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FINAL REPORT
THIN-FILM DEVICE FOR PROCESS MEASUREMENT
U.S. Department of Energy Project DE-FC07-91ID13063

D. S. GOLDMAN
GUIDED WAVE, INC.
5190 Golden Foothill Parkway
El Dorado Hills, CA 95630

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EXECUTIVE SUMMARY

The co-operative agreement for financial assistance entitled "Thin-Film Device for Process Measurement" has fulfilled its original objectives and met its major milestones. A compact, portable planar waveguide spectrometer has been developed and successfully applied to a variety of chemical and petrochemical analytical problems with considerable commercial end-user interest.

This work is an outgrowth of earlier work initiated at the Pacific Northwest Laboratories with DOE funding by the author that led to an R&D100 award and a U.S. Patent (5,082,629). It is a good example of technology transfer from the public to private sectors with the broad goals of energy saving in petroleum and chemical processing and improved U.S. industrial competitiveness.

This planar waveguide technology is ideally suited for liquid samples that are difficult to analyze by conventional means. It is based upon the method of attenuated total internal reflection, which allows spectroscopic analysis without transmitting light across a volume of liquid. As a result, slurries containing light scattering particles can be quantitatively analyzed without time consuming sample preparation. Highly viscous samples are also easy to analyze. The sample is simply "painted" on the flat waveguide plate. For example, seven dark, viscous crude oil samples were analyzed in less than a half hour.

Theoretical and fabrication expertise were gained to produce waveguide plates of high quality for efficient chemical analysis in the near-infrared. To our knowledge, this is the first time that planar waveguides have been used for chemical analysis using a broad wavelength light source with sufficient signal at the detector for excellent quantitative analysis. In fact, the planar waveguide prototype was able to measure below 100 ppm hydroxyl in polymeric systems. Quantitative laboratory studies were conducted and in-plant tests involving sulfonic acid foam and silicone production were completed. Some properties of crude oils were also predicted using sophisticated mathematical models.

The technology did not develop into a fiber optic probe that could be inserted directly into a process pipe. Further technical development should be pursued in this area. The spectrometer is ideal for at-line (perhaps with a flow cell) or quality control laboratory applications.

Considering that significant end-user interest exists for this technology, it is recommended that any remaining funds in the program and other funds that may be made available should be directed toward commercialization and probe development rather than additional plant testing. The device has already been proven. The primary goal should now be delivering the technology to industrial end-users.

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INTRODUCTION

This report summarizes the work performed under this co-operative agreement for financial assistance for the two-year period ending April 9, 1993.

Phase I activities were completed at the Pacific Northwest Laboratory (PNL) in 1989. They proved the feasibility of the concept experimentally with laser sources. The overall optical efficiency of the device was determined to be about 0.1%. This is probably not adequate for a commercially viable instrument. Funding limitations prevented access to state-of-the-art fabrication equipment, so all fabrication was conducted in-house at PNL. Much of Phase I was spent on grating fabrication without any prior experience in sub-micron photolithography. It was felt that access to better grating and waveguide fabrication methods would result in sufficient signal and a practical device. Once rights were obtained to practice the invention conceived at PNL with a non-exclusive license, funding from the current project would be used to assemble a more efficient device by accessing state-of-the-art grating and waveguide fabrication capabilities with outside vendors.

The current project is divided into two Phases. The objectives of Phase II were to (a) overcome the optical efficiency problem with sufficient funding to access improved fabrication capabilities not available in Phase I, (b) begin the prototype design process and (c) conduct laboratory testing. Phase III completes the prototype system development activities, identifies process measurement applications and conducts field testing on relevant process systems.

Thin-film, or planar waveguide technology addresses those process measurements of liquids that scatter light, such as emulsions, suspensions and slurries. Commercial instrumentation for process measurement of clear fluids currently exist. These optical fiber process spectrophotometers generally rely on transmitting light through a volume of liquid. A single fiber or fiber bundle transmits light to the sample, and generally another fiber or bundle receives the light not absorbed by the sample and transmits it to the spectrometer. Light scattering phases in the sample impair these transmission measurements. The

planar waveguide approach operates by a different physical phenomenon, referred to as attenuated total internal reflectance (ATR). ATR is a method of acquiring spectral information without transmitting light through a volume of liquid. As a result, light scattering particles do not significantly impair ATR spectral measurements. ATR evolved in the mid-infrared for laboratory applications in the 60's. The planar waveguide approach allows this method to be used in the near-infrared where much of current process analytical chemistry is conducted. This is because of stable instrumentation, strong light sources, fast and sensitive detectors that operate at room temperature and ease of sample handling.

This project was initially focused upon energy savings from improved chemical process measurements in atmospheric distillation. It was envisioned that the thin-film technology would be configured in the form of a probe that could be inserted directly into a process pipe. The probe would then be connected to the spectral analyzer remotely via optical fibers in order to minimize explosion hazards. The technology first evolved into a compact, stand-alone planar waveguide spectrometer in this project. This device is well-suited for at-line or field lab quality control applications. It has been successfully demonstrated in the laboratory and at plant sites in Phase III activities, as detailed herein. However, due to current technical limitations, it is not in the form of an insertable probe at this point. Thus, it is important to understand that applications demanding in-line chemical analysis from this technology will have to await further technical development.

EARLIER RECOGNITION AND AWARDS

R&D Magazine presented the Planar Waveguide Spectrometer its prestigious R&D100 Award in 1991 as one of the top 100 new technologies based upon Phase I work at PNL. This honor was jointly awarded to PNL and the University of Washington (UW) (Center for Process Analytical Chemistry - CPAC).

A United States Patent (5,082,629) was issued on January 21, 1992 covering the Planar Waveguide Spectrometer concept. It was jointly assigned to the Battelle Development Corporation, representing the PNL, and the UW. The inventors are Lloyd W. Burgess (UW) and Don S. Goldman (formerly at PNL).

