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ULTRAVIOLET-VISIBLE ABSORPTION SPECTROMETERS USING FIBER OPTIC PROBES FOR IN-SITU PRIMARY AND SECONDARY CHEMICAL ANALYSIS

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ABSTRACT

Recent technology advances are making it possible for UV-VIS spectrometers to be used in new ways. While UV-VIS spectrometers are well established laboratory and research instruments, the technology is now capable of being used for in-situ real time analysis of complex chemical solutions in field and factory environments. Fiber optic probes permit contact between the emitted light and a sample in locations remote from the analyzer such as process tanks, flow streams or monitoring wells. Photodiode array detectors permit fast, broad range detection of the absorption signature for a sample solution. Chemometrics permits this information to be interpreted in order to establish the contribution from individual chemical constituents to the absorption signature for the solution. Immobilized reagents may be used to aid detection of some analytes.

I. BASIC ABSORPTION SPECTROMETRY TECHNOLOGY

Ultraviolet-visible absorption spectrometry (UVAS), although a familiar technique for chemical analysis in the laboratory, is not often considered a practical technique for field use in process control, monitoring or other applications where variable multi-constituent chemical solutions are presented for real time analysis. This is usually due to the perception that because so many substances absorb in the uv-visible range, there is no practical or reliable way to capture any meaningful information concerning the individual chemical constituents.

Colorimetry The detection of a color change that occurs in a solution upon the addition of an indicator chemical is fundamental to the field of chemical analysis. Such colorimetric tests rely upon changes in the ability of the chemicals in a solution to absorb light in the visible region of the electromagnetic spectrum.

Many modern laboratories are equipped with a variety of colorimeters and photometers to assist in performance of accurate spectroscopic analysis. Typically, reagents and indicator chemicals are added to the solution to be analyzed to produce strong, selective, detectable reactions with an intensity that is proportionate to the concentration of the analyte being measured. In this way, both qualitative and quantitative analysis can be performed. Such instruments are typically tuned to

specific wavelengths so that each chemical to be detected requires a new analysis.

Absorption and Energy Transitions All forms of absorption spectroscopy are based on the measurement of changes in energy. When a molecule absorbs radiation, its energy increases. The increase in energy is reflected in the form of changes in electronic, vibrational or rotational energy of the molecule [RAO 67]. Quantum mechanics tells us that only certain discrete energy levels are possible in atoms and molecules and that the atoms or molecules must exist at all times in one or another of these "allowed" energy states. The lowest energy level is called the "ground state" and higher levels are referred to as "excited states" (see Figure 1). Under normal conditions, an atom or molecule occupies the ground state, but if energy is acquired from an external source, the energy level can jump from the ground state to one of the permitted excited states [THO 74].

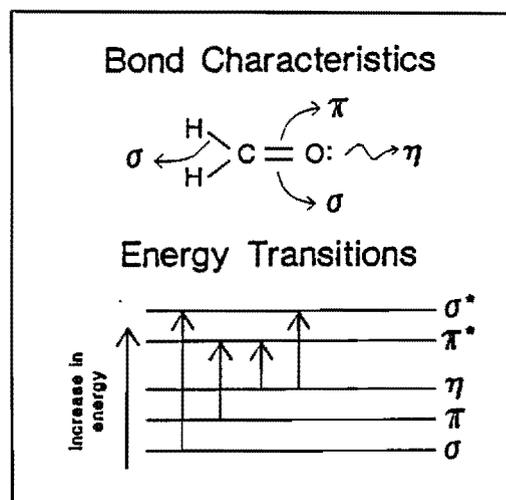


Figure 1. Energy Levels

The transitions that take place as a result of energy absorbed in the ultraviolet region occur in the valence electrons of the molecule [SIL 81]. Since the interaction between electrons to form chemical bonds are also due to the valence electrons and the orbitals comprising the partially filled outer shells of atoms, there is a relationship between bonding characteristics and ultraviolet absorption spectra for atoms and molecules. Thus, it can be said that it is the valence electrons that are responsible for the

electronic spectra of molecules in the visible and ultraviolet regions of the spectrum as well as for the chemical reactivity of these molecules [SCH 77].

