

Detection of trace levels of water in oil by photoacoustic spectroscopy

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Abstract

We have demonstrated the feasibility of non-destructively analyzing trace levels of water in petroleum-based transmission and hydraulic oils and in a synthetic polyol ester engine-lubricating oil using photoacoustic spectroscopy (PAS) at a wavelength of 2.93 μm . Using the method of standard additions, detection limits of 45, 60, and 515 ppm were obtained for water in the transmission, hydraulic, and synthetic engine oils, respectively. Lower sensitivity for water in the synthetic polyol ester oil was due to a 0.16 μm shift in the water absorption maximum from the wavelength used for the other oils. A detection limit of 62 ppm was also observed for analysis of water in standard reference material (SRM) 8507 from the National Institute of Standards and Technology (NIST), which is a petroleum oil having a nominal water content of 77 ppm. The results for the petroleum-based oils exceed the current best detection limits of approximately 100 ppm obtained using Fourier transform infrared spectroscopy (FTIR) and compare favorably with the desired detection limits for water in oil of 10–50 ppm. Factors involved in implementing this technology in on-line sensors are discussed. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Most machinery requires lubrication by oil to operate efficiently and reliably. Oil is also used as a hydraulic fluid in heavy equipment. Both lubrication and hydraulic oils can degrade by contamination from dirt, soot, process or wear materials, process chemicals, fuel dilution, or water. Water is the most common contaminant usually as a consequence of condensation, coolant leak or free water ingress during equipment cleaning or environmental exposure. Water can result in destructive wear and corrosion of parts as well as oxidation or degradation of the oil [1,2]. Knowledge of the condition of oil in equipment is necessary in order to change the oil in a cost effective manner. Premature oil change wastes natural and financial resources and generates additional environmental disposal costs. Changing the oil too late can result in part wear and possible equipment failure.

For early-warning and maintenance-scheduling purposes, detection limits of 10–50 ppm water in oil are desirable. Detection limits as low as 10 ppm are possible using Karl-Fischer titration. However, this technique is unsuitable for accurate, real-time, in situ determinations of water levels in used oil because it requires a substantial sample size, is

sample destructive and time consuming, and is subject to severe interferences from sulfur compounds present in most engine oils (ASTM D6304-00). Accurate, real-time, in situ determinations of water can be made using Fourier-transform infrared (FTIR) spectroscopy, but the best currently achievable detection limits for water in oil are on the order of 100–500 ppm depending on the type of oil [1]. Other analysis techniques are used such as inductively coupled plasma (ICP) spectrometry to measure for metals, wear particle analyzers to monitor particulate debris, and FTIR to analyze for water as well as chemical changes in the oil. Water concentrations greater than 1000 ppm in oil are considered harmful [1]. Although, the current best detection limits for water in oil are about 100–500 ppm using FTIR, it is desirable to be able to measure water at levels as low as 10–50 ppm for early detection of contamination and efficient scheduling of maintenance.

Photoacoustic spectroscopy (PAS), which relies on the absorption of light energy by a sample and then detection of the acoustic wave generated when the sample returns to the ground state, has detection limits that are typically 10–1000 times lower than other purely absorption-based spectroscopies. Sensors based on PAS have recently been designed to monitor serum glucose levels [3], pH and CO₂ [4], oil in water [5], hydrogen gas [6], and biomass fermentation [7]. Lai and Vucic used PAS to monitor the degradation of motor

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oil by exciting the aromatic hydrocarbons at 355 nm [8]. In this paper, we demonstrate the ability of PAS spectroscopy to analyze trace levels of water in petroleum and synthetic lubrication oils using an excitation wavelength of 2.93 μm (3415 cm^{-1}).

2. Experimental

2.1. Samples

Clean samples of unused transmission, hydraulic, and engine oil samples from the US Army tank maintenance facility at the Yakima Firing Range, WA were studied. The transmission and hydraulic oils were petroleum oils. The transmission fluid was a Dextron-type petroleum-based fluid. The hydraulic fluid also was largely petroleum-based and conformed to MIL H 83232. The engine oil was a synthetic polyol ester based oil for use in gas turbine engines (MIL L 23699) and contained few additives. The transmission and engine oils are the types currently used to lubricate M1 Abrams tanks. A standard reference material (SRM) 8507 of petroleum oil from the National Institute of Standards and Technology (NIST) certified to have 76.8 (± 2.3) ppm water was also tested.