Two peer-reviewed papers and one invited conference symposium paper have resulted from the work completed in Phase I (cleared through PNL/DOE-RL):

- Don S. Goldman, P. L. White and N. C. Anheier "Miniaturized spectrometer employing planar waveguides and grating couplers for chemical analysis" *Applied Optics*, v. 29, n. 31, 4583-4589 (1990).

- Don S. Goldman, P. L. White and N. C. Anheier "Planar waveguide spectrometer" SPIE Vol. 1338 Optoelectronic Devices and Applications (1990)
- D. DeGrandpre, L. W. Burgess, P. L. White and D. S. Goldman "A Thin Film Planar Waveguide Sensor for Liquid Phase Absorbance Measurements" Analytical Chemistry, 62(18) 2012-2017 (1990)

CONCLUSIONS

1. The overall goals of the project were achieved in terms of technology development and application to industrially important samples.
2. Further verification from in-plant tests within the scope of the current project is unnecessary. Attention should focus on commercialization. There is a high degree of end-user interest.
3. The first broad-band use of planar waveguide technology for chemical analysis has been demonstrated. Device performance exceeded all original expectations in terms of signal-to-noise and the quality of the resulting spectral data with at least at 50x improvement in efficiency over Phase I results.
4. The technology has been developed into a stand-alone, compact, portable spectrometer for at-line process and quality control laboratory measurements.
5. Further developments are required to evolve the technology into a probe that can be directly inserted into a process pipe for continuous on-line analysis. A technical approach has been devised.
6. The alpha (first) prototype has demonstrated its viability for rapid analysis of difficult-to-analyze liquids and heterogeneous mixtures, including slurries made with silica, titanium dioxide and activated carbon particles. Actual industrial applications for crude oil characterization, silicones and sulfonic acid foams have been successfully completed, including limited in-plant trials.
7. The prototype system was shown to be able to measure 0.1% water in methanol and less than 100 ppm free-hydroxyl in certain polymeric systems.

GLOSSARY

Thin-film or planar waveguide	Similar to an optical fiber, but flat and very thin, typically less than 1 micron, in which the optical modes can be exactly controlled.
Optical mode	An allowed path for a light wave propagating through the waveguide.
Integrated optic	Generally refers to a highly compact optical circuit made of thin-films, various types of couplers, miniature laser sources and detectors mounted on a "chip".
Internal reflection	When considering light as a ray, an internal reflection occurs each time the light ray intersects the surface within the waveguide and reflects back toward the other surface within the waveguide.
Evanescent field	A portion of the beam of light at each internal reflection that actually extends outside the physical boundary of the waveguide and interacts with the sample.
Evanescent penetration distance	The distance into the sample at each internal reflection that the evanescent electric field amplitude decays by 57%. This is the region in the sample that is "sensed" by the planar waveguide device. It is generally less than the wavelength of light.
Effective path length	The effective path is the product of the number of internal reflections times the evanescent penetration distance, and is equivalent of doing a transmission experiment through a liquid-filled cuvette of this length.
ATR- Attenuated Total Internal Reflectance	The process that allows the sample to extract power from the evanescent field at each internal reflection leaving less power in the beam transmitted in the waveguide. This process results in a spectrum of the sample.
Transmission	The process by which light travels through the bulk sample to the detector that results in a spectrum of the sample.
Grating coupler	A series of closely spaced grooves (e.g. 1000 grooves/mm) touching the waveguide as a means to inject light into or extract light from the planar waveguide.
Grating period	The inverse of the number of grooves/distance, typically ranging between 0.4 and 1.0 micron (2500 and 1000 grooves/mm, respectively).
Grating duty cycle	Indicates the relative widths of the troughs and ridges that make up the grating, given in percent.
Photoresist	A light sensitive thin polymer layer deposited on the substrate into which the grating pattern is generated by an electron beam machine or lasers. The regions in the photoresist exposed to the beam are dissolved leaving regions of the bare substrate exposed. Subsequent treatment in an ion beam then etches into the substrate only where it is exposed thus transferring the grating pattern from the photoresist into the substrate. The remaining photoresist is then removed leaving the substrate with the grating.
Photodiode array detector	A solid-state device that is an integrated arrangement of closely adjoining photodiode detectors that are multiplexed so that each one can be illuminated with a different wavelength of light to rapidly acquire a spectrum.
Ion-beam deposition	The process by which an ion beam is used to sputter metal ions from a target so that they can be deposited on a substrate to form a thin film. Often these metal ions are combined with oxygen or nitrogen to produce oxide and nitride films.

SUMMARY OF THE CONCEPT

The planar waveguide concept (U.S. Patent 5,082,629) from Phase I is schematically shown in Figure 1. "White" light, comprised of a continuum of wavelengths, is coupled into the planar waveguide through a grating coupler

over a wide range of angles. Light is transmitted within the planar waveguide. The sample interacts with the evanescent field at each internal reflection. This field extends beyond the waveguide surface into the liquid a distance generally less than the wavelength of light. This evanescent penetration distance is the region in the liquid that the waveguide actually "senses". If the sample absorbs light at various wavelengths in the evanescent region, less power remains in the beam propagating within the waveguide at those wavelengths. Successive internal reflectance interactions with the sample are additive. The light is extracted from the waveguide at the second grating coupler. Each wavelength is directed toward the photodiode array detector at a different angle. The resulting spectrum shows this signal as a function of channel number of the array detector. By using suitable wavelength calibration filters and sources, channel number can be converted into wavelength, if necessary. A transmittance spectrum is obtained by first acquiring the signal over wavelength (i.e. channel number) without the sample on the waveguide and dividing it into the signal obtained with the sample on the waveguide. The negative logarithm of the transmittance spectrum results in the absorption spectrum. The absorbance of various spectral features is often linearly related to the chemical concentration of that species.

