VIAVI Solutions

Application Note

VIAVI

MicroNIR PAT-L Liquid Analysis

Introduction

The new MicroNIR PAT-L and PAT-Lx are the latest innovative near infrared spectrometers for in-line liquid process monitoring offered by VIAVI Solutions. The PAT-L product line provides a scalable multi-point monitoring solution that doesn't rely on central multiplexing systems, which are prone to maintenance, failure, and production downtime. The PAT-L/Lx extends the MicroNIR product line of compact near infrared (NIR) spectrometers for real-time, rapid process monitoring for chemical, pharmaceutical, polymer and oil & gas industrial applications. The PAT-L is built for ordinary process locations, while the PAT-Lx is designed specifically for hazardous locations (ATEX, NEC, and IECEx certified). VIAVI Solutions Linear Variable Filter (LVF) technology and an integrated vacuum tungsten light source with an expected lifetime of over 100,000 hours, the PAT-L requires no periodic maintenance or calibration. The design includes no optical fibers, which ensures that every MicroNIR has nearly identical optical performance. The PAT-L/Lx ships with VIAVI MicroNIR Pro software, a fully Title 21 CFR Part 11- and GMP-compliant data acquisition and chemometric applications development software package.

This application note describes how the PAT-L was used to measure aqueous and non-aqueous liquid samples. Liquid temperature, solute concentration and light scattering were analyzed in water and aqueous solutions, as well as different grades of olive oil. The PAT-L showed exceptional stability and a very high signal-to-noise ratio throughout the analysis, even in the absence of instrument re-referencing.

Figure 1. The MicroNIR PAT-L immersion spectrometer, shown here with a 2 mm transmission path length measurement gap.

Methods

The MicroNIR PAT-L is a NIR spectrometer with a spectral range of 908-1676 nm. This range is very sensitive to the C-H, O-H and N-H bands present in organic materials. Light from an integrated incandescent source is transmitted through the probe section via a reflective light pipe coupled to a sapphire window and then through a measurement gap that contains the analyte of interest. Transmitted light is detected by a linear variable filter bonded to an InGaAs diode array detector. Referencing the spectrum with air in the measurement gap allows the calculation of an absorbance spectrum that is linear in the sample concentration. The absorbance was measured as log10 [(Iref – Id)/(Is – Id)] where Iref is the reference signal intensity, Is the sample and Id the dark signal, measured with lamps off.

Spectra of tap water at temperatures varying from 6 ^{0}C to 39 ^{0}C were acquired over a period of several days using two MicroNIR PAT-L spectrometers with 2 mm and 10 mm path lengths. The probe section was immersed to at least 5 cm below the water level. The water temperature was measured with a mercury thermometer with a precision of better than 1 ^{0}C. 100 scans were averaged, with a typical total scan time of ~350 ms. Using the integration time programmed into the instrument permitted the spectra to be automatically normalized for changes in detector temperature using VIAVI's proprietary Temperature Baseline Normalization (TBN) algorithm. A spectral range of 951-1651 nm was used for the PLS analysis. Spectra were acquired and a model was developed using VIAVI MicroNIR Pro v3.2 software.

The sugar concentration measurements used a different PAT-L with 2 mm path length. Sugar solutions were made up by weight and were analyzed at room temperature.

Spectra of commercial olive oils from multiple countries of origin were acquired at room temperature using a 10 mm path length probe. Both freshly opened and older samples of oil were used for the analysis.

Using NIR spectra to measure water temperature

Figure 2. NIR absorption spectrum of water at 26^{0}C, acquired with 2 mm and 10 mm transmission path lengths

The NIR absorption spectrum of liquid water is shown in Figure 2. The O-H stretching overtone is observed as an intense absorbance centered around 1440 nm, with weaker peaks due to combination bands and higher overtones around 1200 and 970 nm. The spectrum from the 2 mm probe shown in Figure 2 has a maximum absorbance of nearly 2.0 OD (optical density) units, corresponding to a transmission of 1%, while the absorbance is much greater with the 10 mm probe. Under these conditions, Beer's Law does not apply, and the absorbance of the 1440 nm feature does not vary linearly with sample concentration. However, the weaker features remain linear and can readily be analyzed quantitatively, and changes in the shape of saturated bands are meaningful.

