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**NEW TECHNOLOGY FOR ON-LINE ANALYSIS
OF WASTEWATER**

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ABSTRACT

An analyzer featuring a fiber-optic probe, a photodiode array detector and advanced forms of chemometrics and analysis algorithms has been designed and tested for use as a wastewater process analyzer. This technology is a spin-off from a NASA funded effort to develop an on-line analyzer that can simultaneously detect all components of a hydroponic nutrient solution. When used as an on-line absorption spectrometer, a xenon lamp provides a source of light in the ultraviolet and visible wavelength ranges. This analyzer is currently being evaluated for continuous analysis of nitrate in wastewater at Oconomowoc, Wisconsin.

ON-LINE ANALYSIS REQUIREMENTS

Absorption spectrometry is a well accepted laboratory analysis technique, but the use of this technology for on-line analysis without the assistance of reagents is just emerging. On-line detection of natural absorption spectra in the near infrared region has become well established for industrial process control and quality monitoring applications, but on-line applications in the ultraviolet-visible wavelength range have been limited to detection of specific chemicals using immobilized or injected reagents.

There is a strong perception that because so many substances absorb in the ultraviolet-visible range, there is no practical or reliable way to capture any meaningful information concerning the individual chemical constituents without use of reagents to selectively combine with a target analyte and/or suppress interferences. It is typical for many types of spectrometry to obtain information at a single significant (usually peak) wavelength, often because the detector is not capable of being used for more than one specific wavelength at a time. This constraint has limited the use of both absorption spectrometry for multi-component chemical analysis.

There are several laboratory instruments in wide use whose purpose is to detect absorption spectra within a specific region of the spectrum. These instruments are limited to the analysis of static (non-moving) samples and often require a controlled environment for the analyzer because of the sensitivity of the optical components that are mechanically adjusted to permit the analyzer to step through a series of wavelengths in discrete intervals. 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.

Real-time chemical analysis applications, such as process control or quality monitoring, require continuous analytical information. 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 to the analyzer (on-line analysis). This requires a direct connection between the solution and the analyzer.

If the solution to be analyzed contains multiple chemical components, the spectra detected may actually be a function of several components. If absorption or emission spectrometry is to be performed in real time, hardware and software techniques that are capable of rapidly detecting and interpreting these spectral signatures are needed. This implies that the analysis system has the benefit of information concerning the location and intensity of spectra for each absorbing component in the solution over a range of concentrations so that intercomponent effects can be calculated.

ON-LINE SPECTROMETRY TECHNOLOGY

There are three technologies that permit on-line spectrometry to be used for process monitoring.

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 using an optical probe that is designed to be immersed in the solution. Figure 1 illustrates one kind of optical probe used for in-situ absorption spectrometry. Light from a source within the analyzer is conveyed to the probe through a fiber-optic cable, transmitted through a portion of the solution, collected by a companion cable and returned to the analyzer for detection.