Single Wavelength Instruments It is typical for many types of spectrometry to obtain information at a single significant (usually peak) wavelength, often because the detector is capable of being tuned to only one specific wavelength. Some forms of ultraviolet, visible and near-infrared absorption spectroscopy obtain information by observing only a single wavelength, even though a spectrum is available over a RANGE of wavelengths (the absorption band) and can be detected with the proper instrumentation. This is because either the instrument is not capable of detecting the entire spectrum or the analytical software is not capable of performing an analysis at multiple wavelengths.

Multiple Wavelength Instruments There are several laboratory instruments in wide use whose purpose is to detect and record absorption spectra within a specific region of the spectrum. These instruments are limited to the analysis of static (non-moving) samples and require a controlled environment for the analyzer due to the sensitivity of the optical components. Detection is performed in a stepwise manner from one wavelength to the next with adjustments performed immediately before or immediately after transmission of light through the sample. (See Figure 2) These instruments often used special monochromators (prisms or diffraction gratings) which are mechanically adjusted to permit the analyzer to step through a series of wavelengths in discrete intervals. Some instruments use a light source that is specially filtered to step through a series of wavelength intervals. These instruments are not only slow, but are also very sensitive to temperature variation and vibration making them unsuitable for use in many factory or field environments.

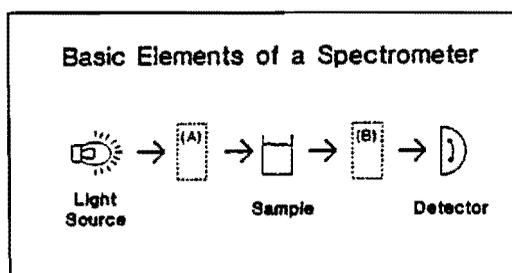


Figure 2. Spectrometer Elements

II. REAL TIME ANALYSIS REQUIREMENTS

If absorption spectrometry is to be used for real time analysis of multiple component chemical solutions, several limitations inherent in the current laboratory technology needed to be addressed.

Static Samples vs. Real Time Analysis Laboratory instruments are designed to analyze a sample that has been extracted from the solution to be analyzed. The sample can, if necessary, be processed or chemically altered in some way prior to analysis. If

laboratory analysis is performed on an instrument that steps through a series of wavelengths, the sample can be held in the instrument for whatever time is required to complete the analysis. In addition, considerable time may transpire between the extraction of the sample from the original solution and the actual processing of the sample in the laboratory.

Real time chemical analysis applications, such as process control or quality monitoring, do not permit analysis that is remote in time or place. The analysis should be performed directly in the solution being analyzed (in-situ analysis) or at least with a fractional sample that is continuously diverted from the solution (on-line analysis). This implies close proximity between the solution and the analyzer.

If the analysis itself is not instantaneous and continuous (such as the "batch" processing of on-line samples) or if sample lines are very long, the fraction of the sample being analyzed may no longer reflect the actual conditions in the original solution at the time of processing. Such forms of analysis, even if automated, may be termed "on-line" analysis but would not be considered "real time" analysis. In solutions that change slowly this may be a distinction without a difference, but if the solution is unstable the distinction may become significant.

Multicomponent Chemical Analysis If the solution to be analyzed contains more than one absorbing component, the absorption spectra detected will be a function of all absorbing components. The overlap of absorption spectra for the individual components will result in smoothed combined spectra as illustrated in Figure 3. If absorption spectrometry is to be performed in real time, hardware and software techniques that are capable of rapidly detecting and interpreting these spectral signatures will be needed. This implies that the analysis system has been armed with some information concerning the shape and positions of spectra for each absorbing component over a range of concentrations so that combination effects can be derived.