Figure 3 shows the absorbance spectra of water at temperatures of 6, 15, 23 and 32 ^{0}C acquired with the 10 mm path length probe. A first derivative Savitzky-Golay transform with 5-point smoothing has been applied in order to highlight the spectral trends. Spectral broadening and shifts to shorter wavelengths with increasing temperature are evident for all three absorbance features. These effects can be used to create a precise quantitative model of the temperature using the PLS algorithm as shown in Figure 4.

The PLS analysis shows that a single PLS factor is adequate to explain 99% of the variance. The spectra were acquired over two days, and no evidence of instrumental drift was observed over that period. The calibration error of the model was less than one degree Celsius and the scores plot shows that spectra at different temperatures can be cleanly separated along the Factor 1 axis.

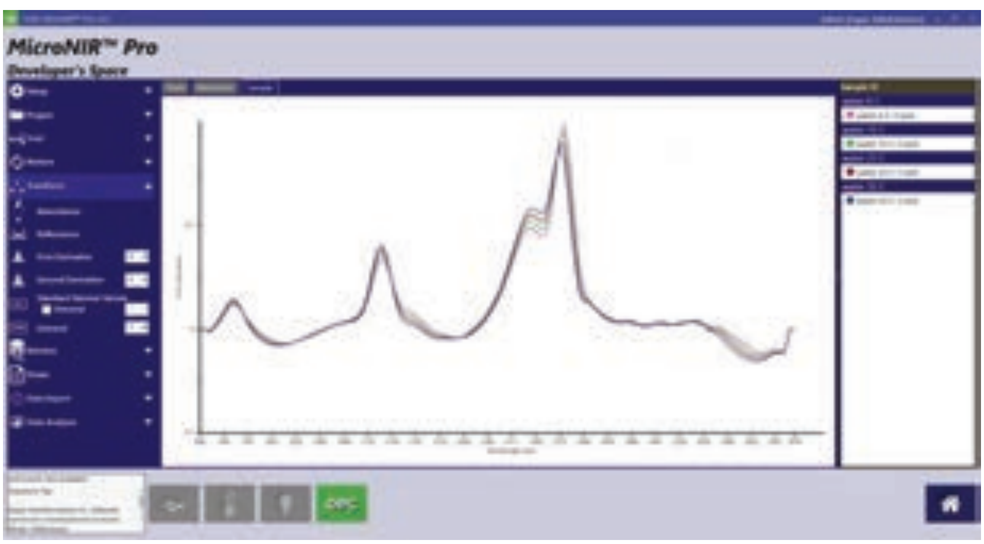

Figure 3. First derivative transformed water spectra at different temperatures

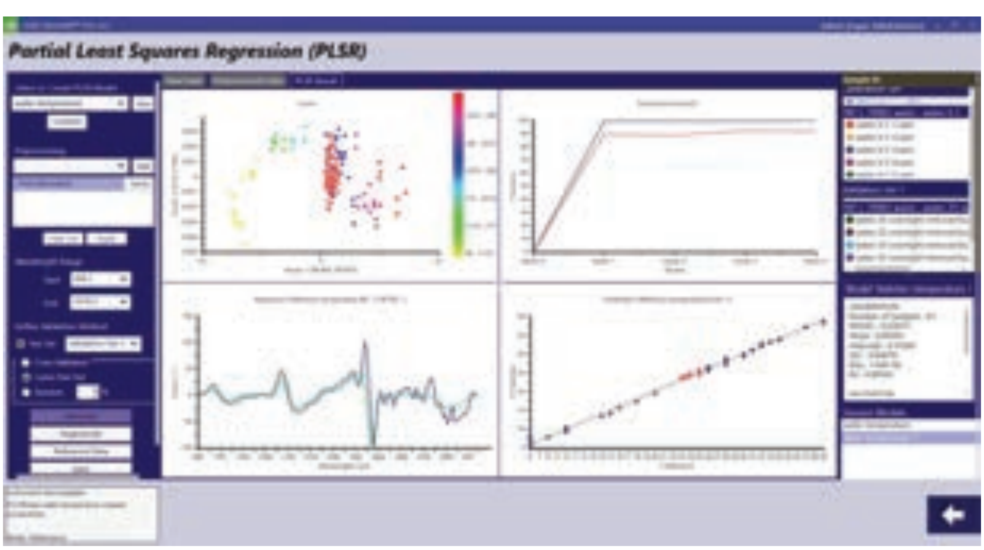

Figure 4. PLS prediction of water temperature with the 10 mm probe

Instrumental stability

The solid state all-reflective design of the PAT-L results in exceptional stability. It is possible to acquire spectra continuously for days with negligible instrumental drift, as shown in Figure 5. First derivative transformed spectra of water between 24 and 26 ^{0}C acquired over three days are shown, with the probe in both vertical and near-horizontal orientations. The spectra overlap almost perfectly, with a slight amount of noise in the 1400-1500 nm region (recall that the transmission in this region is only about 0.2%). The instrument was re-referenced only once during this sequence of measurements. Figure 6 shows spectra acquired over 30 minutes with the 2 mm probe, without stirring. The absence of any change in the spectrum indicates that light absorption by the sample did not heat it to a measurable degree.