The method of standard additions was used to prepare samples of clean oil with known relative water contents. Briefly, 10–20 ml of oil was placed in a tared 22 ml glass vial with a stir bar. While on the balance, aliquots of water (ca. 5–10 μl) were added. The actual amounts added were determined by weight. After capping the vials, the oil/water mixtures were then stirred for 15–30 min or until complete miscibility was obtained as determined by visual inspection. Samples of the clean oils and the reference material were also treated for at least 15 h with a molecular sieve (5 g of 4 \AA pore size, 4–8 mesh pellets from Aldrich were heated 1 week at 120°C, cooled, and then contacted with 10 ml oil) to remove water that might have already been present in the oils.

2.2. Infrared detection

Specimens for FTIR analysis were transferred into a transmission cell [100 μm pathlength, ZnS (IRTRAN) windows]. Between samples, the cell was cleaned by flushing with neat methanol and dried with N_2 gas. Spectra were collected in the mid-infrared region (32 scans, 2 cm^{-1} resolution) using a Bruker IFS66V/S spectrometer equipped with a DTGS detector. The spectra were corrected for background offsets and etalon fringing was removed by smoothing using a 91-point box algorithm.

2.3. Photoacoustic detection

A diagram of the PAS experimental arrangement is shown in Fig. 1. Data were collected using our flow through layered-prism cell [9] with a sapphire entrance prism, quartz

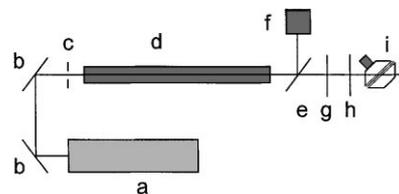


Fig. 1. Schematic of photoacoustic experimental setup: (a) Nd-YAG laser at 1064 nm, (b) 1064 nm high power laser mirror, (c) iris, (d) 1 m Raman cell filled with D_2 (g) at 900 psi, (e) coated-sapphire 1064 nm selective mirror, (f) 1064 nm beam dump, (g) optical filter passing light > 845 nm, (h) optical filter passing 2670–8000 nm light, (i) layered-prism cell with front prism of sapphire, back prism of quartz, and 5 MHz contact transducer. A detailed schematic of the layered-prism cell is given in [9].

exit prism, and an optical pathlength of 0.76 mm. Acoustic contact between the transducer (0.25 in. diameter, 5 MHz, Panametrics) was facilitated by an ultrasonic couplant fluid (Sonic Instruments). Excitation light of 2.93 μm (3415 cm^{-1}) was generated by Raman shifting [900 psi deuterium in a 1 m Raman cell (LightAge, #101PAL.RC-1.0)] 1064 nm light from a pulsed Nd-YAG laser (Continuum, #NY61-20) operating at 20 Hz with a 8 ns pulse width. Because Raman conversion generates several anti-Stokes (807, 650, 544 nm, etc.) and Stokes (1561, 2928 nm, etc.) lines, optical filters and a wavelength-selective mirror were used to remove or reflect the unwanted Raman lines. Energy per pulse was about 20 μJ . The signals from the transducer were amplified using a preamplifier (Panametrics, model 5670, 40 dB) and the waveforms collected on a digital oscilloscope (Lecroy, model 9362). The photoacoustic signal was monitored using in-house data collection software along with a computer interface and a boxcar averager (Stanford Research Systems). All waveforms were signal averaged over 500 shots. The photoacoustic signal was determined by either calculating the maximum peak-to-peak voltage of the waveform or by integrating the signal voltage over the time period selected by the boxcar. Data reported are the averages of twenty 500-pulse signal-averaged events (i.e. 500 s total analysis time). Detection limits were calculated ($S/N = 3$) based on the standard deviation (S.D.) of the signal of the blank ($n = 20$). Between samples, the photoacoustic cell was flushed with methylene chloride and dried with N_2 gas.