The spectral features in the near-infrared region ($0.8 - 3.0 \mu\text{m}$) due to water ($1.4, 1.9 \mu\text{m}$) or organics ($1.1, 1.4, 1.7 \mu\text{m}$) are relatively weak. As overtones and combination modes, they are generally several orders of magnitude less intense than their analogous peaks arising from fundamental molecular vibrations in the infrared. The planar waveguide is so thin that several thousand internal reflections occur within the waveguide between gratings spaced 1 cm apart. The evanescent penetration distance is typically $0.3 - 0.6 \mu\text{m}$ in the near-infrared. The sensitivity of the waveguide is the product of the number of internal reflections with the sample times the evanescent field penetration. This product is referred to as the effective path length, which is equivalent to using a sample-filled cuvette of that width in a conventional transmission analysis. The effective path from the planar waveguide is generally between 1 - 5 mm, which is sufficient to measure many of these spectral features in the near-infrared.

The sensitivity of the planar waveguide in a specific wavelength region can most easily be altered by changing the sample coverage on the waveguide. However, it can also be modified by fabricating a waveguide having a different thickness or different optical properties.

Unlike most optical fibers used for process measurements that have thousands of optical modes, the planar waveguide is designed to have only one. This means that light of one wavelength and polarization only travels one way through the waveguide. Its interaction with the sample can be exactly controlled. This is accomplished by the choice of refractive indices of the substrate and waveguide and the thickness of the waveguide. In addition inert waveguide materials can

be selected that are resistant to most acids and abrasion from particles. Planar waveguides made from Ta_2O_5 suffice for this purpose and have been used throughout Phases II and III.

RESULTS AND DISCUSSION

Tasks 1 and 2. Gratings and Waveguides.

At the beginning of Phase II, a detailed theory was not available that specifically addressed our grating coupler configuration. This relates to coupling electromagnetic radiation into or out of a thin-film planar waveguide through a grating coupler. Considerable theoretical development is available in the open literature in this area. However, these developments did not extend to the case where the evanescent field of electromagnetic radiation propagating in the waveguide extends to a considerable proportion of the grating etch depth, as is our case.

The new code designed by our consultant is versatile, allowing the user to define almost any grating shape (square wave, triangular, trapezoidal, etc.) and etch depth. It also predicts where the light is diffracted out of the waveguide to the photodiode array detector and to what efficiency. There are possibly several grating diffraction orders, so that each wavelength may be diffracted at several angles. The key to making the planar waveguide spectrometer viable is to ensure that only one or a narrow range of consecutive wavelengths illuminates each channel (photodiode) of the detector array and that these wavelengths monotonically increase (or decrease) across the detector. The waveguide is thus designed to only have one mode of light propagation. Furthermore, the grating is designed so that there is only one order of diffraction available for that waveguide mode at that wavelength.

The code indicates that the most efficient grating for our broad wavelength range of interest is rectangular in profile with a 50% duty cycle. All gratings were hence fabricated with this geometry. Blazing the grating (sawtooth shape), a standard approach in many commercial spectrophotometers, does not appear viable in our case. The resulting angle that each wavelength is directed out of the grating coupler is within 2° of the value determined from the earlier, simpler code.

For example, consider the case of a high refractive index waveguide ($n = 2.000$) on a glass substrate ($n = 1.504$) having a linear grating with a period of $0.91 \mu\text{m}$ and a rectangular profile that is etched into the substrate $0.135 \mu\text{m}$ at $1.45 \mu\text{m}$ wavelength in the near-infrared with TM polarization (polarization direction normal to the lines of the grating and plane of the substrate). The code predicts that this light will be diffracted into the substrate at an angle of 1.50° . It also

predicts that 41.1% of the radiation will be diffracted up above the waveguide and 58.9% will be diffracted into the substrate, both with a beam width of about $550\text{ }\mu\text{m}$. These calculations can therefore be used to design the optical system in terms of selecting waveguide material and thickness and grating period and depth.

Technical problems occurred with the first three vendors in making good quality gratings designed from the code. The fourth vendor finally was able to overcome these technical limitations after numerous fabrication runs, and has recently produced excellent gratings.

In addition to the efficiency of the gratings to couple light into and out of the waveguide, it is also important to have waveguide material that readily transmits this light between the gratings with little loss. Loss of signal due to light scattering or absorption within the waveguide is called propagation loss.

High quality waveguides made of Ta_2O_5 were available almost immediately from one vendor in Phase II. However, initial propagation loss measurements indicated values of 5.5 and 3.5 dB/cm for TE and TM polarizations at $1.152\text{ }\mu\text{m}$ in the near-infrared, respectively. This means that 28 and 45% ($T = -10\log(\text{dB}) = 10^{-35}$) of the starting light is propagated 1 cm through the waveguide.

At the time it was not known how important the quality of the substrate surface was in controlling propagation loss in the waveguide. In particular the surface roughness of the substrate is apparently much more significant in this regard than surface flatness. The above losses were measured on standard, flat fused silica plates purchased from optical lens supply houses. Much better surfaces were obtained with commercially purchased glass photoplates. Because these waveguides were more efficient, loss measurements became more difficult. An estimated propagation loss near 1 dB/cm or less ($>79\%$ transmittance) in the near-infrared was achieved. An even better surface would be an oxidized silicon wafer. Mechanical considerations kept our focus on fused silica or glass substrates.

Cleanliness during fabrication was found to be critical because gratings had to be etched into these pristine surfaces prior to waveguide deposition. Thus, the starting pristine surface had to be protected from the etching process and then cleaned of any remaining photoresist material. Once sources of contamination were identified and eliminated, good quality optical parts containing the gratings and waveguides were made in the last 6 months of Phase III. These improvements, in addition to fundamental changes in waveguide and coupler configurations, have led to overall efficiency improvements of at least 50x over Phase I work.

