Superior Water Activity Measurement of Oils and Lubricants Using a Tunable Diode Laser

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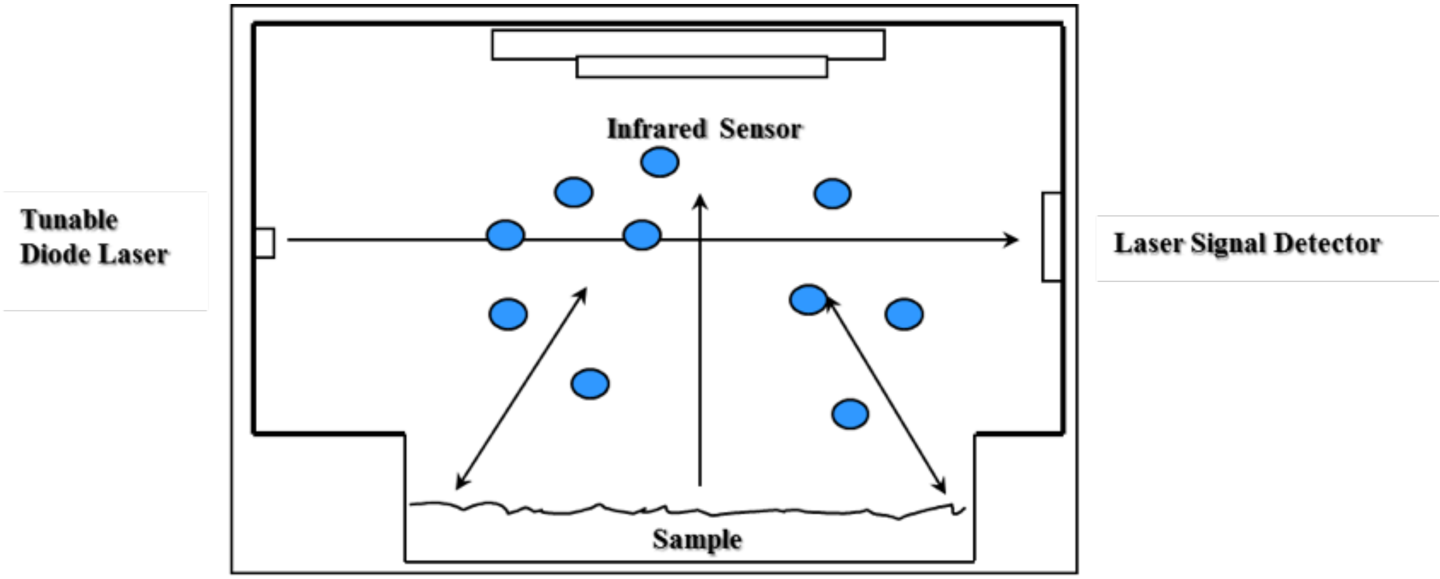
Introduction

The water activity of a sample is measured by equilibrating a sample with a headspace in a sealed chamber and measuring the sample temperature and the vapor pressure of the headspace. The vapor pressure can be measured directly by determining the headspace dew point temperature using a chilled mirror. The water activity is then calculated as the ratio of headspace vapor pressure to saturation vapor pressure at the sample temperature. Alternatively, capacitance or resistance humidity sensors can be calibrated against standards and used as a secondary measure of the equilibrium relative humidity of the headspace, which, when divided by 100, is equivalent to the water activity. However, when volatiles such as Ethanol (Et) or Propylene Glycol (PG) are present in a sample, all of these measurements fail. The volatiles can co-condense on the chilled mirror, changing the point at which dew is detected, and thereby causing the water activity reading to be incorrect. In addition, volatiles can be absorbed by either capacitance or resistance based humidity sensors, causing the properties of the sensor to change, thereby altering their calibration. When volatiles are present, water activity values measured using current sensor technology often are artificially high. Filters are sometimes recommended when testing volatiles, but these alter the equilibrium and disturb the reading. An accurate measurement of water activity in samples with volatiles is not possible with any of these methods. The purpose of this study was to investigate a Tunable Diode Laser (TDL) based technology for measuring water activity with equivalent accuracy to the chilled mirror sensor, but without sensitivity to volatiles.

Experimental Procedure

An AquaLab Series 4TE water activity instrument (Decagon Devices Inc, Pullman, WA) was modified to utilize TDL technology to measure water activity. The AquaLab TDL shines light of through the headspace above a sample in a sealed chamber. The attenuation of the light provides a direct measure of the vapor pressure in the headspace (Figure 1). The TDL is a spectroscopic method in that it sweeps across a single water vapor absorption line at 1854 nm. The absorption at that wavelength is specific to water vapor, which makes it insensitive to the presence of other volatiles. The vapor pressure determined by the TDL is then divided by the saturation vapor pressure at the sample temperature to give water activity. Sample temperature is measured using an infrared sensor similar to existing AquaLab water activity instruments. For comparisons, water activity was also tested using an AquaLab Series 4TEV instrument (Decagon Devices Inc, Pullman, WA) using both a chilled mirror and a capacitance sensor. Temperature was controlled to 25°C during all water activity testing.



Water activity standards of 0.25 a_w, 0.50 a_w, 0.76 a_w, and 1.00 a_w were measured with all 3 sensors. In addition, the water activity of potentially problematic oil and lubricant samples were measured with all 3 sensors, Sample included: brake fluid DOT3, 10W-30 oil, spindle oil, way oil, hydraulic oil, cutting oil concentrate, and diluted cutting oil.

Finally, the water activity of solutions containing 5.0%, 25.0%, 50.0%, and 75.0% concentrations of Et in water were tested. All water activity tests were repeated 4 times and were performed on 3 replications for each sample. Results were averaged across all readings when available. Water activity readings that differed by more than 0.003 a_w (the reported accuracy of the chilled mirror method) were considered to be significantly different.

