A Novel FT-IR Liquid Sampling Device For Analyzing Fuels, Oils And Other Viscous Materials

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Overview

Purpose: Infrared spectroscopy is used extensively to analyze various oils, fuels and lubricants. In many cases the viscous nature of the samples makes sampling and cleaning difficult. The objective of this work is to determine if the variable pathlength technology developed for the Thermo Scientific™ NanoDrop™ UV/Vis products is appropriate for FT-IR applications

Methods: PLS methods were developed from standards run at different pathlengths. Measurements of hexadecane acquired in a sealed liquid cell were employed to calibrate the pathlength

Results: A prototype was evaluated over sample pathlengths from less than 50 microns to over 1.5 mm with excellent precision. Spectra were obtained from less than 100 microliters of sample. The open optical architecture of this design resulted in a total analysis time of less than two minutes per sample including sample deposition, analysis and cleaning.

Introduction

The sampling technology developed for the NanoDrop UV/Vis products provides a fast robust method to analyze small amounts of biological samples. While the requirements for this product are different from those needed for infrared analysis, the basic technology and motor control strategies are appropriate for the shorter pathlength measurements encountered in many infrared spectroscopic applications. One goal of this research was to explore the possibilities of dynamically adjusting the pathlength to optimize the analysis. Based on a preview spectrum, the pathlength increases for weak peak and decreases for overly strong peak.

Experimental

Instrumentation: All spectra were acquired with a Thermo Scientific™Nicolet™iS™5 FT-IR spectrometer using the Thermo Scientific™ OMNIC® software suite at 4 cm-1 resolution. 32 scans were averaged to reduce noise. Hexadecane was selected as a validation and calibration standard due to it’s low volatility and similarity to the hydrocarbon oils frequently analyzed by infrared spectroscopy.

Data Analysis: OMNIC TQ Analyst™ was used to perform all spectral measurements and quantitative analysis. Results were automatically stored in an Excel® readable format for further statistical analysis.

FIGURE 1. The NanoDrop instrument with drop down arm and computer adjustable sample pathlength.

Design Details

A high-precision computer controlled stepper motor assembly was designed to allow the optical pathlength to be adjusted to within one micron. The total travel of the assembly was greater than 1.5 millimeter. The infrared beam is focused through the lower window through the sample to a detector above the upper window.