Task 3. Preliminary System Development.

A block diagram of the spectrometer system is presented in Figure 2 and a picture of the system is shown in Figure 3. To our knowledge, this is the first time that broad-band, incoherent light has been used with planar waveguides. It provides the means necessary to perform analytical chemistry of liquid samples. The prototype system will be described in general below.

A small wattage tungsten light bulb was used as the light source. Focusing optics were used to produce a collimated beam of light. This is the region that polarizing filters, cut-off wavelength filters and calibration components can be placed. A shutter to interrupt ("blank") the beam is also in the optical system to provide a "dark" signal for the detector. The light is appropriately focused to couple into the waveguide. The light exits the waveguide at the grating coupler, and is dispersed as a function of wavelength. A 256 element photodiode array detector (Epitaxx) made of indium-gallium-arsenide (InGaAs, often pronounced as "ingas") was used. Each element of the array is 0.5 mm tall and 0.03 mm wide, with a 0.05 mm center-to-center spacing. Thus, the active area of the entire array is 12.8×0.5 mm. The light emanating from the grating was conditioned by a lens assembly to be accepted by this active area of the photodiode array detector. Electronic circuitry purchased from EG&G Reticon were used for amplification and pre-amplification of the multiplexed array detector. A 16-bit analog-to-digital (A/D) converter (Analogic DASH16) was used for data acquisition and was placed in the one available slot of the Toshiba T6400DXC laptop computer. An external power supply was purchased and several DC-DC converters were assembled. The waveguide part was placed in a custom stainless steel mounting which can be readily inserted into the prototype, as shown in Figure 3.

Conventional ATR used in the infrared has one to perhaps a dozen or so internal reflections within the ATR element. Complete coverage of the crystal by the sample ensures that all locations of internal reflection will be covered. Hence, the exact number of internal reflections with the sample will not vary from sample to sample. However, it is difficult to achieve this invariance with thin-film planar waveguides having several thousand internal reflections/cm of beam travel. Applying samples to the waveguide that cover the beam differently on the order of fractions of a millimeter will lead to differences in the number of internal reflections by hundreds. [In fact, calculating the number of internal reflections for such a waveguide is useful, but is a mathematical simplification using ray optics. The beam is actually a propagating surface wave.]

It is also desirable not to cover the gratings with the liquids of interest, unlike what is shown in Figure 1. The primary signal of interest is from the ATR

phenomenon occurring between the waveguide and the sample. Changes in the refractive index of the liquid will not significantly change this process on the waveguide when using a high index waveguide, such as Ta_2O_5 . However, covering the grating with the liquid sample can change the angle at which each wavelength is directed toward the detector when the refractive index of the liquid changes. It is important decouple these phenomena and only analyze the ATR interaction on the waveguide. Therefore, some means to contain the sample on the waveguide reproducibly was sought.

One means was "wicking" liquid underneath a microscope cover slip placed on the waveguide, as shown in Figure 4 (right). Capillary forces cause the sample to fill the space between this piece of glass and the waveguide with reasonably defined boundaries without touching the grating. Cover slips of differing widths were used to adjust sensitivity by controlling the number of internal reflections. Later in the program it was demonstrated that a thick overcoat of a non-porous, inert material on the waveguide containing an opening in the middle of the overcoat that exposes the waveguide is perhaps the most reliable means to reproducibly contain the sample (Figure 4, left). The overcoat must be several times thicker than the evanescent penetration distance. It was experimentally demonstrated that samples applied to the overcoat are not sensed by the waveguide.

The overcoat can also be used to seal a flow cell to the waveguide. This may allow the planar waveguide spectrometer to be used at line on a slip-stream of process liquid diverted from the main process pipe. Bonding directly to the waveguide may present problems. Using polymeric gaskets against the waveguide may produce a spectral signal of the gasket material.

Task 4. Applications Development

Wavelength Calibration

As mentioned previously, photodiode element (sometimes referred to as a channel) number can be converted into wavelength using suitable standards. Figure 5 shows several such standards. The peaks labeled 1152 and 1523 nm originate from Helium-Neon lasers used in place of the tungsten light bulb. The peak labeled 1544 represents the tungsten bulb and a 1544 nm interference filter placed in the collimated portion of the beam before the waveguide. The peak labeled 1304 nm is from a diode laser, and the peak labeled 1700LP represents a tungsten bulb and a long pass filter. This filter allows light having wavelengths longer than 1700 nm through the system. The appearance of a peak results from the decaying sensitivity of the InGaAs detector at wavelengths longer than 1700 nm. A calibration graph shown in Figure 6 is made with these and other

sources. A second order polynomial provides an acceptable fit to the data and is used subsequently to convert element number into wavelength.

Water: Comparison with Transmission Spectra

Water is a common spectroscopic benchmark. Figure 7 uses such a wavelength conversion to compare planar waveguide spectra of water with that derived from conventional transmission measurements through a 1 mm wide cuvette. The data show reasonable agreement. The planar waveguide spectrum was obtained by wicking water under a microscope slide having a width of 6.5 mm. Thus, about 7 mm of coverage on the waveguide by water will produce about the same spectrum as obtained from 1 mm of transmission.

The shape of the planar waveguide spectrum slightly differs from the transmission spectrum. The wavelength of maximum absorption near 1450 nm is slightly shifted (as is often times found in the infrared between ATR and transmission). Also, there is an increasing baseline toward longer wavelengths in the planar waveguide spectrum. The sensitivity or effective path of the planar waveguide increases with increasing wavelength. This is a combined effect of the number of internal reflections and the depth of the evanescent field that change with wavelength. A planar waveguide spectrum "corrected" for these changes is also shown in Figure 7 for direct comparison with the transmission spectrum.