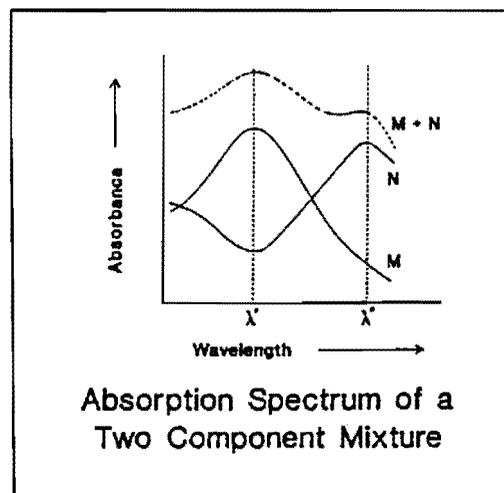


Figure 3. Multiple Component Spectra

III. NEW ABSORPTION SPECTROMETRY TECHNOLOGY

A. FIBER OPTICS

Fiber optic cables permit substantial distance between the analyzer and the solution to be analyzed while providing the means for continuous analysis of the solution. The analyzer can therefore be located in a benign environment protected from the more extreme environment containing the solution being analyzed. This is accomplished using either an in-situ or an on-line strategy.

In-Situ Analysis The analysis is performed directly in the flow stream, process tank or other vessel. An optical probe is designed to be immersed in the solution. Light that was generated within the analyzer is conveyed to the probe through a fiber optic cable, transmitted through a portion of the solution, collected in a companion cable and returned to the analyzer for analysis. Figure 4 illustrates one kind of optical probe used for in-situ analysis.

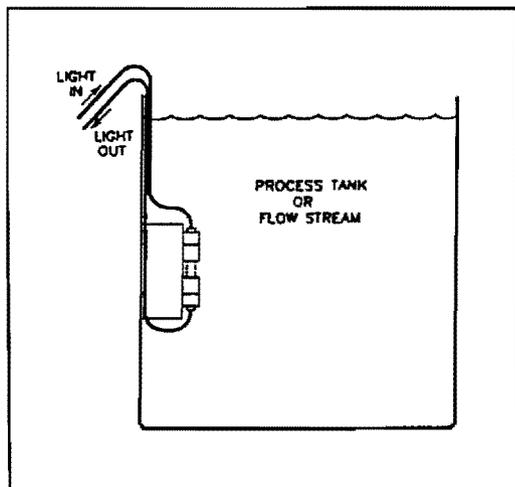


Figure 4. Submerged Optical Probe

On-Line Analysis The analysis is performed in a flow through optical probe, such as the one illustrated in Figure 5. This design allows a continuous flow of sample through the probe while light is being continuously transmitted through the sample. Since no chemical alteration of the sample has occurred, the sample can usually be returned to the solution from which it was extracted.

B. PHOTODIODE DETECTOR ARRAYS

The development of photodiode detector arrays has made it possible to rapidly scan an entire wavelength range and thus read spectral signatures in real time, even in a flowing sample. These detectors eliminate the need to mechanically index through wavelength intervals with movable gratings or mirrors, thus eliminating the moving parts that would otherwise compromise use of the instrument in field or factory environments. Since a wide wavelength range can be detected in as many as 1024 increments a broadband source of light can be used. The light is

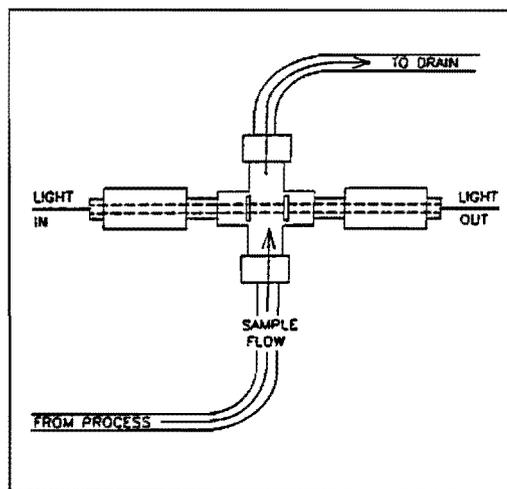


Figure 5. Flow Through Optical Probe

transmitted through the solution with the unabsorbed fraction returned to the analyzer. The returned light is projected onto a fixed diffraction grating, where it is separated into discrete wavelengths and reflected onto the array. This basic arrangement is illustrated in Figure 6. Each element in the detector array is matched with a dedicated integrating capacitor that can be rapidly scanned to record the intensity detected by a specific segment of the array. The Ultraviolet-Visible Array Spectrometer described in this paper detects absorption in the 200 nm to 800 nm wavelength range using a 1024 element array.