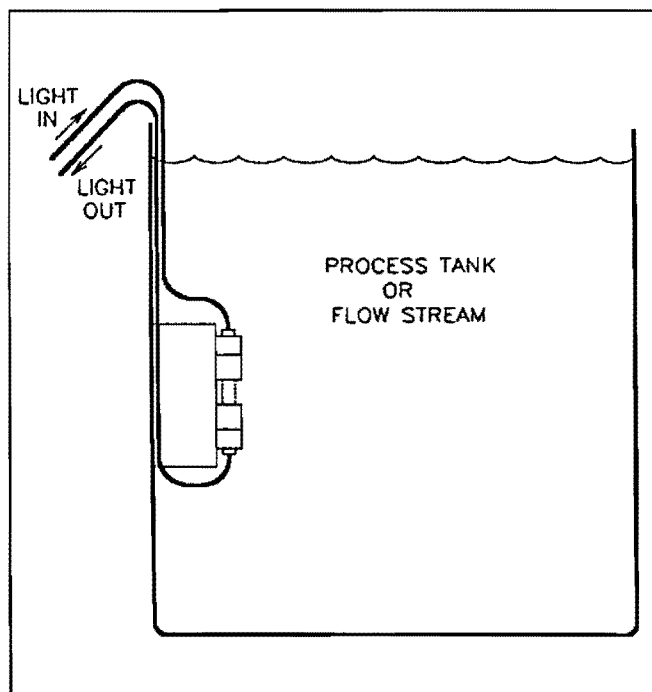


Figure 1

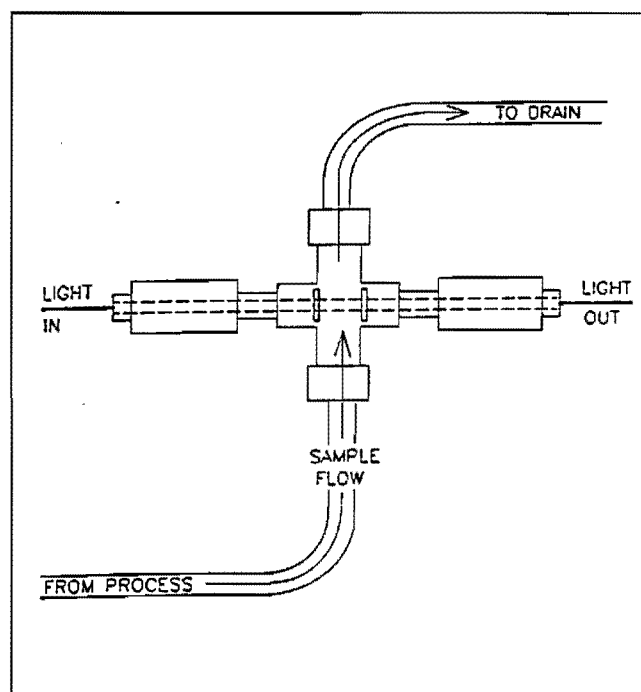


Figure 2

On-Line Analysis

The analysis is performed in a flow-through optical probe, such as the one illustrated in Figure 2. This design allows a continuous flow of sample through the probe while light is being continuously transmitted through the sample. Because no chemical alteration of the sample has occurred, the sample can usually be returned to the solution from which it was extracted.

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. These detectors eliminate the need to mechanically index through wavelength intervals with adjustable optics, thus eliminating the moving parts that would otherwise compromise use of an instrument in field or factory environments. In absorption spectrometry applications, the light to be analyzed is projected onto a fixed diffraction grating, where it is separated into discrete wavelengths and reflected onto the array detector. This basic arrangement is illustrated in Figure 3. 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 system being used for wastewater analysis at Oconomowoc detects spectral features in the 200 to 450 nm wavelength range using a 256 element array. The original NASA system uses a 1024 element array to detect wavelengths from 200 to 800 nm.

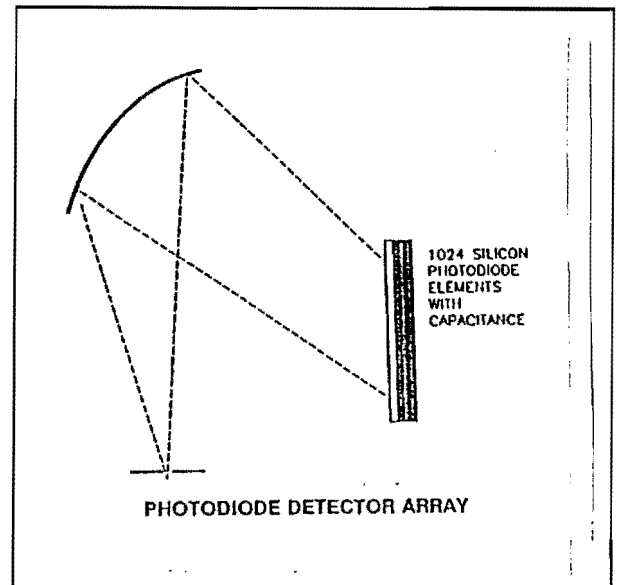


Figure 3

CHEMOMETRICS

Chemicals must often be analyzed in solutions that contain numerous components, resulting in overlapping or closely grouped spectra. Chemometrics is a term used to describe the application of statistical methods, mathematical methods and methods based on mathematical logic to problems in analytical chemistry. This includes the effects of multiple chemical constituents on the observed spectral pattern for a solution. Although many different chemometric techniques are used for absorption spectrometry some general observations can be made. There are three basic steps involved in the process of using chemometric techniques for analysis of spectra, as illustrated in Figure 4.

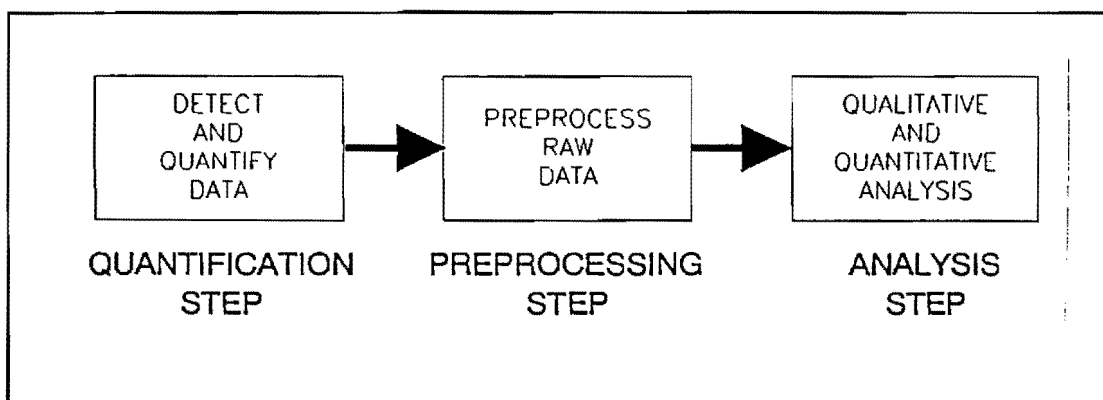


Figure 4

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 spectral information into forms that permit more efficient analysis.