Testing Results

The TDL a_w sensor performed better than the capacitance sensor in accuracy and precision on the a_w standards, and was equivalent to or better than the chilled mirror sensor (Table 1). This would indicate that the TDL technology can be considered equal to the chilled mirror sensor in water activity testing performance. The chilled mirror water activity method is generally accepted as the fastest and most accurate way to measure water activity. The TDL method is similar in test time to chilled mirror, since the time determining step of both methods is vapor equilibrium of the sample to the headspace.

Table 1. Water activity performance on salt standards for the TDL, chilled mirror, and capacitance water activity sensors.*

	0.25 a_w		0.50 a_w		0.76 a_w		1.00 a_w	
Sensor	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
TDL	0.2490	0.0007	0.5017	0.0007	0.7611	0.0009	0.9999	0.0016
Chilled	0.2519	0.0017	0.4906	0.0004	0.7580	0.0016	0.9961	0.0015
Cap	0.2506	0.0053	0.5004	0.0115	0.7467	0.0105	0.9983	0.0011

** A difference >0.003 a_w of average values from the actual value of the standard and a standard deviation > 0.001 a_w are considered out of specification.*

The TDL water activity sensor measured water activity values that were significantly lower than the chilled mirror for all of the samples tested, indicating a lack of sensitivity by the TDL sensor (Table 2). The chilled mirror sensor is particularly sensitive to the 10W-30 motor oil and diluted cutting oil, as evidenced by the inability to make readings, but the TDL sensor was able to read both correctly with no issues. The capacitance sensor reported water activity values similar to the TDL sensor and followed the trend of being lower than the chilled mirror sensor for spindle oil, way oil, and hydraulic oil. However, for the cutting oil concentrate, the capacitance sensor reported water activity values higher than even the chilled mirror sensor, while the TDL was significantly lower than both of the other sensors. These results provide evidence that while the capacitance sensor can handle many samples with volatiles better than the chilled mirror sensor, even the capacitance sensor can be impacted by some products. The TDL however showed no such weakness.

Table 2. Average water activity values and standard deviations of volatile containing products as measured using the TDL, capacitance, and chilled mirror sensors.*

	Brake Fluid DOT3		10W-30		Spindle Oil		Way Oil	
Sensor	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
TDL	0.0298a	0.0004	0.2132b	0.0001	0.2224c	0.0004	0.2251c	0.0001
Chilled	0.0279b	0.000	NA	NA	0.3049a	0.001	0.2881a	0.001
Cap	0.0233c	0.001	0.2494a	0.001	0.2616b	0.001	0.2406b	0.001

	Hydraulic Oil		Cutting Oil Concentrate		Cutting Oil Diluted	
Sensor	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
TDL	0.2362c	0.0001	0.8883c	0.001	1.00a	0.0006
Chilled	0.3202a	0.001	0.9261b	0.002	NA	NA
Cap	0.2943b	0.001	0.9371a	0.003	NA	NA

** Average values in columns followed by the same letter are not significantly different ($p<0.05$).*

The trend of both the capacitance sensor and the TDL sensor reading lower than the chilled mirror continued for solutions of Ethanol at all concentrations (Table 3). The chilled mirror sensor could not even make measurements of the 50% and 75% ethanol solution, due to an inability to determine an accurate dewpoint temperature. Even though both the capacitance and TDL sensors recorded lower water activities than chilled mirror at all of the concentrations, the TDL sensor was significantly lower than the capacitance sensor for all of the solutions. A reference to freezing point data, the only other water activity method not susceptible to the presence of volatiles (but with many other challenges), indicates that the lower TDL water activity values are more accurate for these solutions (Table 3). The values reported for the TDL are not statistically equivalent to the freezing point data, but the trend of being lower than the chilled mirror and capacitance sensor holds true for the freezing point data. Agreement to the freezing point data is made further difficult by the freezing point data being only appropriate for water activity values higher than 0.90 a_w.

Table 3. Average water activity values and standard deviations of solutions containing 4 different concentrations of Ethanol (Et) as measured by the TDL, chilled mirror, and capacitance sensors compared to Freezing Point (Fr Pt) data.*

	5% Et		25% Et		50% Et		75.0% Et	
Sensor	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
Fr Pt	0.9712c	NA	0.8724d	NA	0.6723c	NA	0.6118c	NA
TDL	0.9651d	0.0010	0.8807c	0.0006	0.8121b	0.0002	0.6722b	0.0004
Chilled	0.9959a	0.0006	0.9967a	0.0018	NA	NA	NA	NA
Cap	0.9937a	0.0067	0.9390b	0.0044	0.8834a	0.0025	0.7889a	0.0018

** Average values in columns followed by the same letter are not significantly different ($p<0.05$).*

Summary

As expected, the water activity readings of the chilled mirror sensor were significantly impacted by the presence of volatiles. The capacitance sensor was not as sensitive as the chilled mirror to the presence of volatiles, but it was also shown to be susceptible to some types of volatile-containing samples. In addition, the capacitance sensor, being a secondary water activity method is not as fast or accurate as the chilled mirror sensor.

The performance of the TDL water activity sensor on water activity standards was equal to or better than the best currently available water activity testing options. Its accuracy, precision, and speed are equivalent to the chilled mirror sensor (currently the fastest and most accurate sensor available). In addition, it was the only sensor to completely lack sensitivity to the presence of volatiles, as indicated by its lower water activity readings and closer agreement with freezing point data. The top performance in water activity testing combined with ease of use and the lack of sensitivity to any sample types makes TDL the superior method for measuring water activity.

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