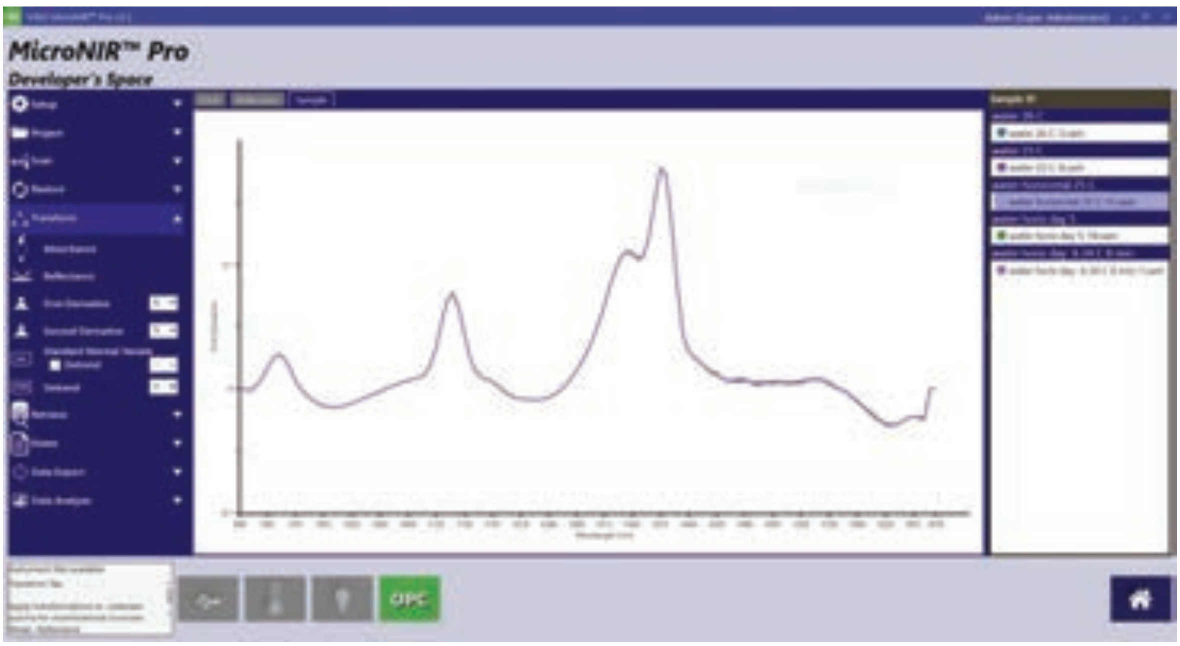

Figure 5. Water spectra at constant temperature acquired over three days with the 10 mm probe

Figure 6. Water spectra acquired over 30 minutes with the 2 mm probe, indicating the absence of local heating

Effect of air bubbles

Experiments were performed using water that had not been degassed. Over time, air bubbles formed around the optical windows. These bubbles could easily be detected by an increase in the spectral baseline due to light scattering. However, even when air bubbles were present on both windows, there was no increase in the error of the water temperature measurement made using the 10 mm probe. After degassing, air bubbles were no longer observed, and easily removed. With the 2 mm probe, it is important to keep the transmission gap clear of air bubbles.

Light scattering measurements with the PAT-L

Figure 7. Spectra of whole milk diluted with water

Transmission measurements can be used to detect light scattering in liquids. Applications of light scattering measurements include solvent recrystallization of pharmaceutical APIs and detection of carbonate precipitation in carbon capture research. Figure 7 shows spectra of water and of various dilutions of whole milk, acquired with the 10 mm probe. The absorbance spectrum of water below about 1350 nm is in the linear regime. Milk diluted with water to 3% or lower concentration can readily be quantified by NIR transmission measurements (note that the measured absorbance must then be interpreted as light scattering). At concentrations above 3%, the detector receives too little light for reliable measurements to be made with the 10 mm probe, but the PAT-L is available with path lengths as short as 2 mm, enabling measurements to be made even with highly scattering samples.