3. Results and discussion

The absorption maximum for free water ($A = 12\,000\text{ cm}^{-1}$, $\epsilon = 216\text{ M}^{-1}\text{ cm}^{-1}$) is at 2.94 μm (3401 cm^{-1}) [10]. Although, the absorption maximum for water in an oil matrix was unknown, this wavelength region was selected as the most likely to yield the low detection limits required. To demonstrate the selectivity of the approach, water and a series of four neat organic solvents that did or did not contain hydroxyl functional groups were tested at an excitation wavelength of 2.93 μm (3415 cm^{-1}). For the solvents that

contained the hydroxyl functional groups (water, methanol and decanol), strong absorption at $2.93\ \mu\text{m}$ due to O–H stretching vibrations was expected. Little absorption was expected for the other solvents that lacked the hydroxyl functional group (methylene chloride and carbon tetrachloride). The PAS results obtained for these five solvents were:

Solvent	PAS signal (peak-to-peak, mV)
Methylene chloride	1.8 ± 0.5
Carbon tetrachloride	5.7 ± 1
Water	47 ± 1
Methanol	228 ± 2
Decanol	230 ± 2

These results show the clear selectivity of the PAS technique for substances that contain hydroxyl groups when a $2.93\ \mu\text{m}$ excitation wavelength is used. The four-fold higher sensitivity to methanol and decanol than to water stems from the more favorable acoustic transmission properties of the alcohols. The very low signal levels observed for the non-hydroxylated solvents may actually reflect the presence of trace levels of water in these nominally neat solvents.

Standard curves for the photoacoustic analysis at $2.93\ \mu\text{m}$ of clean hydraulic, transmission, and engine oils with different levels of water are plotted in Fig. 2. Detection limits for water were calculated to be 60 ppm in hydraulic oil, 45 ppm in transmission oil and 515 ppm in engine oil. Fig. 3 shows FTIR absorbance spectra for transmission oil with increasing amounts of water. To determine the amount of water present in the original oil, molecular-sieve material was added to this oil to remove all water. The signal obtained corresponded to an “added water” concentration of $-120\ \text{ppm}$, indicating that the original concentration of

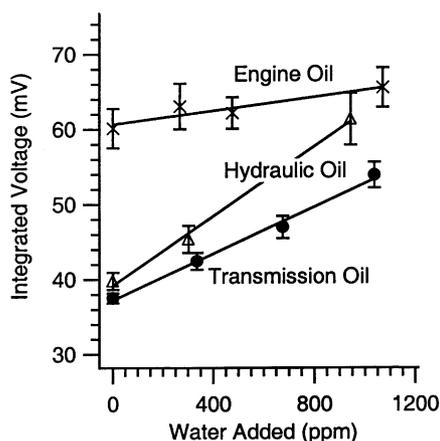


Fig. 2. PAS calibration curves for clean hydraulic (Δ), transmission (\bullet), and engine (\times) oils with varying amounts of added water. Detection limits for water were calculated to be 60 ppm in hydraulic oil, 45 ppm in transmission oil and 515 ppm in engine oil. The error bars represent ± 3 S.D.

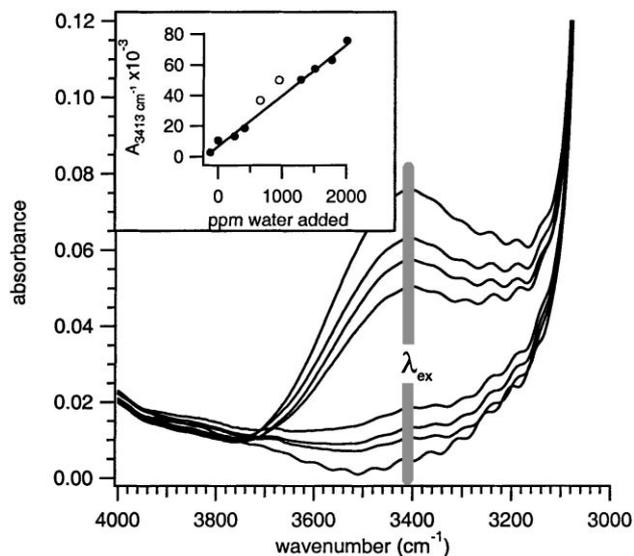


Fig. 3. FTIR absorbance spectra of transmission oil with different amounts of added water (0–2000 ppm). The least absorbing spectrum is for “dried” oil that had been reacted with molecular-sieve material to remove all water. Parameter λ_{ex} represents the wavelength of excitation ($3415\ \text{cm}^{-1}$) used in the photoacoustic experiments. The inset shows the absorbance at λ_{ex} as a function of water added. Data represented by open circles were not included in the linear regression or shown in the spectral plot. These two specimens were likely contaminated with residual methanol in the FTIR cell as a result of incomplete drying between samples.

water in the unamended oil was 120 ppm. The estimated detection limit for the FTIR analysis of this oil was about 100 ppm water. Thus, the detection limits for the hydraulic and transmission oils using PAS are two times lower than those obtainable with FTIR.