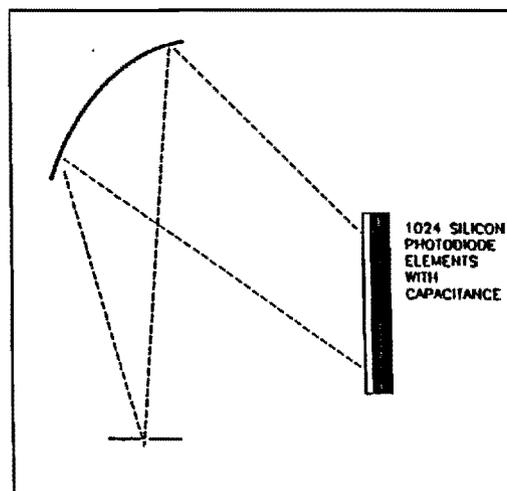


Figure 6. Photodiode Array Detector

C. CHEMOMETRICS

Chemicals must often be analyzed in solutions that contain numerous components, resulting in overlapping or closely grouped spectra. The overall absorption spectra for the liquid is a smooth pattern that results from the effects of absorption by these individual components. There are three basic steps involved in the process of using absorption spectra for chemical analysis illustrated in Figure 7.

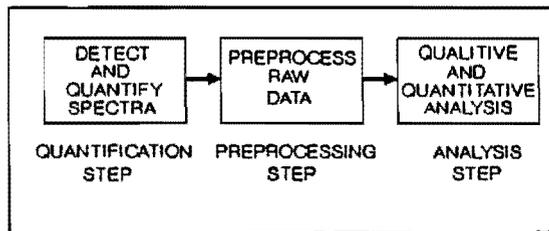


Figure 7. Spectral Analysis Steps

QUANTIFICATION involves converting detected spectra for calibration solutions and unknowns into numerical values that can be processed using mathematical and statistical procedures.

PREPROCESSING of raw data reduces the effects of noise and transforms absorption information into forms that permit more efficient analysis.

ANALYSIS of absorption values identifies individual components and calculates an estimate of their concentrations in the liquid.

Development of Analysis Models These three steps are the result of a process that is performed at the beginning of a monitoring project to select the combination of wavelengths, preprocessing techniques and analysis models that are capable of providing the most accurate analysis of the analytes of interest in a specific application. This process uses information from several site specific samples that contain known concentrations of the target analytes. These samples, known as a "learning set" are used in parallel calculations to evaluate the combination of techniques that produces the lowest error when actual and predicted values are compared. Several "test sets" are then processed to verify the model. This process is illustrated in Figure 8.

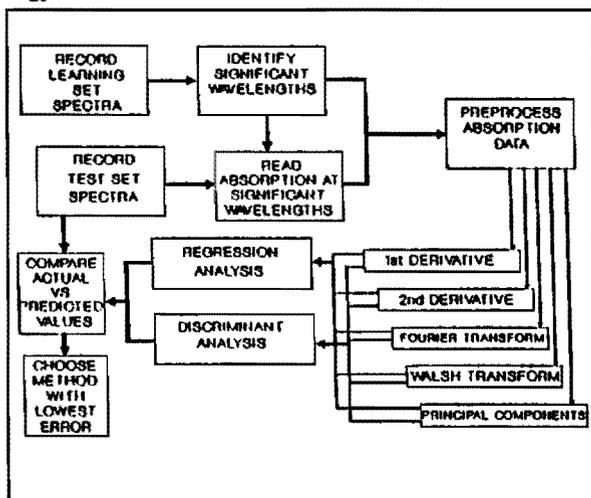


Figure 8. Analytical Model Development

Quantification The quantification step is fairly straightforward. Absorption of light is governed by

Bear's Law (see Figure 9), which relates absorption to the absorptivity of the media, path length through the media, and concentration of the absorbing components within the solution.