FIGURE 2. Schematic of infrared transmittance device based on NanoDrop technolog

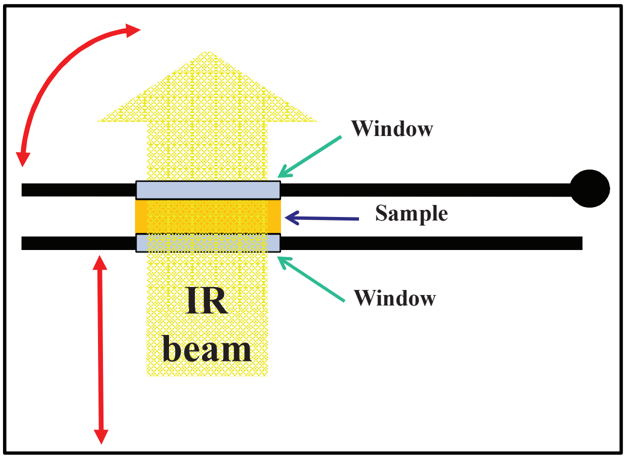


FIGURE 3. Variable pathlength transmittance prototype in Nicolet iS5 FT-IR

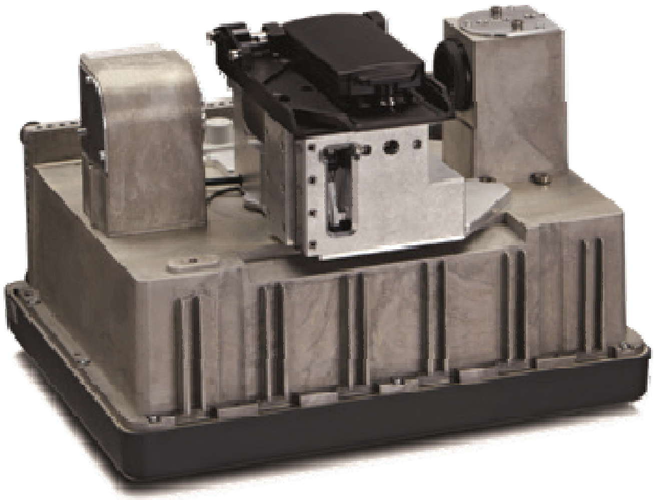
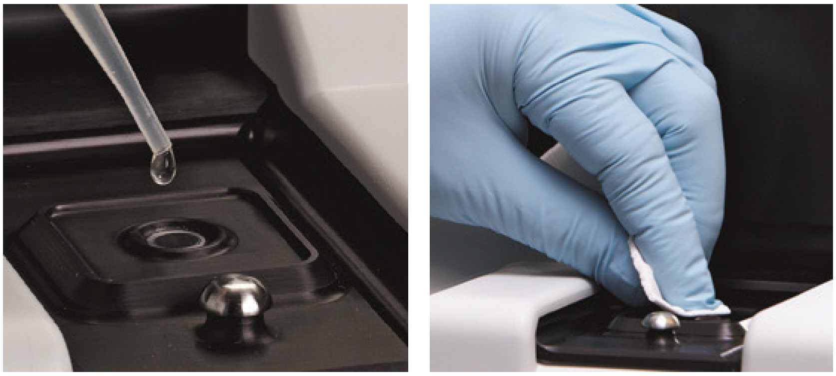
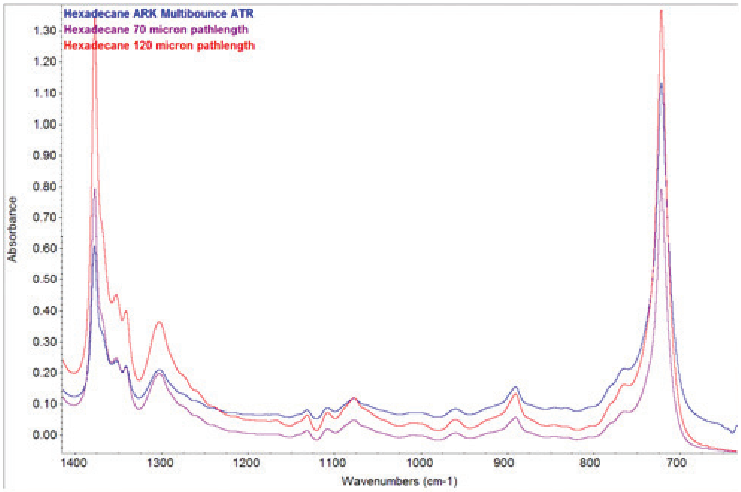


FIGURE 4. The design utilizing small diameter windows and a sample containment system requires less than 100ul of sample and is easily cleaned with a lint free wipe



A number of laboratories have developed methods based on attenuated total reflectance (ATR) spectroscopy for characterizing oils and other viscous samples. While ATR techniques work well, it is not easy to optimize the sampling pathlength and the majority of the signal is produced by the material in contact with the ATR crystal. For situations where a pathlength of less than 50 microns is best, the spectral intensities of the transmittance device are similar to a multi-bounce ATR accessory but the noise level is generally lower with transmittance. In many applications the longer pathlength available in transmittance provides much lower detection limits than ATR.

FIGURE 5. Comparison of Multi-bounce ATR spectrum with spectra acquired in transmittance with a 70 micron and 120 micron pathlength.



Calibrating Sample Pathlength

Creating a device that can precisely set a pathlength with an accuracy of less than one micron for values as low as 50 microns was quite challenging. While the stepper motor on the prototype moves approximately 200 nanometers per micro-step, we observed significant variance between different motors. We decided to base our pathlength on spectral intensity. Reference spectra were acquired from n-hexadecane in sealed liquid cells with nominal pathlengths of 50 and 100 microns. We used the fringe technique to determine the actual pathlength to better than one micron. Based on replicate spectra acquired on several instruments, we calibrated a method to predict the pathlength from the spectral features in the 4400 cm-1 region. This method has proven accurate for pathlengths less than 400 microns. To maintain a linear response at pathlengths greater than 500 microns, a second method based on the weak hydrocarbon peak at 2020 cm-1 was created, and the results are shown below.

FIGURE 6. Spectra from Hexadecane measured at 4400 cm-1 and 2020 cm-1 as a function of pathlength