Fig. 4 shows FTIR absorbance spectra for the petroleum transmission and synthetic engine oils, both as received and

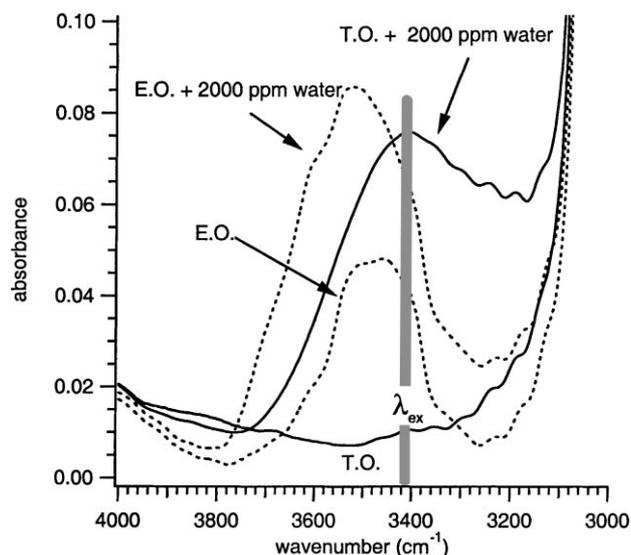


Fig. 4. FTIR absorbance spectra of clean transmission oil (T.O.) and engine oil (E.O.); as received and after amendment with water to a level of 2000 ppm. Parameter λ_{ex} represents the wavelength of excitation ($3415\ \text{cm}^{-1}$) used in the photoacoustic experiments.

after addition of water to a final concentration of 2000 ppm. The absorption maximum for water in this synthetic engine oil shifts to $2.84 \mu\text{m}$ (3520 cm^{-1}). Light absorption by the unamended synthetic oil at $2.93 \mu\text{m}$ (3415 cm^{-1}) was due to a combination of an ester overtone band centered near 3470 cm^{-1} and a weak band associated with antioxidant additives near 3390 cm^{-1} . With addition of water, an increase in the absorption was observed at this wavelength, albeit to a significantly lesser degree than at the absorbance maximum near $2.84 \mu\text{m}$ (3520 cm^{-1}). Because of these interferences, the optimal excitation wavelength for detection of water in the synthetic polyol ester oil is around $2.78 \mu\text{m}$ (3600 cm^{-1}). At the excitation wavelength used in this study, one would not expect to be able to detect water in the synthetic engine oil by PAS with the same sensitivity achieved for the hydraulic and transmission oils.

In a second PAS experiment, we focused on the transmission oil and a wider range of water contents, including a sample of the oil treated with a molecular sieve to remove water initially present. The results showed a linear response to about 1800 ppm added water (Fig. 5). Above this value incomplete miscibility occurred (emulsification of the sample was not attempted) and so a lower signal was obtained than expected. To determine the amount of water present in the original oil, we added the molecular-sieve material to this oil to remove all water and measured the PAS signal. The signal obtained corresponded to an “added water” concentration of -170 ppm , suggesting that the original concentration of water in the oil was 170 ppm. Statistically, this value is not significantly different from the 120 ppm value determined by FTIR.

