Spectroscopy
Method 70-18
Job No. 8903209

INFRARED DETERMINATION OF PETROLEUM OIL CONTAMINATION IN PYDRAUL 625 AND PYDRAUL 625A

INTRODUCTION

The German Mine Authority has set a limit of 4% maximum petroleum oil (mostly paraffinic type) in Pydraul fluids. They requested Monsanto provide a method that would indicate oil quantities to insure the amounts of contaminants are below the 4% level.

SUMMARY

A differential infrared method has been developed covering the range of 0-4.5 wt. % petroleum oil contamination in Pydraul fluid. A pair of matched 0.05 mm NaCl cells are used with new Pydraul fluid in the reference cell and the used Pydraul fluid in the sample cell. Petroleum oil contamination is determined by measuring the absorbance of the symmetrical C-H stretching band of the methylene group at 2855 cm^{-1}. A 0.1 wt. % oil contamination level produces a change of 0.01 absorbance units. The accuracy and reproducibility of the method have not been established for used fluids. Based on our measurements with new fluids, $\pm$0.2% can be expected.

CALIBRATION

Two absorbance bands can be used to determine the oil contamination level in used Pydraul fluids; the asymmetrical C-H stretching band at 2925 cm^{-1}, and the symmetrical C-H stretching band at 2855 cm^{-1}. Although the 2925 cm^{-1} band is more intense than the 2855 cm^{-1} band, by a factor of two, absorbance measurements of the 2855 cm^{-1} band were used to develop the analytical method. This was done because in plotting absorbance of the 2925 cm^{-1} band versus oil concentration, serious deviations from Beer's Law were obtained. The plot of the data for the 2855 cm^{-1} band was linear.

Standards are prepared by weighing known amounts of a reference petroleum oil (Mobil DTE-26 oil) into weighed quantities of Pydraul 625 or 625A. The mixtures are heated in a 100°C oven for about 10 min. and then stirred magnetically for about five minutes to completely mix and uniformly disperse the oil in the Pydraul fluid.

Fill both NaCl cells with new Pydraul 625 or 625A. Place one cell in the sample beam of the infrared spectrophometer and the other in the reference beam. Scan and record the spectral region from 3100 to 2800 cm^{-1}. Reverse the cells by moving the cell that was in the sample beam to the reference beam, and the cell that was in the reference beam to the sample beam. Scan and record again the region of 3100 to 2800 cm^{-1}. Determine which arrangement gives a positive pen deflection (higher absorbance or lower transmission) at 2855 cm^{-1} and label the cells appropriately as sample cell and reference cell.

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A blank run is made with new Pydraul 625 or 625A in both cells. The differential spectrum is recorded from 3400 to 2500 cm^{-1} at a speed of one minute/100 cm^{-1}. A base line is drawn tangent to the absorbance minima at 3250 and 2550 cm^{-1}. The base line technique is used to compensate for background variations in used Pydraul samples. The absorbance of the base line at 2855 cm^{-1} is measured. The spectrum is rerun between 3000 and 2800 cm^{-1} at a speed of three minutes/100 cm^{-1} for more precise measurements of the absorbance at the analytical frequency.

The absorbance of the blank at 2855 cm^{-1} is obtained by:

$$A_O = A_B - A_L$$

where A_O = absorbance of the blank at 2855 cm^{-1}
A_B = measured absorbance at 2855 cm^{-1}
A_L = measured absorbance of the base line at 2855 cm^{-1}

The sample cell is cleaned by flushing with carbon tetrachloride. Residual solvent is removed by aspiration. The sample cell is filled in turn with each of the standards and the spectrum of each recorded under both the base line and analytical conditions. For each standard, draw a base line tangent to the absorbance minima at 3250 and 2550 cm^{-1} and measure the absorbance of the base line at 2855 cm^{-1}.

The absorbance of the standard is obtained by:

$$A = A_S - A_L$$

where A = standard absorbance at 2855 cm^{-1}
A_S = measured absorbance at 2855 cm^{-1}
A_L = measured base line absorbance at 2855 cm^{-1}

The corrected absorbance for each standard is obtained by:

$$A^* = A - A_O$$

The instrument parameters used to develop the method are:

Base Line Conditions

Spectral region:	3400 to 2500 cm^{-1}
Scan time:	one minute/100 cm^{-1}
Base line points:	3250 and 2550 cm^{-1}

Analytical Conditions

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Spectral region:	3000 to 2800 cm^{-1}
Scan time:	three minutes/100 cm^{-1}

Common Parameters

Analytical frequency:	2855 cm^{-1}
Instrument:	Perkin-Elmer Model 221G spectrophotometer or equivalent instrument with a linear frequency presentation
Sample Cell:	0.056 mm
Reference Cell:	0.055 mm
Slit Program:	980 (311 μ at 3000 cm^{-1})
Source:	0.34 amps
Gain:	5.5
Abscissa Scale:	4 cm/100 cm^{-1}

The calibration data for Pydraul 625 obtained with the 0.0056 and 0.0055 cm cells is:

A* Absorbance	C Wt. % Oil	a Absorptivity (l/% cm)
0.057	0.62	16.4
0.141	1.53	16.5
0.239	2.59	16.5
0.316	3.44	16.5
0.426	4.66	16.3
		16.4 Average

The calibration data for Pydraul 625A is:

A* Absorbance	C Wt. % Oil	a Absorptivity (l/% cm)
0.057	0.62	16.4
0.143	1.55	16.5
0.236	2.58	16.4
0.322	3.52	16.3
0.411	4.51	16.3
		16.4 Average

PROCEDURE AND CALCULATIONS

The sample and reference cells are filled with new Pydraul 625 or 625A and the blank differential infrared spectrum recorded under the base line conditions. A base line is drawn tangent to the absorbance minima at 3250 and 2550 cm^{-1}. The absorbance of the base line, A_L, is measured at 2855 cm^{-1}. The spectrum is then run between 3000 and 2800 cm^{-1} under the analytical conditions and the absorbance, A_B, measured at 2855 cm^{-1}. The absorbance of the blank is obtained by:

$$A_o = A_B - A_L$$

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The sample cell is cleaned by flushing with carbon tetrachloride and filled with the used Pydraul 625 or 625A. The spectrum is recorded under the base line conditions and a base line drawn tangent to the absorbance of the base line at 2855 cm^{-1}, A_L, is measured. The spectrum of the used fluid is run under the analytical conditions and the absorbance at 2855 cm^{-1}, A_S, measured. The absorbance of the sample is obtained by:

$$A = A_S - A_L$$

The corrected absorbance, A*, is calculated by:

$$A^* = A - A_o$$

The level of oil contamination in the used Pydraul 625 or used 625A is calculated by:

$$\text{wt. \% oil} = \frac{A^*}{17.9 \times 0.0056} = \frac{A^*}{0.0918}$$

db

Monsanto Company
Organic Chemicals Division
Applied Sciences Section
St. Louis, Missouri

8/70 - B. Katlafsky, M. W. Dietrich

DSW 620497

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