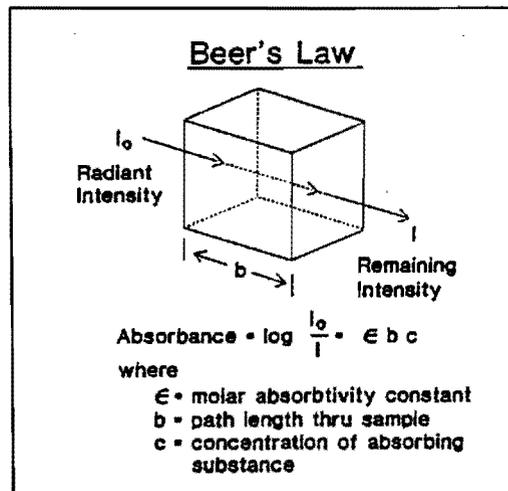


Figure 9. Beer's Law

When all of the absorbing components in the media are known, total absorption at each wavelength is a function of the sums of all of the absorbing components. A series of simultaneous equations can be used to calculate absorption. Most often, however, all of the absorbing components are not known, in which case an inverse technique that defines concentration as a function of absorbance must be used.

Preprocessing of Spectra Preprocessing of spectra is often performed for multi-component solutions or to adjust for noise or drift. Typical techniques include the use of first or second derivatives of the absorption spectrum or the use of Fourier or Walsh transformations. Examples of how the raw absorption signature is affected by various transformation techniques is shown in Figure 10. Another frequently

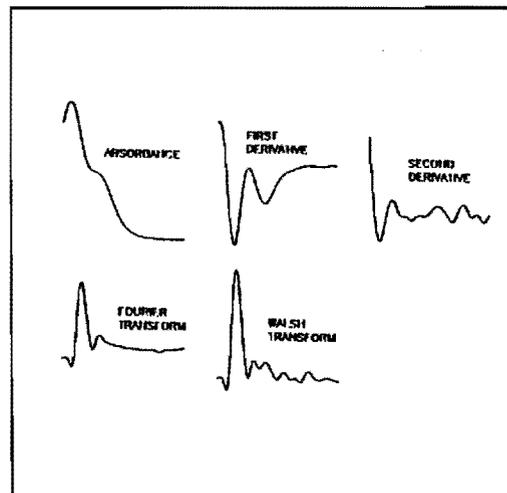


Figure 10. Transformations

used transformation technique is Principal Components Analysis (PCA). PCA uses statistically determined quantities to rotate the coordinate system such that the original information that may have been aligned on several axes becomes aligned on only a few axes. In effect, the variables that are highly correlated with one another can be treated as a single variable, thus simplifying the analysis.[8,9]

Analysis Techniques The analysis techniques currently used include stepwise linear regressions and discriminant analysis. Discriminant analysis is a clustering process which defines linear decision boundaries between information clusters for known concentrations of analytes, and assigns unknowns to an appropriate cluster based upon detection of significant characteristics for the unknown.[10] An illustration of this technique can be seen in Figure 11.

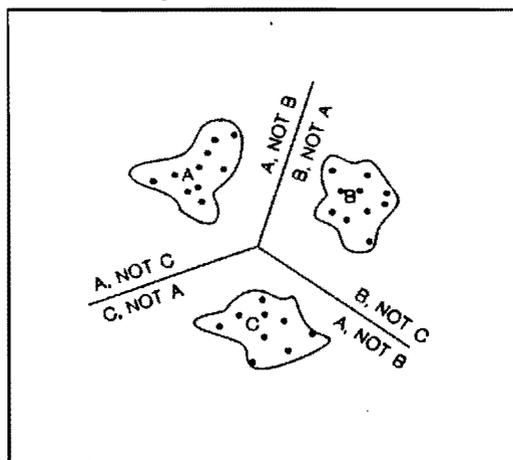


Figure 11. Discriminant Analysis

Emerging techniques for analysis include experimental methods such as inductive learning and neural networks, especially for problems that cannot be simplified through principal components analysis. A technique that shows great promise is the Lattice-K Nearest Neighbor technique, where known values for variables are organized into the nodes of a lattice. Predicted values for an unknown are based upon relative distances of variables for the unknown with those of the nearest neighbors in the lattice.

