of the Analysis A intermediate blend solution prepared, g

5. Prepare 10 g or more of the Analysis A calibration blend containing approximately 5.0 mass-% of Analysis A intermediate blend solution in p-xylene. Thoroughly mix the solution by shaking. Record all weights to the nearest 0.0001 g.
 - If refrigerated, the stock solution, secondary blend solution and calibration blend should remain stable for six months. If the response factors change more than 10% from when the blend was initially prepared and analyzed, prepare and use a new stock solution, secondary blend solution and calibration blend.
6. Calculate the concentration of p-DEB and indan in Analysis A calibration blend to the nearest mg/kg using Equation 3 or the procedure described in ASTM Practice D4307. Using the above dilutions, the resulting Analysis A calibration blend should contain approximately 5 mg/kg of each added component.

$$J = 10^4 \frac{DG}{H} + I \quad (3)$$

where:

D = concentration of each analyte in the Analysis A intermediate blend solution, from Equation 2, mass-%

G = mass of the Analysis A intermediate blend solution in the calibration blend, g

H = total mass of the Analysis A calibration blend solution prepared, g

I = concentration of p-DEB or indan, if any, in the p-xylene, mg/kg

J = concentration of p-DEB or indan in the calibration blend, mg/kg

10⁴ = factor to convert mass-% to mg/kg

7. 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 daily 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.
8. Use the average peak areas to calculate the absolute response factor for p-DEB and indan in p-xylene, by weight, to three significant figures, using Equation 4.

$$L = \frac{J}{K} \quad (4)$$

where:

L = absolute response factor for p-DEB or indan

J = concentration of p-DEB or indan in the calibration blend, from Equation 3, mg/kg

K = average peak area for p-DEB or indan in the calibration blend

Calibration – Analysis B

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 the Analysis B 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 ethylbenzene, m-xylene, o-xylene and p-xylene in decane, by weight. Thoroughly mix the solutions by shaking. Record all weights to the nearest 0.0001 g.
 - Obtain the purest decane possible to prepare the blend. Analyze it, looking for impurities that elute at the ethylbenzene, m-xylene, o-xylene and p-xylene sites. If an impurity in the decane is present, obtain decane from a different vendor and check for the impurity. If no decane can be found without an impurity at the ethylbenzene, m-xylene, o-xylene and p-xylene 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 Analysis B stock solution to three significant figures using Equation 5 or the procedure described in ASTM Practice D4307:

$$N = 100 \frac{O}{P} \quad (5)$$

where:

- N** = concentration of each analyte in the Analysis B stock solution, mass-%
- O** = mass of each analyte in the Analysis B stock solution, g
- P** = total mass of the Analysis B stock solution prepared, g
- 100** = factor to convert to mass-%

3. Prepare 20 g or more of the Analysis B calibration blend containing approximately 0.5 mass-% of Analysis B stock solution in decane. Thoroughly mix the solutions by shaking. Record all weights to the nearest 0.0001 g.
 - If refrigerated, the stock solution and calibration blend should remain stable for six months. If the response factors change more than 10% from when the blend was initially prepared and analyzed, prepare and use a new stock solution and calibration blend.
4. Calculate the concentration of ethylbenzene, m-xylene, o-xylene and p-xylene in the Analysis B calibration blend to the nearest mg/kg using Equation 6 or the procedure described in ASTM Practice D4307. Using the above dilutions, the resulting calibration blend should contain approximately 50 mg/kg of each added component.

$$Q = 10^4 \frac{NR}{S} + T \quad (6)$$

where:

- N** = concentration of each analyte in the Analysis B stock solution, from Equation 5, mass-%
- R** = mass of the Analysis B stock solution in the Analysis B calibration blend, g
- S** = total mass of the Analysis B calibration blend prepared, g
- T** = concentration of ethylbenzene, m-xylene, o-xylene or p-xylene, if any, in the decane, mg/kg
- Q** = concentration of ethylbenzene, m-xylene, o-xylene or p-xylene in the Analysis B 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 daily 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 ethylbenzene, m-xylene, o-xylene and p-xylene in decane, by weight to three significant figures, using Equation 7.