The slope of the response curve for the transmission oil is about three times greater in Fig. 5 than Fig. 2. However, a decrease in signal-to-noise was also observed leading to an estimated detection limit of 85 ppm water for transmission oil in this experiment. The differences in slope and signal-to-noise likely stem from changes in one or more experimental

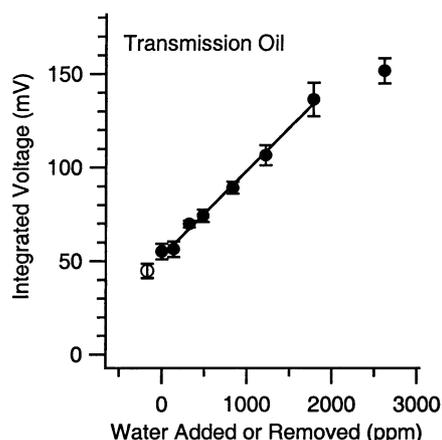


Fig. 5. PAS signal for transmission oil with standard additions of water. Molecular-sieve material was added to this oil to remove any water initially present (open circle), yielding an estimate of 170 ppm water in the unamended oil as received. The error bars represent $\pm 3 \text{ S.D.}$

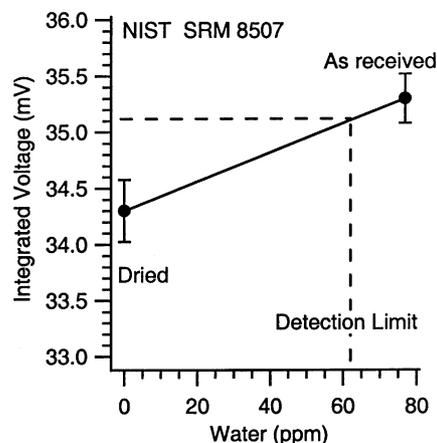


Fig. 6. PAS response for NIST SRM 8507 and this oil ‘dried’ with molecular-sieve material for 48 h. The error bars are $\pm 1 \text{ S.D.}$ The dashed line represents the calculated detection limit of 62 ppm water.

parameters (laser power, laser stability, Raman-conversion efficiency, and sample-cell alignment) between the two experiments.

In a third PAS experiment, two samples of the NIST reference oil, one as received and one after treatment with the molecular sieve for 48 h to remove water, were run. The results of these analyses (Fig. 6) clearly show the ability of PAS to distinguish between 77 and 0 ppm water in this sample (the error bars in the figure are 1 S.D. of the data). The calculated detection limit ($S/N = 3$) for this sample was 62 ppm water.

The results of these three PAS experiments demonstrate that water in petroleum oils can be detected at levels at least two times lower than those accessible to conventional absorption spectroscopic techniques such as FTIR. Detection limits on the order of 50 ppm are easily obtainable. Limits as low as 10–20 ppm might be achieved routinely with further optimization (e.g. better laser stability and transducer sensitivity, higher laser power). The optimal analysis of water in synthetic polyol ester oils would require light at a different wavelength [i.e. $2.78\text{--}2.86 \mu\text{m}$ ($3600\text{--}3500 \text{ cm}^{-1}$)] than used in these experiments, due to the shift in the water absorption band, and to interferences from the ester overtone band and antioxidants in the synthetic oil.

For application to miniaturized, on-line analyses of machinery, a stable, rugged, inexpensive light source is needed. Because the Raman conversion used in our experiments was expensive, inefficient, and had large shot-to-shot variability, it is unsuited for sensor applications. Given the success we observed at the $20 \mu\text{J}$ per pulse level, however, laser diodes should be able to provide sufficient monochromatic light for this purpose. Use of an inexpensive Xe flash lamp and a notch filter [11] may be another option, if sufficient intensity in the mid-IR region can be achieved. A third option would be an Er-YAG laser, which has a fundamental wavelength of $2.94 \mu\text{m}$. Because current pulse-widths for this laser are 100–700 μs , which is much longer

than the 10–100 ns optimal for PAS work, a new design that yields significantly shorter pulse widths is needed. Preliminary discussions with laser manufacturers suggest such a laser could be produced at a size and cost that make it competitive with diode lasers. The short-pulse Er-YAG would offer more power than the diode lasers, if such was needed.

4. Conclusions

Trace levels (≥ 50 ppm) of water in petroleum oils can be determined accurately by PAS with at least two-fold greater sensitivity than conventional FTIR spectroscopy. For synthetic polyol ester oil, the optimal absorption maximum differs by about 0.16 μm and sensitivity is decreased 10-fold if the excitational wavelength is not shifted accordingly. Eventual use of PAS in sensor applications awaits development of a stable, rugged, and inexpensive pulsed light source.

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