

FOOTS OIL IN METHYL ISOBUTYL KETONE BY GC

UOP Method 968-00

SCOPE

This gas chromatographic method is for determining the total amount of foots oil (residue) that accumulates in the recycled methyl isobutyl ketone (4-methyl-2-pentanone) stream of the UOP MIBK Wax DeOiling® process. The range of quantitation for the foots oil composite is 50 to 500 mass-ppm.

OUTLINE OF METHOD

A reproducible sample volume is injected into a gas chromatograph that is equipped with a deactivated stainless steel wide-bore column internally coated with dimethyl polysiloxane, and a flame ionization detector. The total concentration of foots oil in methyl isobutyl ketone (MIBK) is determined by the external standard method of quantitation, wherein the total peak area of foots oil is compared to the peak area of 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, 6 m of 0.53-mm ID deactivated stainless steel wide-bore, internally coated to a film thickness of 0.15- μ m with cross-linked dimethyl polysiloxane, Restek, Cat. No. 70101

Gas chromatograph, capable of temperature ramping, built for wide-bore open tubular 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 50 mass-ppm foots oil when operated at the recommended conditions, Hewlett Packard, Model 6890

Gas purifier, helium, used to remove oxygen from the carrier gas, Mat/Sen, Cat. No. P100-1

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.

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

Integrator, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that the narrow peaks can be accurately measured.

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 introducing a repeatable 2- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307. An autoinjector is recommended.

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

Foots oil, local supply from the process

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 methane

4-Methyl-2-pentanone (methyl isobutyl ketone - MIBK), 99.5+% purity, Aldrich, Cat. No. 29,326-1

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 wide-bore steel column in the gas chromatograph.
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, Fig. 1.
4. Program the column oven to 350°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.

5. Cool the column oven to a stabilized 100°C.
6. Analyze the sample in duplicate as described in Steps 7 through 9.
7. Mix the sample thoroughly by shaking it vigorously to ensure the sample is homogeneous.
8. Inject 2.0 µL of sample into the gas chromatograph and start the integrator and the column oven programming sequence.
9. Identify the foots oil peak profile and measure the total area of the foots oil peak profile using the Typical Chromatograms as a guide, Figs. 1 and 2.

Table 1
Recommended Operating Conditions

Carrier gas	Helium
Column head pressure @ 100°C,	
Constant pressure	20 kPa gauge (3 psig)
Equivalent flow	14.9 mL/min
Injection port temperature	275°C
Column temperature program	
Initial temperature	100°C
Initial time	5 min
Programming rate	15°C/min
Final temperature	350°C
Final time	8.5 min
Detector	
Temperature	355°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup helium flow rate*	5 mL/min
Sample size	2.0 µL

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

10. Average the total peak areas from the duplicate runs.
11. Use the average total foots oil peak area to calculate the total amount of foots oil.
 - The peak areas from each of the two runs should not deviate from the average by more than 3% of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make further runs until the required repeatability is obtained on two consecutive runs.

Calibration

Quantitative results are based on the injection of a reproducible volume of a sample and a reference blend. Absolute response factors are used to relate the peak area of the total foots oil to mass-ppm.

1. Prepare a calibration blend as described in ASTM Method D 4307 to contain 100 mass-ppm of foots oil in MIBK.
 - Obtain foots oil material from the process.
2. Analyze the blend in triplicate as described under Steps 7 through 8, *Chromatographic Technique*.
 - A calibration blend is run when the method is initially set up and thereafter when changes have been made to the equipment or periodically to verify proper calibration.
3. Identify the foots oil peak composite profile and measure the peak composite area using Typical Chromatograms as a guide, Figs. 1 and 2.
 - The peak areas from each of the three runs should not deviate from the average by more than 3% of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make further runs until the required repeatability is obtained on three consecutive runs.
4. Average the total peak areas and use the average total peak area to calculate the absolute response factor for foots oil to three decimal places by using Eq. 1:

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

where:

F = absolute response factor for foots oil
M = concentration of foots oil in the blend, mass-ppm
P = average total peak area for foots oil in the blend

CALCULATIONS

Calculate the concentration of the total amount of foots oil in MIBK using Eq. 2:

$$\text{Total amount of Foots Oil in MIBK, mass-ppm} = FS \quad (2)$$

where:

F = absolute response factor for foots oil
S = average total peak area for foots oil in sample

PRECISION

The precision statements were developed using UOP Method 999.

ASTM Repeatability

A nested design was carried out for foots oil analysis with four analysts. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 16. Using a stepwise analysis of variance procedure, the within day estimated standard deviation (esd) was calculated and is listed in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 2 with 95% confidence. The data in Table 2 was obtained using an autoinjector.