Olive Oil analysis

NIR spectroscopy is often used to analyze the quality and authenticity of olive oil. One example is the use of the MicroNIR 1700 ES in Diffuse Reflectance mode to distinguish extra virgin olive oil from lower grades[1], while another paper used NIR to detect the adulteration of extra virgin olive oil[2]. Olive oil is composed primarily of mixed triglyceride esters of long-chain fatty acids and, like hydrocarbon-based materials such as biodiesel, which are best studied with a long path length transmission probe. Raw and first derivative spectra of olive oil acquired with the 10 mm path length PAT-L probe are shown in Figures 8 and 9 and a PCA analysis of the samples is shown in Figure 10.

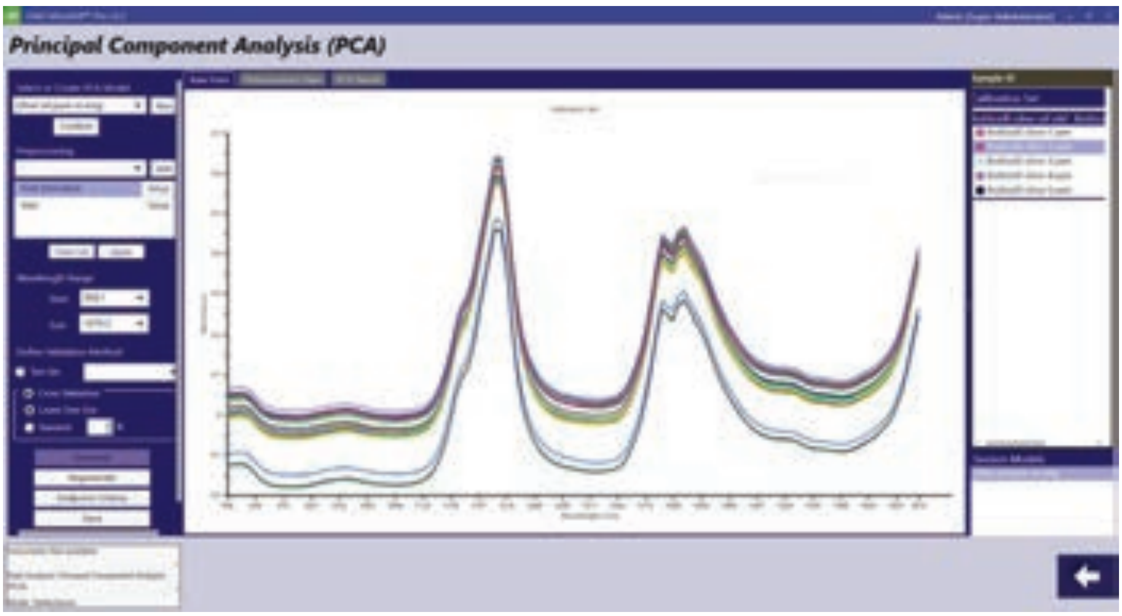

Figure 8. Spectra of commercial olive oil samples acquired with the 10 mm probe

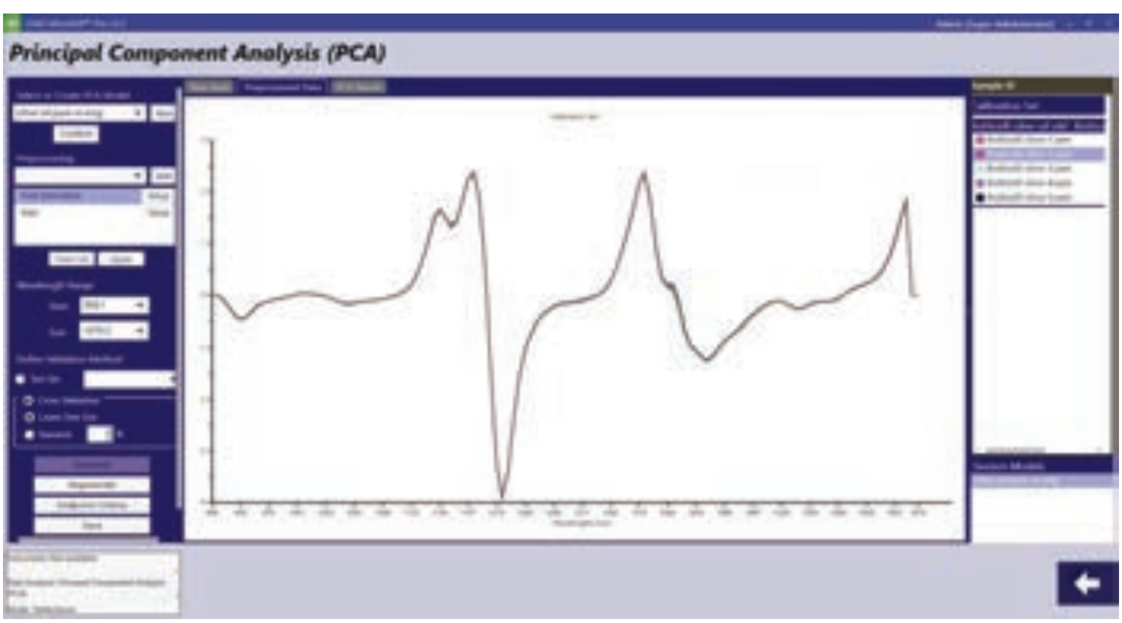

Figure 9. First derivative transformed spectra of pure grade and extra virgin olive oil