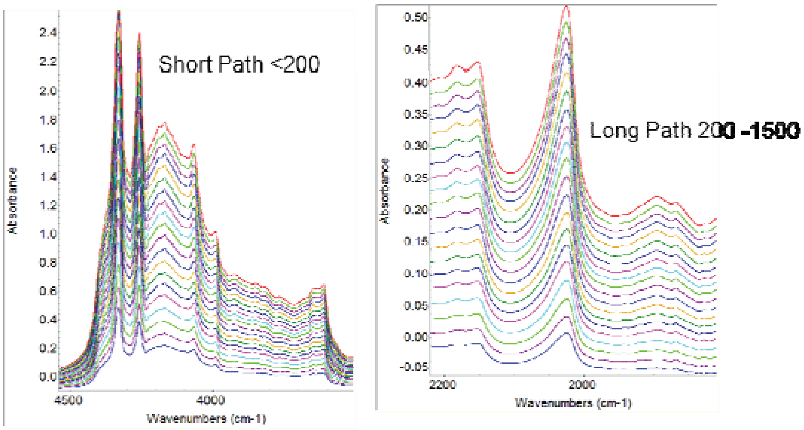
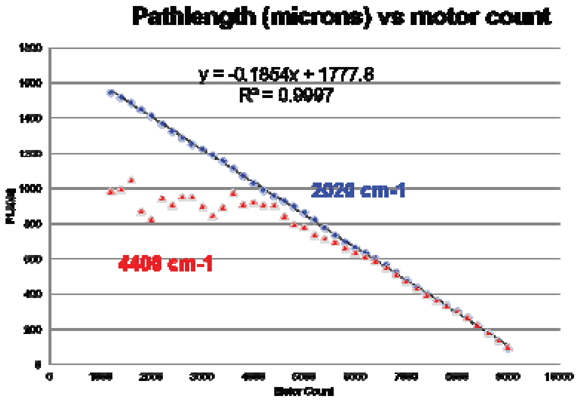


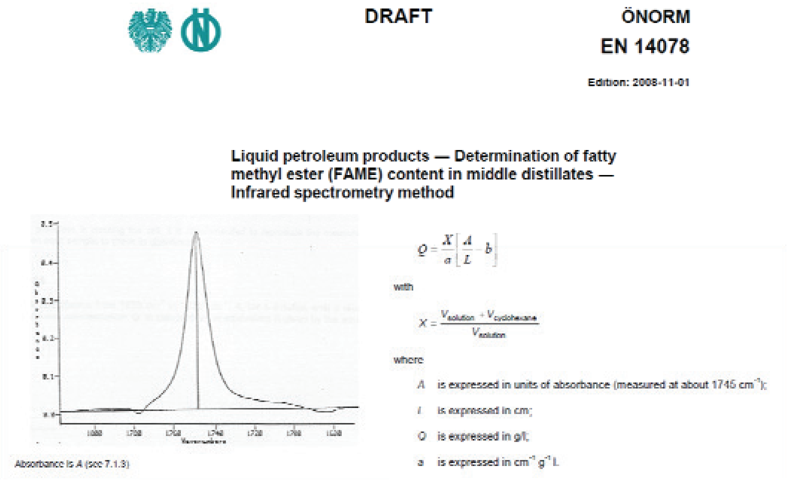
FIGURE 7. Graph showing extended linearity at pathlengths greater than 500 microns for the 2020 cm-1 peak.



Measuring FAME In Jet fuel from the percent to ppm levels

Infrared spectroscopy provides a fast and accurate method that can not only determine the amount of fatty acid methyl esters (FAMEs) in biodiesel , but also screen for low level FAME contamination in jet fuel. For levels of FAME in fuel blends greater than 10%, a short pathlength (50 micron) is required. However a pathlength of at least 500 microns is necessary to measure low ppm levels of FAME contamination in jet fuel.

FIGURE 8. Summary of European method to determine the amount of Fatty Methyl Ester (FAME) in jet fuel



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Liquid petroleum products — Determination of fatty methyl ester (FAME) content in middle distillates — Infrared spectrometry method

$$Q = \frac{X}{a}\left[\frac{A}{L} - b\right]$$

with

$$X = \frac{V_{solution} + V_{cyclohexane}}{V_{solution}}$$

where

A is expressed in units of absorbance (measured at about 1745 cm^{-1});

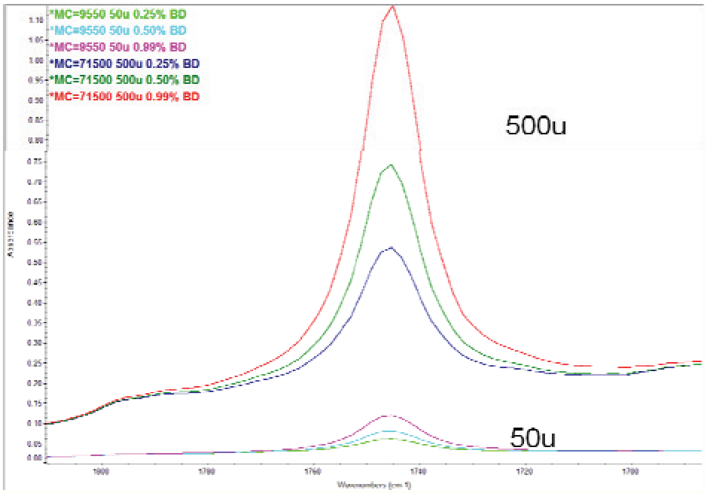
l is expressed in cm;

Q is expressed in g/l;

a is expressed in cm^{-1} g^{-1} l.