UOP Repeatability

A nested design was carried out for foots oil analysis with four analysts. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 16. Using a stepwise analysis of variance procedure, the within-lab standard deviation (esd) was calculated and is listed in Table 2. 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 2 with 95% confidence. The data in Table 2 was obtained using an autoinjector.

The data in Table 2 is 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

<u>Component</u>	<u>Mean</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>
Total Foots Oil	94	1.6	5	1.6	5

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.25 hours. The labor requirement is 0.5 hour.

REFERENCES

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

SUGGESTED SUPPLIERS

Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)
Hewlett Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
Restek Corp., 110 Benner Circle, Bellefonte, PA 16823-8812 (814-353-1300)
Mat/Sen, 4509 Golden Foothill Pkwy., El Dorado Hills, CA 95762 (916-939-8800)
UOP, Process Information and Control (PIC), 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (847-391-2529)

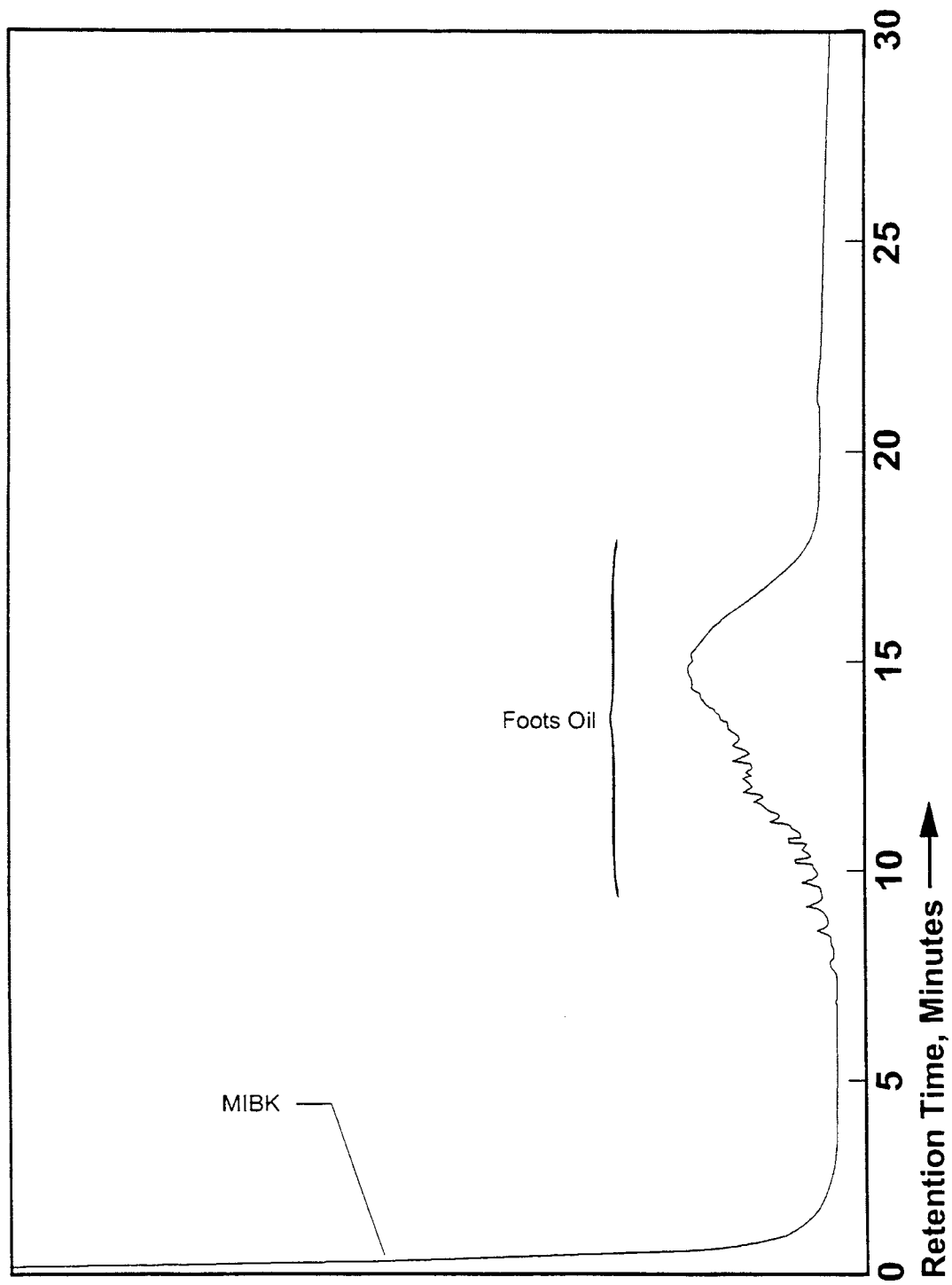


Figure 1
 Typical Chromatogram
 Fools Oil Calibration Blend, 100 mass-ppm (Complete Chromatogram)

