

TRACE DESORBENT IN C₁₀-C₁₈ MOLEX PRODUCTS BY GC

UOP Method 863-01

SCOPE

Molex[®] is an adsorptive separation process that separates normal paraffins from branched chain and cyclic hydrocarbons.

This method is for determining trace amounts of Molex desorbent (*n*-pentane, isooctane, *p*-xylene) in C₁₀-C₁₈ Molex products. The lower limit of detection for *n*-pentane and isooctane is 5 mass-ppm. Early eluting Molex product may cause interference at the *p*-xylene site. Therefore, the lower limit of detection for *p*-xylene can be as high as 50 mass-ppm.

OUTLINE OF METHOD

A repeatable sample volume is injected into a gas chromatograph that is equipped with a fused silica capillary column internally coated with dimethyl polysiloxane, and a flame ionization detector. The concentrations of the desorbent components are determined by the external standard method of quantitation, wherein, the peak areas of the desorbent components in the sample are compared to the peak areas of desorbent components in a calibration blend.

APPARATUS

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

Balance, readability 0.1-mg

Chromatographic column, 50 m of 0.20-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked dimethyl polysiloxane, Agilent Technologies, Cat. No. 19091-S

Gas chromatograph, capable of temperature ramping, built for capillary column chromatography utilizing 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 5 mass-ppm isooctane when operated at the recommended conditions. Agilent Technologies, Model 6890

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 19428-2959, 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

Gas purifier, hydrogen, used to remove oxygen from the carrier gas, Mat/Sen, Fisher Scientific, Cat. No. P200-1

Integrator, electronic, for obtaining peak areas, ChemStation, Agilent Technologies

Leak detector, gas, Alltech Associates, Cat. No. 21-250

Recorder (optional), used to supplement integrator plot

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, helium, two-stage, high purity, Matheson Gas Products, Model 3122-580

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350

Sample injector, syringe or injector capable of injecting a reproducible 2- μ L volume of sample. Use of an automatic injection system (autosampler) is strongly recommended, Agilent Technologies, Model 7683

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 ppm as methane

Helium, zero-gas, total hydrocarbons less than 0.5 ppm as methane

Hydrogen, zero-gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Isooctane (2,2,4-trimethylpentane), 99% minimum purity, Acros Organics, Cat. No. 42456-5000

n-Undecane, 99% minimum purity, Acros Organics, Cat. No. 14066-5000

p-Xylene, 99% minimum purity, Acros Organics, Cat. No. 15877-5000

PROCEDURE

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph
 - Column life is significantly reduced if a gas purifier is not used.
2. Install the column in the gas chromatograph.
 - **CAUTION:** Hydrogen gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, 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.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figure).

4. Program the column oven to 250°C 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.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Column head pressure @ 100 °C,	
Constant pressure	105 kPa gauge (15 psig)
Equivalent flow	0.7 mL/min
Equivalent linear velocity	25 cm/sec
Injection port temperature	250 °C
Column temperature program	
Initial temperature	50 °C
Initial time	0 min
Programming rate A	4 °C/min
Intermediate temperature	120 °C
Intermediate time	0 min
Programming rate B	20 °C/min
Final temperature	230 °C
Final time	38 min
Detector	
Temperature	275 °C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup helium flow rate*	30 mL/min
Sample size	2.0 µL

* Consult the manufacturer's instrument manual for suggested flow rates.

6. Inject 2.0 µL of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
7. Identify the desorbent components using the Typical Chromatogram as a guide (Figure).

Calibration

Quantitative results are based on the injection of a repeatable volume of a sample and of a reference blend. Absolute response factors are used to relate the peak area of the desorbent components to mass-ppm. Since *n*-pentane is quite volatile, and it has about the same detector response as isooctane, the isooctane in the blend is used to calibrate for both *n*-pentane and isooctane in the sample; *p*-xylene in the blend calibrates for *p*-xylene in the sample.

1. Prepare, following ASTM Method D 4307, one or more calibration blends containing isooctane and *p*-xylene in *n*-undecane at the concentrations expected in the samples.
2. Analyze the blend in triplicate as described under Steps 6 and 7, *Chromatographic Technique*. Average the peak areas for each desorbent component from the three runs.
 - The peak areas from each of the three runs should not deviate from the average by more than 2%. If greater deviation is found, check equipment and technique, and make further runs until the required repeatability is obtained.
3. Calculate the response factor for each desorbent component as follows:

$$F = \frac{M}{P} \quad (1)$$

where:

F = absolute response factor for desorbent component

M = concentration of desorbent component in the blend, mass-ppm

P = average peak area for the desorbent component in the blend

CALCULATIONS

Calculate the concentration of the total amount of each desorbent component in the sample as follows:

$$\text{Molex desorbent component, mass-ppm} = FS \quad (2)$$

where:

F = absolute response factor for the component (use the isooctane factor for *n*-pentane)

S = peak area for the component in the sample

Report results to the nearest 1 mass-ppm.

PRECISION

The GC used to perform the precision study was equipped with an autoinjector. Precision statements were determined using UOP Method 999.