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[1] Yan, van Stuijvenberg and van Ruth, Eur. J. of Lipid Sci and Tech (2019), 121: 1900031 DOI: 10.1002/ejlt.201900031

[2] Vanstone, Moore, Martos and Neethirajan, Food Qual. Safety (2018), XX: 1-10 doi:10.1093/fqsafe/fyy018

While the NIR spectra of pure grade (a mixture of refined and extra virgin oils) and extra virgin olive oil are extremely similar, Principal Component Analysis (PCA) can easily distinguish them in scores space. Classification methods such as Linear Discriminant Analysis (LDA) or VIAVI's proprietary Counter False Positives-Support Vector Machine algorithm, available as an add-in for VIAVI MicroNIR Pro v3.2 software, can be used to distinguish these grades of olive oil or to detect the adulteration of extra virgin oil.

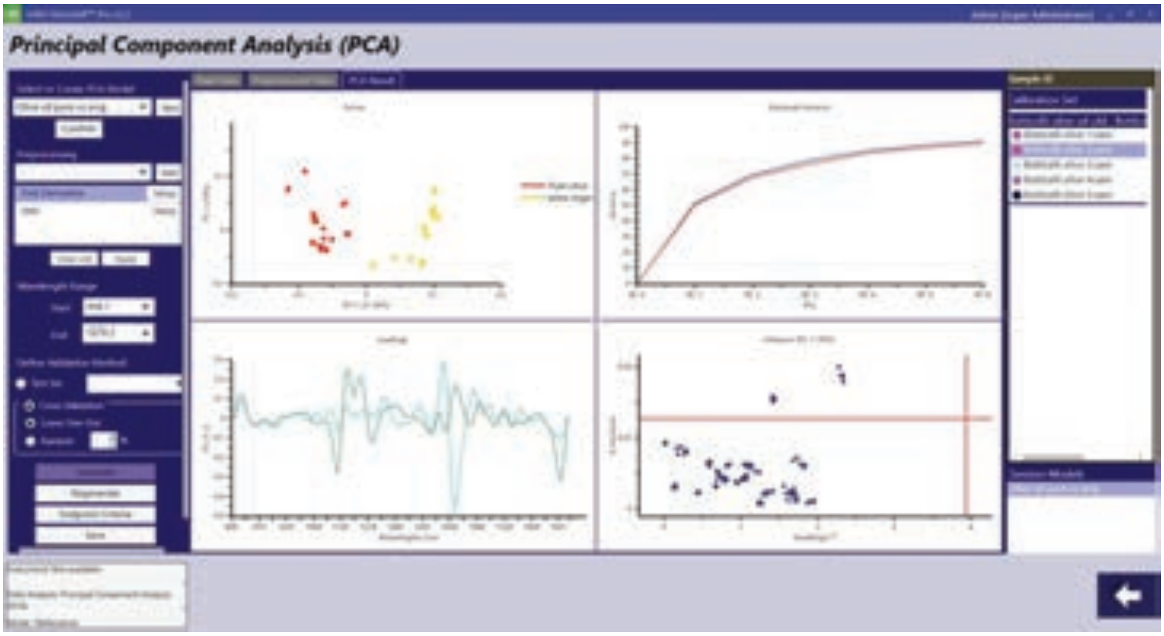

Figure 10. PCA analysis of pure grade and extra virgin olive oil. The pure grade (red markers) and extra virgin (yellow markers) oils are easily separated in the scores plot.