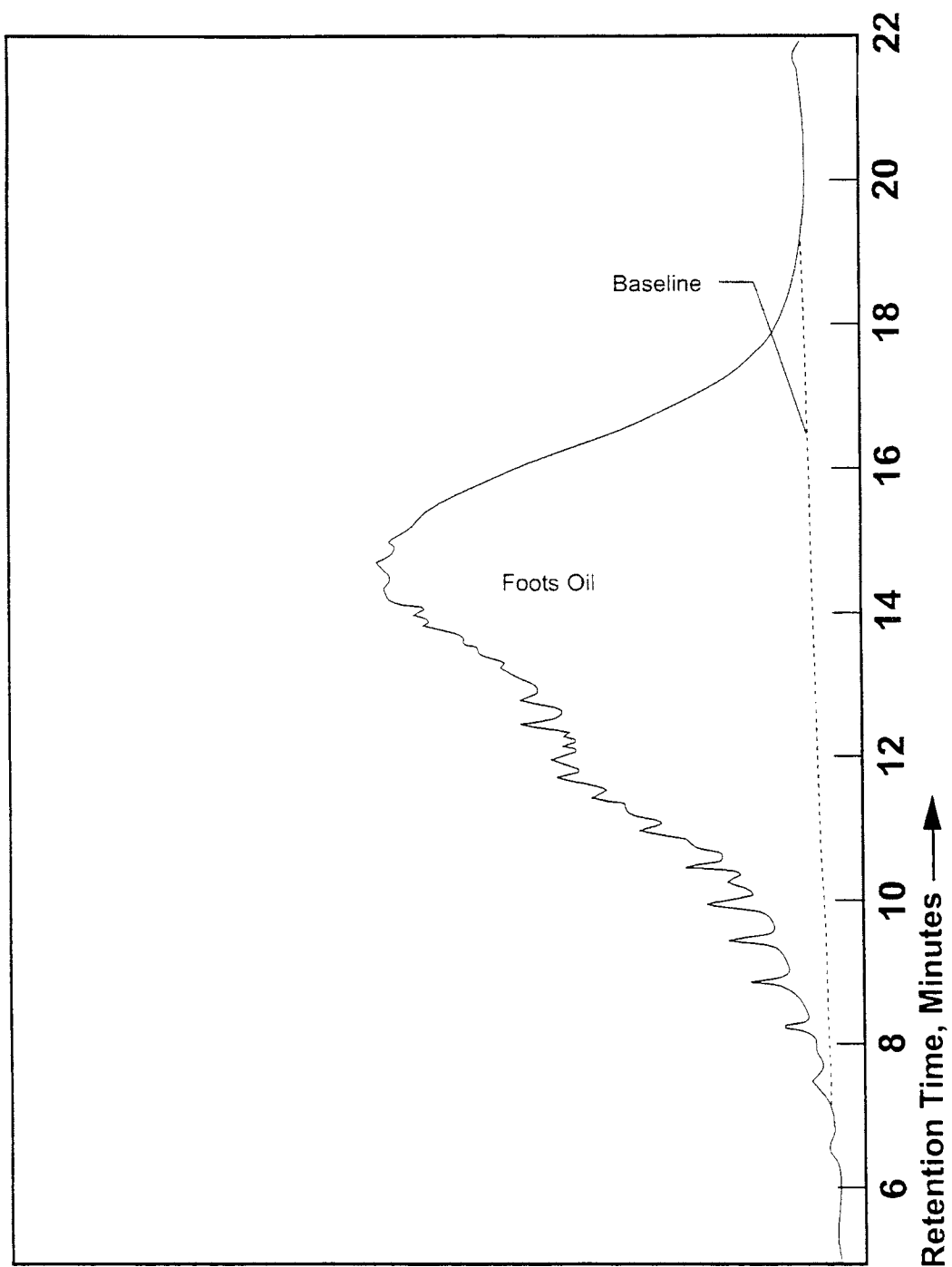


Figure 2

Typical Chromatogram
Foots Oil Calibration Blend, 100 mass-ppm (Enlargement of Foots Oil Peak)