ANALYSIS of information at multiple wavelengths identifies individual components and calculates an estimate of their concentrations in the solution.

Quantification

The quantification step is fairly straightforward. Absorption spectrometry is governed by Beer's Law, which quantifies absorption as a function of the absorptivity of the media itself, the path length through the media, and the concentration of any absorbing components within the media. Total absorption at each wavelength is a function of the sums of all of the absorbing components at that wavelength, as illustrated in Figure 5. This differs substantially from the familiar pattern of discrete emission responses that are characterized by distinct narrow lines that represent the atomic elements present in the sample as illustrated in Figure 6. (An on-line emission spectrometer has also been developed for NASA as a companion technique to be used with absorption spectrometry in a hybrid instrument that shares a common detection system.)

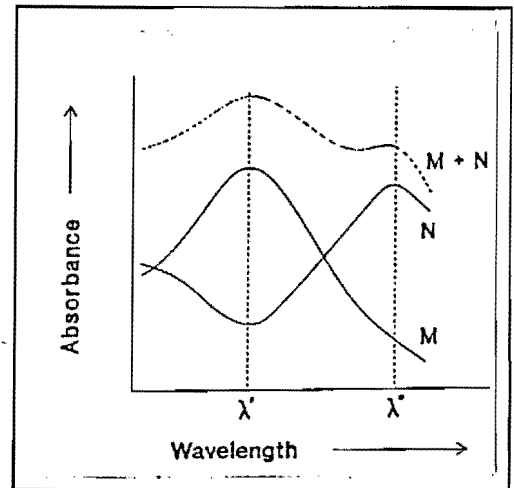


Figure 5

Preprocessing

Preprocessing of emission spectra is often performed to analyze multi-component solutions or to adjust for noise or drift. The preprocessing is performed using applied mathematical techniques known as deconvolution, which attempt to restore a distorted signal or image. Typical techniques include the use of first or second derivatives of the absorption spectra or the use of Fourier or Walsh transformations. Another frequently used transformation technique is principal components analysis. Principal components analysis 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.

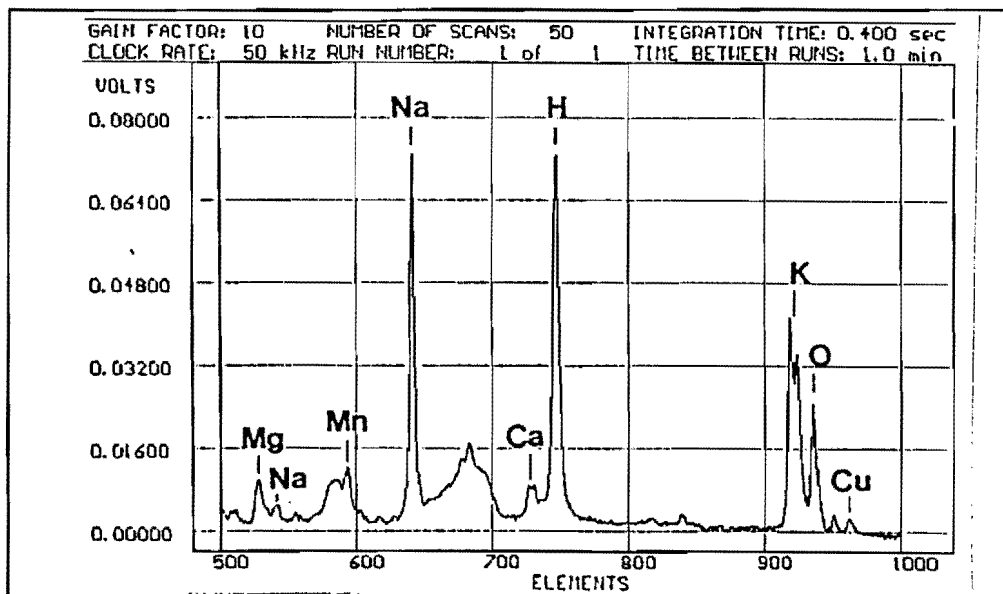


Figure 6

Analysis Techniques

The analysis techniques currently used for analysis of linear functions include stepwise regressions,

discriminant analysis and principal components analysis. Emerging techniques for analysis include experimental methods such as neural networks, especially for problems that cannot be simplified through principal components analysis. Neural networks combined with genetic algorithms show great promise for analysis of complex problems, often achieving significant improvements in error compared to more conventional methods.