From a practical standpoint, it is unnecessary to convert the spectrum from element number to wavelength or correct for changes in effective path length with wavelength (unless uniform spectral resolution over all wavelengths is required). These modifications may simply add noise to the system. Calibration can readily proceed with absorbance vs. channel data, as will be demonstrated later in this report.

Slurries

Figure 8 is an interesting comparison that illustrates the usefulness of the near-infrared ATR method. Glycerin and glycerin containing 1% titanium dioxide particles are compared. In conventional transmission through 1 mm wide cuvettes, light scattering from the particles causes a 1.5 absorbance unit (AU) increase in the overall baseline of the spectrum. This means that about 97% of the light is scattered by the sample away from the detector, and the scattering is not always predictable. Thus, any calibration must be done on the remaining 3% signal. These spectra are almost directly superposed when measured by the planar waveguide spectrometer (no baseline adjustments). As is well known in the infrared, ATR has now been demonstrated in the near-infrared not to be significantly impaired by particle scattering.

Figure 9 is a comparison of slurries made with activated carbon particles and the same mixture of mono-, di- and triglycerides. Samples 1 and 2 differ in hydroxyl number by about 20. The planar waveguide spectra of these samples show a significant spectral difference between 1500 and 1600 nm, where absorption from hydrogen-bonded hydroxyls occur. Figure 9 also shows this comparison with 5 mg activated carbon added per 50 ml of solution. About the same difference is obtained in this spectral region between these two samples. The carbon prevents conventional transmission even through 1 mm. The baselines of all spectra were fixed to 0.0 at 1100 nm where little absorption occurs. This type of spectral adjustment is a common part of calibration procedures. Nevertheless, all spectra were within 0.04 AU of 0.0 at 1100 nm, so these adjustments are minor.

It is noted that identical spectra were acquired for pure water, and water that was cloudy white due to finely divided, suspended silica particles (no figure presented).

In one additional example, RTV sealant materials (Dow Corning 732) were examined with the planar waveguide spectrometer. RTV means "Ready to Vulcanize". This material is dimethylsiloxane containing a large hydroxyl content and a silica filler. The results are presented in Figure 10. One sample was colorless and translucent, one was white (containing titanium dioxide) and one was black (containing carbon). Although there are some baseline changes, the spectral features arising from carbon-hydrogen groups and hydroxyl are readily observed.

Kinetic Studies of Polymer Curing

The colorless RTV sealant was smeared onto the waveguide to form a thin film. Spectra were taken frequently over time and the absorbance at 1550 nm was determined. This absorbance plotted as a function of time is presented in Figure 11.

It is assumed that the curing of this thin RTV film is being observed on the waveguide. The data appear to exponentially decay with little change occurring after about 300 seconds, which suggests that the thin film is completely cured. It is important to realize that the entire change in absorbance from start to cure is 0.006 AU. Although this is a very small change, it is about a factor of 30 larger than the background noise of this first planar waveguide prototype spectrometer. In another experiment, a similar initial decrease was observed, but no change was detected from 360 to 2400 seconds (standard deviation = ± 0.0006 AU). It may even be possible to derive a rate equation from the type of data presented in Figure 11, although further work is required to prove that these spectral changes result from curing. The flat geometry of the planar waveguide spectrometer is

conducive for making such measurements of film curing, or perhaps film adhesion properties.

Single Wavelength Calibration

Acetonitrile and water are miscible. Various mixtures were analyzed as the first quantitative test of the planar waveguide device from 0 to 60% water by volume. For quantification, about a microliter of liquid was pipetted adjacent to a cover slip resting on the waveguide after a suitable reference spectrum was taken. After the mixture wicked under the cover slip completely, a sample spectrum was taken and the absorbance determined. The results are presented in Figure 12.

An analysis of the correlation coefficient between the absorbance at a particular wavelength and percent water in the mixture for all samples revealed that the optimum correlation occurs at 1550 nm. Figure 13 shows a linear regression analysis of the absorbance data at 1550 nm against percent water. An excellent linear calibration was achieved (r -squared = 0.986).

Multivariate Spectral Analysis Methods

Single wavelength calibrations often work for such simple binary mixtures as acetonitrile and water. However, more complicated mixtures often require additional spectral information. Powerful mathematical procedures are utilized for this purpose to relate spectral data covering many wavelengths to either physical (e.g., specific gravity) or chemical data. This is how octane is now being measured in refineries on-line in the process pipe from near-infrared spectra.

Such techniques include stepwise multivariate regression in which the best combination of data at individual wavelengths is determined systematically until the number of wavelengths selected provides acceptable predictive capability.

More powerful techniques include principal component regression (PCR) and partial-least squares (PLS), with the latter methods perhaps being the most popular. These techniques are in essence pattern recognition algorithms. They are operationally similar. They analyze the variation in spectral data over the selected wavelength range. They determine the most important linear combination of spectral data (i.e. those wavelengths that contribute most strongly to the spectral variation). They proceed to find the next most important linear combination, and so on.

Mathematically, this is an eigenvector problem with each eigenvector representing the linear combination, and the length of the eigenvector, i.e. its

eigenvalue, representing the relative amount of variance of the sample set accounted for by that linear combination. The eigenvectors are commonly referred to as FACTORS. It is generally found that one to five FACTORS account for >95% and often >99% of the overall variation in spectral data. This means that other spectral variation does not add significant information and may, in fact, add noise when performing a regression analysis. Thus, these methods eliminate unnecessary spectral variation without throwing away spectral data at any particular wavelength. All original absorbance data at each wavelength are still contained in each FACTOR (although some wavelengths may carry little weight).