D. SECONDARY ANALYSIS

Although many chemicals have natural absorption spectra in the ultraviolet-visible range (principally heavy metals, unsaturated organics and aromatic compounds), many others do not. When UV-VIS absorption spectrometry is used for direct detection of the natural absorption spectra the term "primary" analysis is used. When chemical reagents must be employed to induce a detectable absorption spectra, the techniques are termed "secondary" analysis.

The preferred form of secondary analysis is the use of immobilized reagents. These chemicals form

chelates with the analytes of interest which vary in proportion to analyte concentration. The reagent is bonded to a transparent substrate and positioned such that the reagent is in contact with the solution being analyzed. Light is transmitted through (or reflected off of) the substrate. This technique allows secondary analysis techniques to be used in both in-situ and on-line analysis.

IV. SPECIFIC DESIGNS

The foregoing principals have been incorporated into the design of an ultraviolet-visible absorption spectrometer for real time chemical analysis. A block diagram of this analyzer is shown as Figure 12. The design incorporates a fiber optic link to an optical probe, a spectrograph with a diffraction grating and a 1024 element photodiode detector array, and internal processors for execution of chemometric algorithms, operator interface routines and communications tasks.

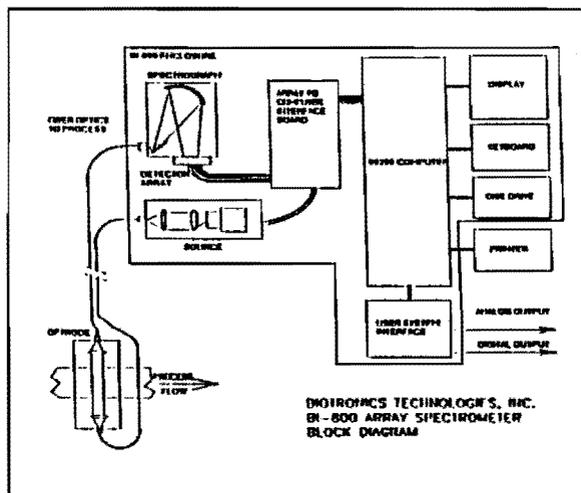


Figure 12. BI-800 Block Diagram

Major Applications The potential of ultraviolet-visible absorption spectrometry to perform multi-component chemical analysis has been demonstrated under a recent NASA contract. Iron and nitrates were identified in nutrient solutions using stepwise regressions of primary absorption spectra. Iron was measured over a range of concentrations from 0 to 10.0 ppm with an error of less than 0.03 ppm. Nitrates were measured with errors of less than 1.0 ppm over a range of 10.0 to 500.0 ppm.

Under another study, Walsh transformations and discriminant analysis were used to identify iron and copper in boiler feed water at trace levels. Various heavy metals and industrial chemicals have also been identified in process waters and wastewaters.

Another environmental application of this technology is for groundwater monitoring. In one approach, conventional calibrated pattern recognition

techniques are used to identify and measure the presence of known contaminants or indicators of contamination from a known source. In another approach, a baseline spectra for uncontaminated groundwater is identified at a particular site to be monitored. The appearance of certain contaminants produces a deviation in the baseline absorption spectra. Contaminants such as gasoline, toluene, benzene, kerosene, ammonia, chloroform, cleaning solutions, and 1,2-dichloroethane have been demonstrated to produce deviation responses at trace levels in groundwater.

V. CONCLUSION

New technology is converting ultraviolet-visible absorption spectrometry from a laboratory technology to one that can successfully be used in field and factory applications for real time chemical analysis of multi component solutions. These technology improvements include fiber optics, photodiode detector arrays and chemometric analysis routines.

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