Development of Algorithms

A process is performed for each major application to select the combination of wavelength quantification, preprocessing techniques and analysis models that are capable of providing the most accurate analysis of the analytes for a specific application. This process uses information from a "learning set" to perform parallel calculations that evaluate the combination of techniques that produce the lowest error when actual and predicted values are compared. The resulting algorithm can then be used to process the on-line information, using the original learning set or a new set of samples for calibration.

SPECTROMETER DESIGN FEATURES

The foregoing principals have been incorporated into the design of a ultraviolet absorption spectrometer (UVAS) system for real-time analysis of wastewater and other process solutions. This technology is commercially available under the ChemScan™ UV-6100 Process Analyzer brand name. A block diagram of this analyzer is shown as Figure 7. The design incorporates a fiber-optic link to a flow cell or optical probe, a spectrograph with a diffraction grating and a 256 element photodiode detector array plus internal processors for execution of chemometric algorithms, operator interface routines and communications tasks.

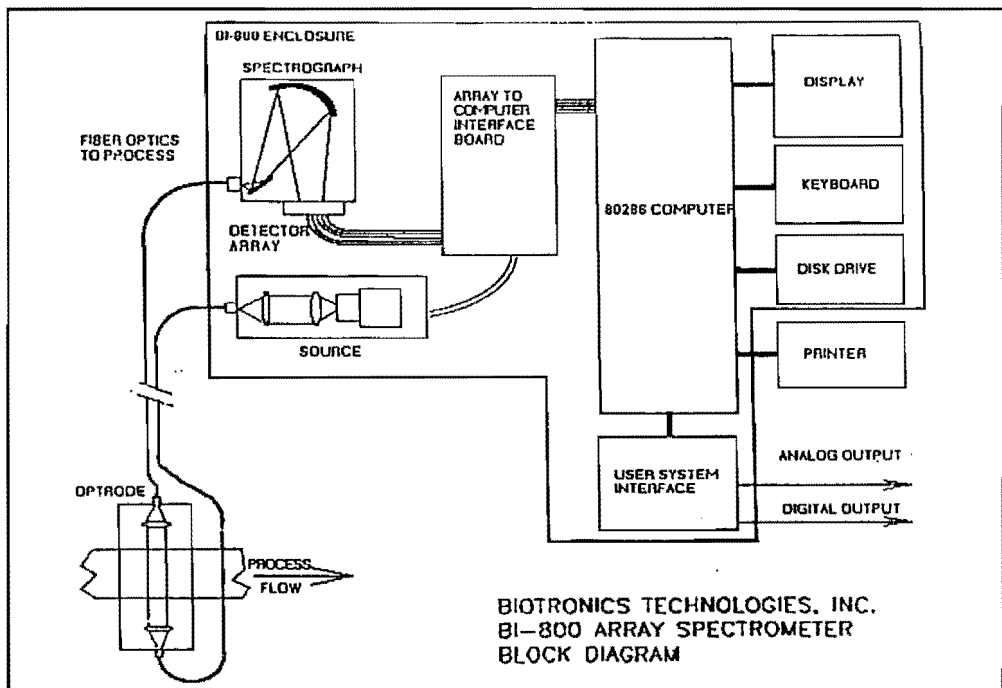


Figure 7

A xenon flash lamp located within the analyzer is used to provide a source of light with a known output across a broad wavelength range. The light is conveyed from the analyzer to the optical probe through the fiber optic cable. The light remaining after transmission through the media being analyzed is returned to the analyzer through a companion fiber-optic cable, where it enters the spectrograph for separation and detection.

CURRENT USES

During an earlier phase of the NASA project, iron and nitrates were identified and measured in the 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. Nitrate was measured with errors of less than 1.0 ppm over a range of 10.0 to 500.0 ppm. Methods for on-line analysis of additional nutrient components using UVAS technology are currently under development for NASA, the US Navy and others. These include detection of ions such as ammonium, nitrite, phosphate, and chloride; certain heavy metals; and organics such as unsaturated hydrocarbons and aromatic compounds. Major uses for this technology include oceanography, process control and environmental monitoring, including a variety of wastewater treatment process monitoring applications.

CONCLUSION

New technology is converting ultraviolet absorption spectrometry from a laboratory technology to one that can successfully be used for real-time chemical analysis of multi-component solutions such as wastewater. The technology improvements that make this possible include fiber optics, photodiode detector arrays and chemometric analysis algorithms.

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