Regression with the chemical or physical parameter is performed with the FACTORS selected. This leads to a model which applies coefficients to the absorbance data at each wavelength to predict the property of interest. PLS is popular because it utilizes the chemical or physical property data to assist with analysis of the spectral data (i.e. the decomposition of spectral data into FACTORS) and thereby achieves the most robust mathematical model that predicts the parameter from the spectral data.

PLS Model of Methanol and Water

Figure 14 shows the planar waveguide spectra of methanol and methanol containing 6% water by volume. These data and others were taken with a waveguide containing a blocking overcoat with a 6.5 mm opening that exposes the waveguide. A cell was constructed with a cap to contain the fluid, since this fluid wets the waveguide completely and would otherwise flow over the overcoat.

The presence of water is indicated near 1450 nm as increased absorption on the low wavelength side of the methanol peaks (compare with pure water in Figure 7).

As an aside, store-bought baking soda (sodium carbonate) was added to the 6% water mixture to produce a wet packed powder resting on the waveguide without significant spectral deterioration, as is also shown in Figure 14..

A PLS model using the UNSCRAMBLER™ software package from CAMO (Norway) was used to produce the calibration model presented in Figure 15. This figure compares the percent water predicted from the spectral data with the actual or measured water data. An excellent calibration was achieved with only 4 FACTORS producing an r-squared value of 0.999.

The minimum detection limit of the planar waveguide method (3x of background noise) is about 0.07% water in methanol, which is sufficient for a number of industrial applications.

PLS Model of Crude Oil

One of the primary factors that led to the funding of this project was the potential of this technology to assist in petroleum processing because of the large potential energy savings. As soon as the technology evolved in Phase II to the point of collecting near-infrared spectra, attention was focused on crude oil analysis.

A set of well characterized crude oil samples was provided for this purpose. These samples ranged from sticky and highly viscous to lightly colored and fluid, and included both sweet and sour crudes. Initial measurements failed. It took nearly the remainder of the first year of the project to understand how to make good quality measurements with the system. The importance of sample presentation to the waveguide was realized. Now it is a matter of routine, aided by the overcoat technology. The results presented in Figures 17 and 18 were taken some time ago on this well characterized sample set before the overcoat technology was in place. This last week a set of seven crude oil samples were brought to the laboratory from one of the major oil companies. These samples included very waxy, sticky samples that had to be scooped out of the glass vials. Nevertheless, all seven samples were analyzed with the prototype in 28 minutes with spectral quality superior to those presented in Figure 17. A representative spectrum from this sample set is shown in Figure 16. The first and second C-H overtones occur near 1750 and 1200 nm, respectively. The methyl groups absorb near 1400 nm. The shape of the 1200 nm peak changes with the aromatic and aliphatic contents of the crude oil.

Figure 17 shows the typical spectra of crude oils plotted as photodiode array channel (element) number against absorbance from the earlier data set. There is an overall increasing baseline to shorter wavelengths (lower channel numbers) due to electronic absorption mostly likely arising from the asphaltene component.

PLS models of two important parameters were developed and presented in Figure 18. Crude oils are often analyzed in laboratory instruments to provide a simulated distillation (volume yield within a defined temperature range). The distillation yield measured in this way for these samples for the volume fraction above 1000° F is predicted from the planar waveguide near-infrared spectra in Figure 17 using only 1 FACTOR. SEP means the standard error of prediction, but since this calibration on this limited data set has not been used on additional samples to test the model, this statistic is actually a standard error of calibration.

Figure 17 also shows a 1 FACTOR PLS model for the Ramsbottom carbon number. It is realized that this is a small data set, and claims to the efficacy of the planar waveguide method must await further testing. It should be noted

that transmission through 1 mm of crude is often achievable, so long as the crude is not too darkly colored or is absent of scattering particles, such as wax. In fact the recent crude oil set of samples described at the beginning of this section had scattering problems due to particles even at 80° C in transmission, but no measurement problems with the planar waveguide method. Ease of use of the planar waveguide device is a significant advantage over filling cuvettes with sticky crude oil for conventional transmission. Its portability will allow for measurements at remote locations, if needed, as on a cargo ship or at a pipeline, for example.

PLS Model of Sulfonic Acid Foam - First On-Site Plant Test

The planar waveguide prototype was assembled in the latter part of the second quarter of Phase III and was taken to a chemical plant in the early part of the third quarter to analyze sulfonic acid foam. This material is made from injecting SO₃ vapor into a reactor containing an alcohol to produce the foam. It is eventually neutralized to make sodium laureth sulfate for shampoos, as well as other products. The foam is a pourable, frothy liquid that is opaque and light brown in color. It is difficult to readily sample this material for an automated flow injection analysis or an autotitrator chemical analysis, since bubbles prevent a known liquid volume from being measured. Typical procedures are to frequently sample the reactor, bring the sample to the plant laboratory and perform a chemical titration analysis.

The objective of the visit was just to demonstrate the ability of the prototype planar waveguide spectrometer to measure this difficult material. However, the goal of the plant personnel was to have the device measure product changes as a function of a process change. This was the first test of the device to collect and analyze the data with a PLS model in a plant environment. Plant personnel extracted a sample, measured the titration value and supplied the sample for immediate planar waveguide analysis.

The results are shown in Figure 19 in which the measured titration values are compared with those values determined from the near-infrared spectra. An excellent preliminary calibration on this limited data set was obtained. The numbers show the time sequence of the samples started near 26 (mEQ/g titrant), overshoot the target of about 24 down to nearly 21 and then stabilizing near 24. These results are encouraging, again showing the potential of the device on this limited data set. This would be a good application for utilizing a flow cell over the waveguide for an at-line analysis instead of manual sampling.

PLS Model of Silicones - Second On-Site Plant Test

Measuring the chemical and physical properties of commercial silicones (dimethylsiloxanes) is important for quality control. Analytical costs for measurements in quality control laboratories are quite high for many products.