$$U = \frac{Q}{V} \quad (7)$$

where:

U = absolute response factor for ethylbenzene, m-xylene, o-xylene or p-xylene

Q = concentration of ethylbenzene, m-xylene, o-xylene or p-xylene in the Analysis B calibration blend, from Equation 6, mg/kg

V = average peak area for ethylbenzene, m-xylene, o-xylene or p-xylene in the Analysis B calibration blend

Calculations – Analysis A

Obtain peak areas for each individual component and calculate the composition of the sample to the nearest 0.1 mg/kg below 10 mg/kg, and to the nearest mg/kg above 10 mg/kg, using Equation 8.

$$\text{Component, mg/kg} = LM \quad (8)$$

where:

L = absolute response factor, previously defined, Equation 4

M = peak area of individual component

Calculations - Analysis B

Obtain peak areas for each individual component and calculate the composition of the sample to the nearest 0.1 mg/kg below 10 mg/kg, and to the nearest mg/kg above 10 mg/kg, using Equation 9.

$$\text{Component, mg/kg} = 0.847 UW \quad (9)$$

where:

U = absolute response factor, previously defined, Equation 7

W = peak area of individual component

0.847 = correction for the difference in density between the decane external standard solution and the p-DEB sample, $0.730 \div 0.862$

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 a p-xylene sample by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 12 analyses for Analysis A. Using a stepwise analysis of variance procedure, the within-day and within-lab 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

Component	Mean	Repeatability		Site Precision	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
p-DEB	11.0	0.05	0.2	0.09	0.6
Indane	2.3	0.05	0.2	0.05	0.2

A nested design was carried out for determining impurities in a p-diethylbenzene sample by three analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 18 analyses for Analysis B. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. 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 3 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 3 with 95% confidence.

Table 3
Repeatability and Site Precision, mg/kg

Component	Mean	Repeatability		Site Precision	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
Ethylbenzene	8.4	0.15	0.5	0.15	0.5
p-Xylene	12.5	0.11	0.3	0.18	0.6
m-Xylene	35.5	0.32	1.0	0.44	1.4
o-Xylene	5.0	0.21	0.7	0.33	1.1

The data in Tables 2 and 3 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 Analysis A is 0.3 hour. The elapsed time for Analysis B is one hour. The labor requirement is 0.3 hour for each analysis (A and B).

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 Ave., 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