Absorbance is A (see 7.1.3)

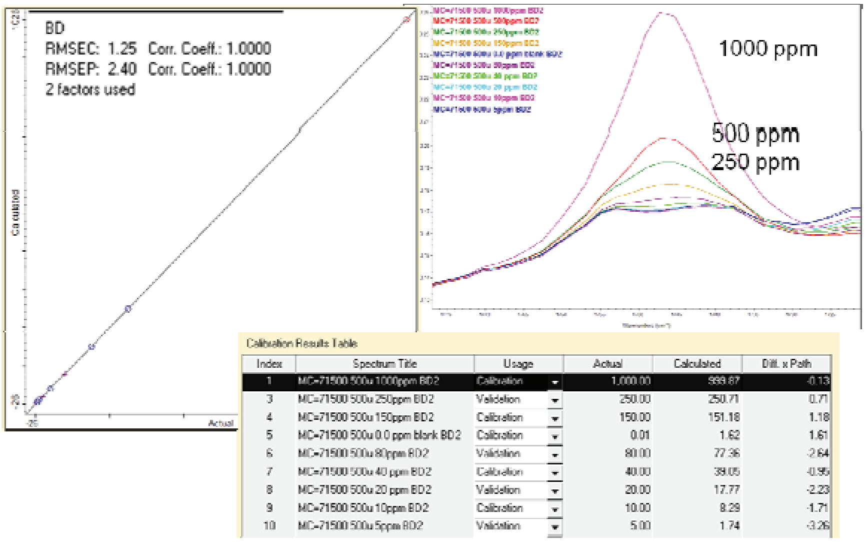
FIGURE 9. A comparison of the FAME carbonyl peak measured at 50 micron and 500 micron pathlengths



A workflow was developed using OMNIC Macros Basic to acquire a preview spectrum and then to automatically set the optimal pathlength, based on the intensity of the 1745 cm^{-1} peak corresponding to the carbonyl band of the ester.

In this example, two PLS methods calibrated for different pathlengths were developed using the TQ Analyst multivariate analysis software, from standards acquired at a 50 micron pathlength and then at 500 microns, respectively. The method based on the 500 micron standards yielded a root mean square of prediction (REMSEP) of 2.4 ppm using two factors, including a second factor to compensate for the baseline variance observed in low level standards. An overlay of the standard spectra and the results of the calibration are shown in Figure 10.

FIGURE 10.Calibration results for a PLS method to measure low ppm levels of FAME in jet fuel showing a RMSEP of less than 3ppm.



BD
RMSEC: 1.25 Corr. Coeff.: 1.0000
RMSEP: 2.40 Corr. Coeff.: 1.0000
2 factors used

Calibration Results Table

Index	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	MC=71500 500u 1000ppm BD2	Calibration	1,000.00	999.87	-0.13
3	MC=71500 500u 250ppm BD2	Validation	250.00	250.71	0.71
4	MC=71500 500u 150ppm BD2	Calibration	150.00	151.18	1.18
5	MC=71500 500u 0.0 ppm blank BD2	Calibration	0.01	1.62	1.61
6	MC=71500 500u 80ppm BD2	Validation	80.00	77.36	-2.64
7	MC=71500 500u 40 ppm BD2	Calibration	40.00	39.05	-0.95
8	MC=71500 500u 20 ppm BD2	Validation	20.00	17.77	-2.23
9	MC=71500 500u 10ppm BD2	Calibration	10.00	8.29	-1.71
10	MC=71500 500u 5ppm BD2	Validation	5.00	1.74	-3.26

Conclusion

In this presentation, we have described a sampling technique to expedite quantitative measurements on viscous samples. We have demonstrated that with pathlength calibration, the device can precisely adjust the pathlength from less than 50 microns to over 1000 microns. Preliminary tests demonstrate that the appropriate pathlength for a specific sample can be determined with a quick preview scan and set automatically in the analytical workflow. PLS methods were optimized using spectra acquired at desired pathlengths and then selected based on the preview spectrum.

- Successfully measured low ppm levels of FAME in jet fuel with a RMSEP of less than 3ppm
- High quality spectra were acquired from less than 100 microliters of sample
- Varied pathlength from less than 50 microns to over 1.5 mm
- Obtained better sensitivity at longer pathlengths than found with ATR measurements

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