The planar waveguide device has the potential of making such measurements quickly, thereby freeing analytical time for other measurements. A trip was made to one facility for the purpose of developing a calibration set on 20 - 30 well-characterized silicone samples during the last half of Phase III as a prelude to a plant trial.

The planar waveguide spectrum of silicone is presented in Figure 20. The goal is to measure the hydroxyl concentration in the < 1000 ppm range. The results of a 5 FACTOR PLS model of 23 samples are presented in Figure 21, resulting in an r-squared value of 0.988 for the predicted vs. measured comparison.

A return trip to the plant was made near the end of this project. Recent silicone samples collected from a production facility were analyzed using the calibration model presented in Figure 21. The results are shown in Figure 22. The planar waveguide data (PWG) are compared to two other data sets. A similar prediction was made from spectra taken with a state-of-the-art, commercial Fourier Transform Near Infrared Spectrometer (FTNIR). The FTNIR data were predicted from a model using the same calibration samples as was used for the planar waveguide shown in Figure 21. Data from the reference method, based upon a chemical extraction procedure, are also presented for comparison. The results show excellent agreement between the two near-infrared methods (PWG and FTNIR), which appear to differ from the reference method by a constant factor. This could suggest that a constant error exists in the assumed hydroxyl content of the synthesized calibration set used for both near-infrared calibration models. The near-infrared data clearly follow the trend of the reference data.

The important point to note is that the alpha prototype planar waveguide spectrometer favorably compared to an expensive, commercial FTNIR spectrometer. Because of the ease of "paint on - wipe off" sample preparation for the planar waveguide, at least twice as many samples were analyzed in comparison with filling and cleaning cuvettes for the FTNIR.

ACKNOWLEDGMENTS

This technology began at the Pacific Northwest Laboratories in Richland, Washington with a small project funded by Dan Wiley and Tom Gross in the Office of Industrial Technologies at DOE Headquarters. Without their willingness to take a risk on this new idea, it is doubtful that this report would exist. I would like to thank my former colleagues at PNL, Patti White and Norman Anheier, and my collaborators at the University of Washington, Lloyd Burgess and Mike DeGrandpre, in the initial phases of this work that led to our R&D100 award and a U.S. Patent. I would also like to thank Dan Wiley and Linda Schilling at the DOE's Office of Industrial Technology for funding and support the Phase II and III work at Guided Wave, and to Elmer Fleischman, my technical monitor at EG&G Idaho, for most of this project, for his interest and involvement. In particular, I would like to thank my colleagues at Guided Wave, Terry Todd and Steven Wilcox, for assisting me with the design and fabrication of the prototype device. I only wished that Guided Wave's management provided an atmosphere more conducive toward the development of this technology. I would also like to especially thank Nelson Lytle for his interest and involvement during the testing of this device. Corporate technology "champions" are hard to find.

Figure 1. Initial Planar Waveguide Concept

Figure 2. Block Diagram of Planar Waveguide Spectrometer

Figure 3. Picture of Planar Waveguide Spectrometer Prototype

Figure 4. Controlling Sample Application

Figure 5. Wavelength Calibration Sources

Figure 6. Typical Wavelength Calibration for Photodiode Array Detector

Figure 7. Planar Waveguide and Transmission Spectra of Water

Figure 8. Comparison of Glycerin with and without TiO_2 Particles

Figure 9. Glyceride Mixtures with and without Activated Carbon

Figure 10. RTV Sealants

Figure 11. Curing of RTV Thin-Film on Planar Waveguide

Figure 12. Acetonitrile-Water Planar Waveguide Spectra

Figure 13. Calibration for Acetonitrile-Water Spectra at 1550 nm

Figure 14. Water-Methanol Mixtures and Slurry

Figure 15. PLS Model of Methanol-Water Spectra

Figure 16. Crude Oil Spectrum Made with Latest Planar Waveguides

Figure 17. Planar Waveguide Spectra of Characterized Crude Oils

Figure 18. PLS Models of Carbon Number and Distillation Yield of Crude Oil

Figure 19. PLS Model of Sulfonic Acid Foam from In-Plant Test

Figure 20. Planar Waveguide Spectrum of Silicone

Figure 21. PLS Model of Silicones

Figure 22. Results of In-Plant Silicone Trial Using PLS Model in Figure 21

April 1, 1993

Ms. Linda Schilling
U.S. Department of Energy
Office of Industrial Technologies (CE-142)
1000 Independence Avenue S.W.
Washington, D.C. 20595

RCO WHILE ON VACATION
4/14/93 TO 4/15/93
READ 4/14/93 EHF

Dear Linda:

The purpose of this letter is to discuss plans for the final commercialization of the technology.

Please find attached the final report for the project entitled "Thin Film Device for Process Measurement", DE-AC07-91ID16303. I am mailing by separate cover a copy of this letter and the report to Dan Wiley (DOE/HQ/IT), Dave Blanchfield and Robert Chappel (DOE/Golden) and Elmer Fleischman (EG&G/ID). The report includes a one page executive summary, table of contents, a conclusions section, 20 pages of text and 22 figures. I have stressed industrial applications rather than device development.

I had a wonderfully successful plant test this week, measuring ppm concentrations of hydroxyl in silicone. The results were in general agreement with existing commercial instrumentation costing \$80,000, and the samples were analyzed in about one third the time. I was recently able to measure crude oil samples in one fifth the time of a commercial device. As you will hopefully see from the final report, the technology has been proven. Spending the balance of projects funds for more plant testing is wasteful. Funds should be focused toward commercialization, and getting this technology to end-users. I already have letters of commitment for the sale of the planar waveguide spectrometer when it becomes available.