ASTM and UOP Repeatability

A nested design was carried out for determining Molex desorbent components in Molex product with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day for each sample. The total number of tests for each constituent was 16. The precision data are summarized in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference 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 with 95% confidence.

The data in Table 2 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.

Table 2

ASTM and UOP Repeatability, mass-ppm

Compound	Mean Conc.	ASTM Repeatability		UOP Repeatability	
		Within- Day esd	Allowable Difference	Within- Lab esd	Allowable Difference
Sample 1					
<i>n</i> -Pentane	8	0.32	1.3	0.29	1.1
Isooctane	8	0.25	1.0	0.26	1.0
<i>p</i> -Xylene	9	0.50	2.0	0.50	2.0
Sample 2					
<i>n</i> -Pentane	73	0.38	1.5	1.0	5.
Isooctane	73	0.56	2.2	0.56	2.2
<i>p</i> -Xylene	77	0.52	2.1	0.52	2.0

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.3 hour. The labor requirement is 0.3 hour.

REFERENCES

ASTM Method D 4307, www.astm.org
 UOP Method 999, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Acros Organics, Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
www.fishersci.com
 Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com
 Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600) www.alltechweb.com
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com
 Matheson Gas Products, P.O. Box 85, East Rutherford, NJ 07073 (201-933-2400)
www.mathesontrigas.com

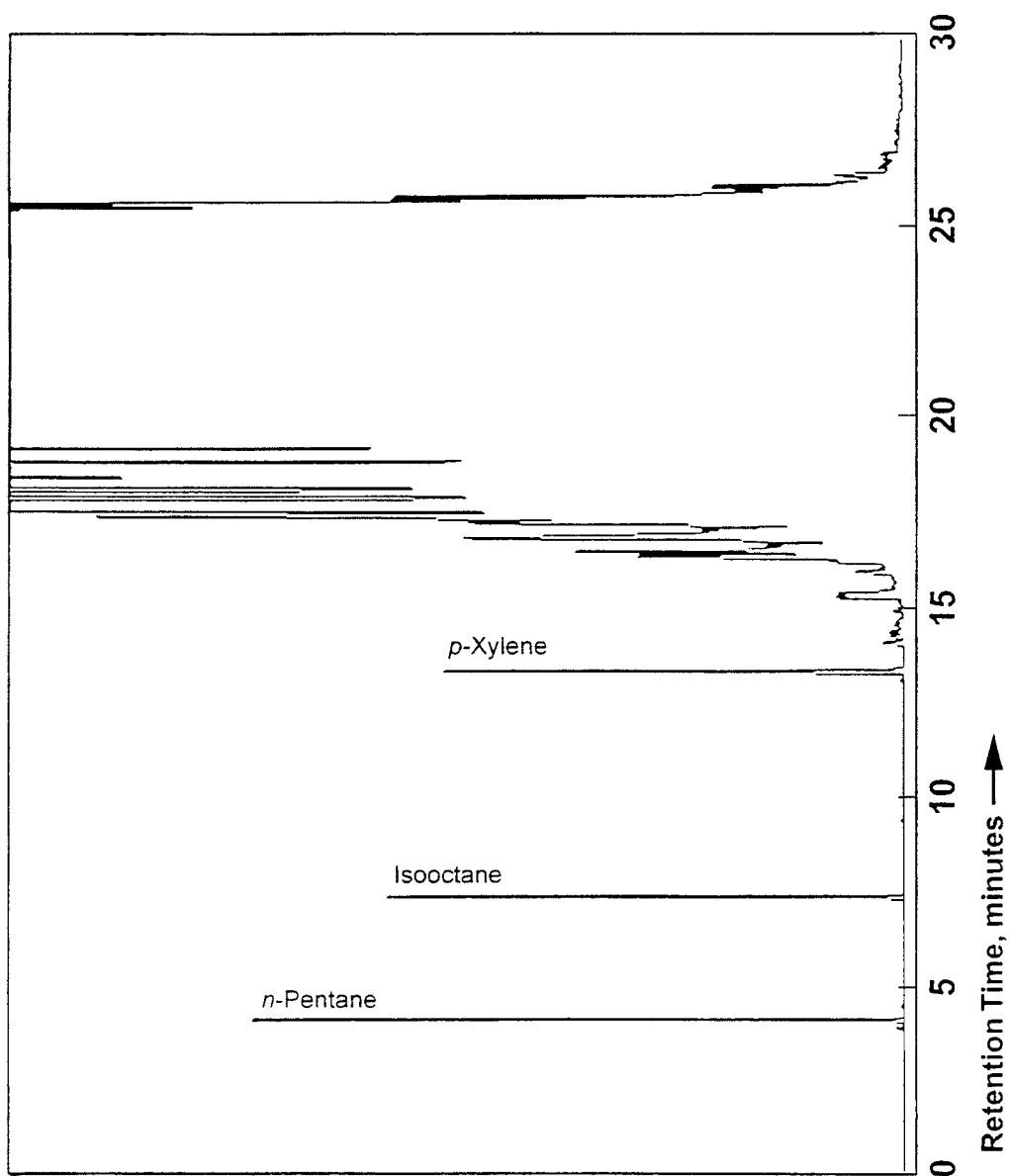


Figure
Typical Chromatogram
Molex Product