Measurement of sugar concentration

The MicroNIR PAT-L spectrometer with 2 mm transmission path length was used to measure the concentration of table sugar dissolved in water. As observed in the water temperature measurements, the most obvious effect of the added solute was a change in shape of the water spectrum. A single-factor PLS model was created to quantify the sugar concentration between 1% and 13% with a prediction error of 0.25% as shown in Figure 11.

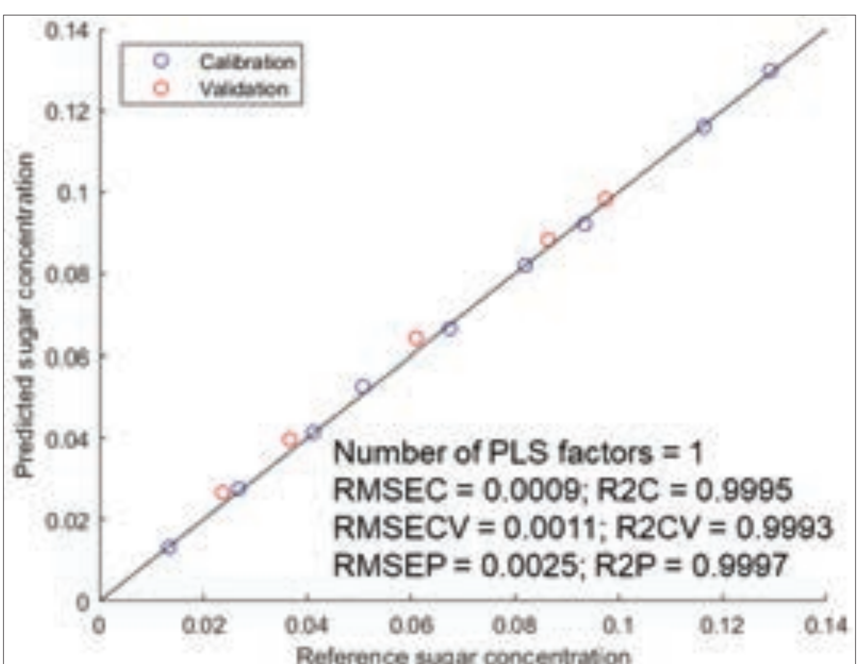

Figure 11. PLS predicted vs. refence plot for aqueous sugar concentration measurements

Conclusions

The VIAVI MicroNIR PAT-L is highly stable, both mechanically and electronically. It is possible to acquire spectra with negligible drift over a period of days, irrespective of the orientation of the spectrometer. While the sample spectra themselves are highly sensitive to temperature, VIAVI's built-in calibration algorithm normalizes the MicroNIR detector response for changes in ambient temperature over the 0-40 ^{0}C range. The PAT-L probe can be immersed in liquids at temperatures up to 400 ^{0}C with an optional water-cooling jacket, which isolates the spectrometer from the elevated temperature.

The PAT-L is available with transmission path lengths of 2 mm to 10 mm. While shorter path lengths are preferred for aqueous solutions and longer path lengths for hydrocarbons, both material classes can be analyzed by both qualitative and quantitative measurements using probes with the multiple path lengths. The methods used to develop chemometric models are robust and automatically adjusts for regions of the spectrum where linear measurements do not apply.

The PAT-L can be used to perform not only conventional transmission/absorbance measurements, but also light scattering to monitor turbid media or precipitation reactions.

While the PAT-L is not rated for hazardous locations, a similar instrument, the PAT-Lx, is available from VIAVI solutions and is rated for use in explosive atmospheres. The optical performance of the two models is identical.

VIAVI Solutions

Contact Us **+1 844 GO VIAVI**
(+1 844 468 4284)

To reach the VIAVI office nearest you,
visit viavisolutions.com/contact

micronir-pat-l-liquidanalysis-an-osp-ae
30193639 900 1222