I believe about \$90,000 remains unspent in the project. In addition, the \$30,000 probe development funds for Task 6 has been funded, but I could not get corporate approval to proceed. No one wanted to incur the 26.47% cost share.

Please find below my current understanding and recommendations to proceed with commercialization under Optical Solutions, Inc.:

1. Technical success has been achieved and considerable market interest for the technology has been generated in a company environment at Guided Wave that was and still is hostile to this new technology. The 2 principals have refused to pursue patent protection, turned customers away, hid crude oil samples brought for analysis with the planar waveguide technology, claimed there is no market to justify further development and created an "ours vs.

yours" situation. Further development at Guided Wave will not be successful for these reasons.

2. Guided Wave, Inc. has existed since January with me as its only employee solely for the DOE project based upon an agreement between UOP and Perstorp, Inc. The building and all equipment are now owned by UOP of Des Plaines, IL who purchased the assets of Guided Wave from Perstorp, Inc. in November, 1992. All Guided Wave employees were transferred to UOP on January 1, 1993, except me.
3. Perstorp has informed me in writing that they have no further interest in the technology and that my employment will terminate on April 9, 1993 (the end of the original contract period).
4. As Project Director, I extended the budget period at no additional cost to December 31, 1993 under 10CFR600.31(d).
5. I felt compelled to complete this last field test quickly and write the final report by April 9, 1993, since it was uncertain what would follow. I informed Bob Chappel of this, since one of the milestones was DOE approval of the test plan. He told me to proceed. I did not inform UOP since they have no direct involvement in the project at this time, and because they already prevented me from traveling to Perstorp to discuss this technology earlier this year. I could not afford any further entanglements and needed this plant trial to complete the remaining milestones.
6. I submitted an extensive invention report (20 pp, >10 Figures) to my supervisor at Guided Wave (Dr. Roger Schirmer, VP R&D) in October, 1991 regarding new developments in the project. The company president, David LeFebre, still claiming no interest in the technology refused to let Dr. Schirmer submit it to the corporate patent attorney. Dr. Schirmer finally submitted it on February 27, 1992. Unfortunately, Dr. Schirmer left Guided Wave in June of 1992. Although numerous phone calls occurred with this patent attorney for the next 10 months, I never saw a first draft. My last communication with him was by phone during the first week of December, 1992. He has refused to return all calls since. Because I felt strongly that this technology must be protected, I pursued it with a patent attorney in the Bay area at my own expense. It was filed on March 5, 1993. We included in the application that this intellectual property was developed with government funds, and will shortly notify the Chicago office of this development.
7. Because I have ownership rights to this technology based upon my 2 year employment contract with Guided Wave Inc., and because UOP was not willing to establish an appropriate employment arrangement with me, I

have incorporated a new company in California, Optical Solutions, Inc., on March 23, 1993 for the purpose of commercializing this and other technologies. UOP most likely has limited rights to this technology, as well.

8. Discussions are underway with UOP to arrive at a mutually beneficial arrangement to pursue commercialization and avoid a competitive situation.
9. Optical Solutions has the technical expertise and market contacts to develop and sell planar waveguide products in less than 1 year. It proposes that the balance of the project funds and obligations be transferred into Optical Solutions for this purpose of commercialization, rather than pursuing additional, unnecessary plant testing. Optical Solutions also wishes to acquire the \$30,000 probe development funds to serve applications requiring in-line process measurement.
10. Rather than spending time and funds to rebuild the prototype spectrometer system shown in Figure 3 of the Final Report, it is also requested that this prototype equipment be transferred to Optical Solutions as a basis for commercial design and for customer demonstration. This is being proposed to UOP, since it apparently owns all equipment at Guided Wave.
11. The expertise in planar waveguide technology resides only at Optical Solutions, including marketing, spectroscopy, chemical analysis and electro-optic engineering. Optical Solutions will be dedicated toward bringing this technology into the commercial marketplace. Transferring the remaining project to other organizations to learn about the technology is not an efficient use of funds.
12. As a new, small business, Optical Solutions requests that the current cost-share of 26.47% be maintained, even though it is understood that based on the recent Energy Policy Act of 1992, the cost-share for commercialization is generally 50%. Part of the effort will still be technology development for planar waveguide probes.
13. It is estimated that \$240,000 will be required over the course of the following year to efficiently complete the commercialization process with a quality product. The additional \$30,000 for probe development is adequate for that task and is an addition to the commercialization funds. The goal of this effort will be product release in the first quarter, 1994 and a product introduction at the Pittsburgh National Instrument Conference in March, 1994. I will provide a further breakdown of costs and milestones at your request.

14. As with most small companies, including Guided Wave, Optical Solutions will generally have outside vendors fabricate most parts. Assembly, product testing, quality control and product support are handled by the company. Optical Solutions has access to these suppliers. Planar waveguide devices have few parts and can be quickly assembled. I have generated a substantial customer base, so direct sales will be relied upon initially augmented by advertising in some of the trade journals. One company is preparing to write a purchase order for multiple units. Because of the compact size of the device, it can be expressed-mailed back to Optical Solutions for rapid repair, instead of incurring the cost of a service call. Optical Solutions will use experienced accountants to comply with DOE bookkeeping requirements.
15. As we understand it, all that is required is to have Guided Wave, Inc. (managed by Perstorp, Inc. of Florence, MA) agree to sign the agreement over to Optical Solutions.
16. Optical Solutions, as owners of the technology, will oppose attempts by other organizations to access the remaining funds in this project. It would hope that closing down the project and having to submit a completely new unsolicited proposal to accomplish this work, and its inherent time delays, can be avoided.

I look forward to hearing from you regarding the commercialization of this technology.

Sincerely,

Don S. Goldman, Ph.D.
President
Optical Solutions, Inc.
1009 Folsom Ranch Drive, Suite 101
Folsom, CA 95630
Phone/FAX (916) 987-8680