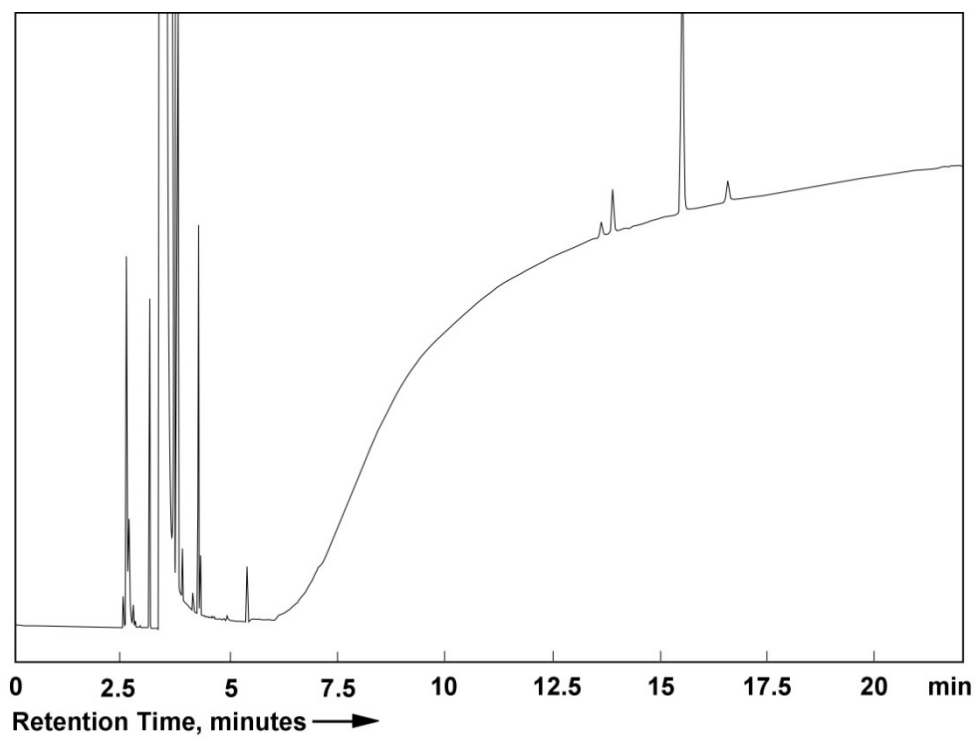


Figure 1
Typical Chromatogram, Analysis A

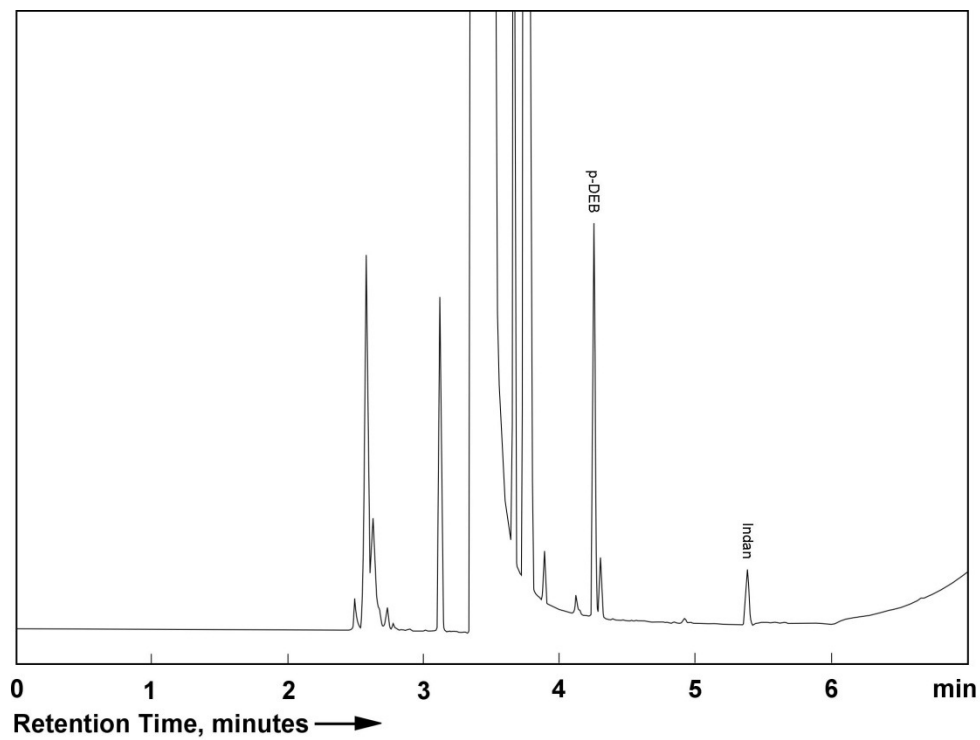


Figure 2
Typical Chromatogram, Analysis A Expanded

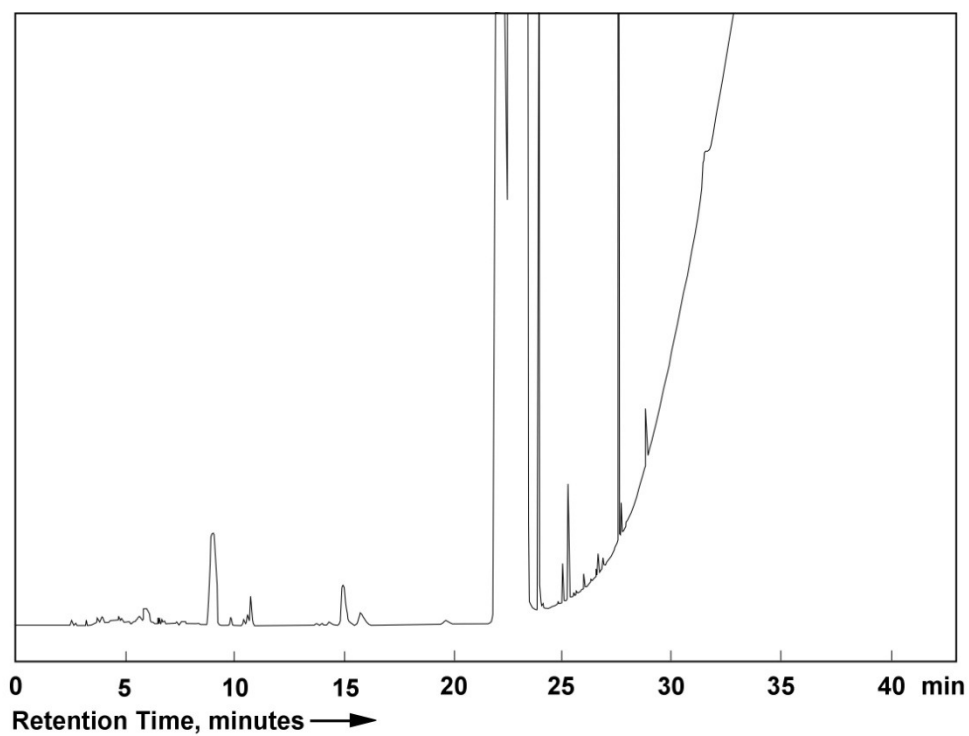


Figure 3
Typical Chromatogram, Analysis B

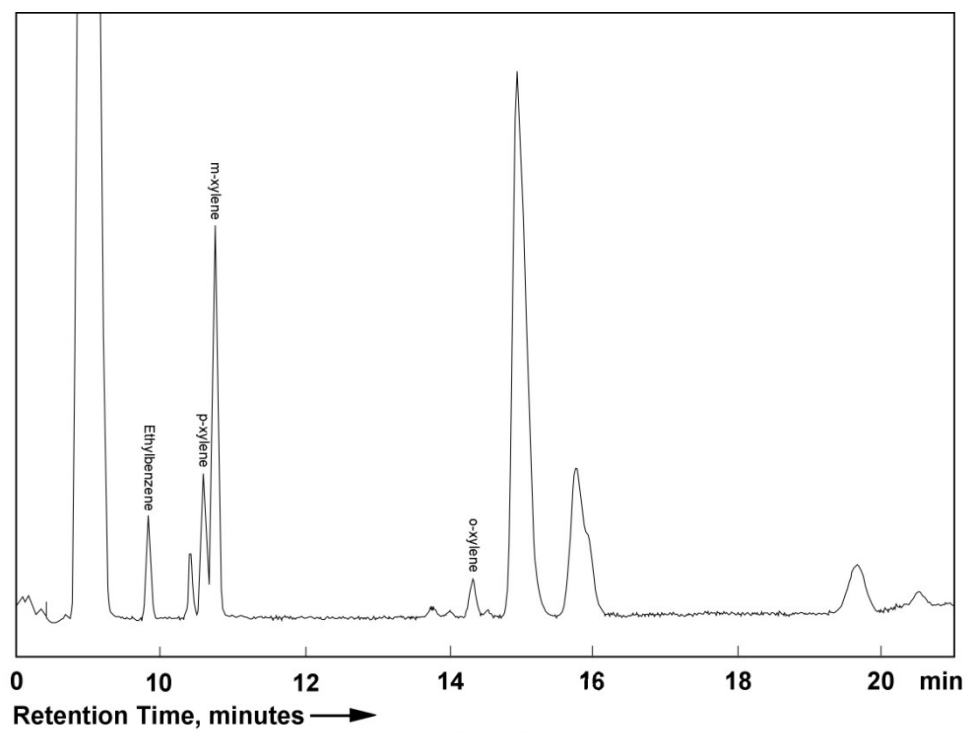


Figure 4
Typical Chromatogram, Analysis B, Expanded