HAES - A HYBRID ABSORPTION/EMISSION SPECTROMETER FOR ON-LINE MULTICOMPONENT ANALYSIS OF LIQUIDS

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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 hybrid absorption/emission spectrometer (HAES). When used as an absorption spectrometer, a xenon lamp provides a source of light in the ultraviolet and visible wavelength ranges. When used as an emission spectrometer, an arc discharge in the optical probe provides the excitation energy. This analyzer is currently being evaluated for continuous monitoring of nutrient solutions, process waters, wastewaters and groundwater.

ON-LINE ANALYSIS REQUIREMENTS

Absorption and emission spectrometry are both well accepted laboratory analysis techniques, but their use for on-line analysis is just emerging. On-line detection of natural absorption spectra in the near infrared region is becoming well established, 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 and emission spectrometry for multicomponent chemical analysis.

There are several laboratory instruments in wide use whose purpose is to detect absorption or emission 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 or emission spectrometry is to be used for real-time analysis of multiple-component chemical solutions, several limitations inherent in the current laboratory technology need 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 will be 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

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.
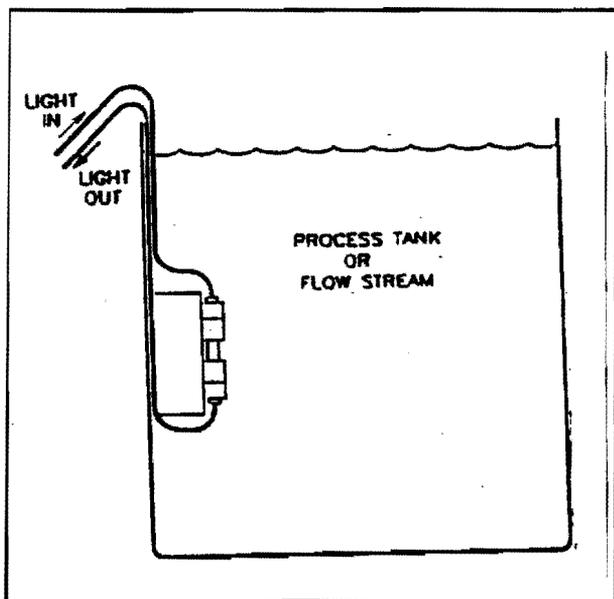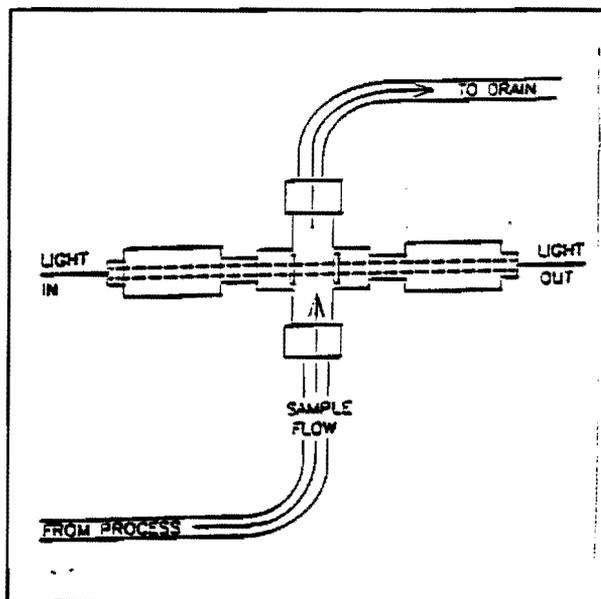

Figure 1

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, even in a flowing sample. 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 or emission 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 HAES system described in this paper detects spectral features in the 200 to 800 nm wavelength range using a 1024 element array.
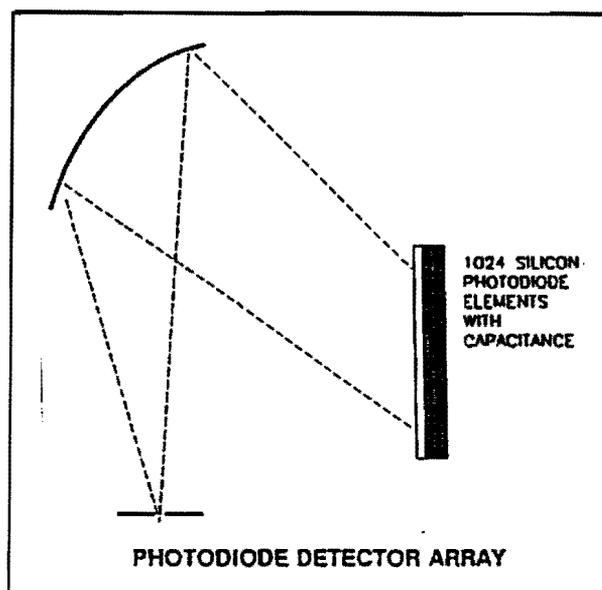
1024 SILICON PHOTODIODE ELEMENTS WITH CAPACITANCE

PHOTODIODE DETECTOR ARRAY

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 different chemometric techniques are used for absorption spectrometry and emission spectrometry, several 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.
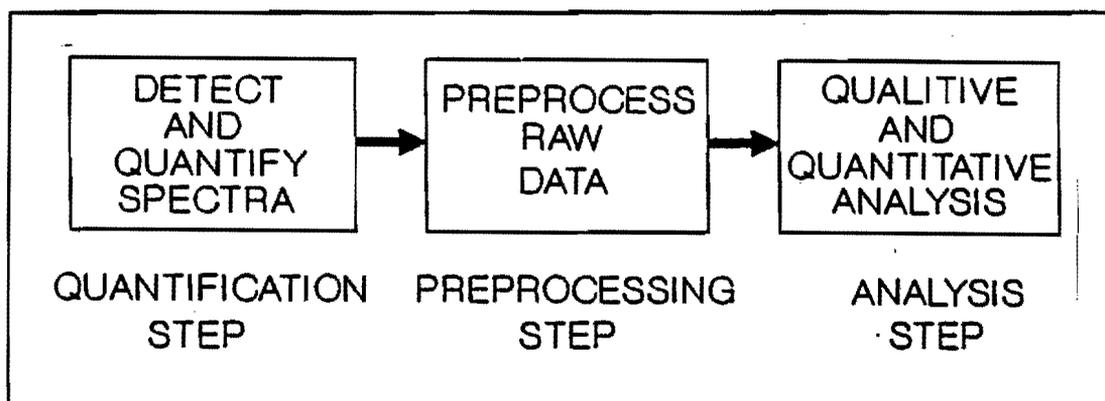
| DETECT AND QUANTIFY SPECTRA | → | PREPROCESS RAW DATA | → | QUALITIVE AND QUANTITATIVE ANALYSIS |

| QUANTIFICATION STEP | PREPROCESSING STEP | ANALYSIS STEP |

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.

Emission spectra of gaseous media are typically characterized by distinct narrow lines that represent the atomic elements present in the sample. When spectra are obtained from a liquid, however, the emission bands for elements are broadened by matrix effects from other constituents in the media and from optical distortion within the instrument. This effect is illustrated in Figure 6.
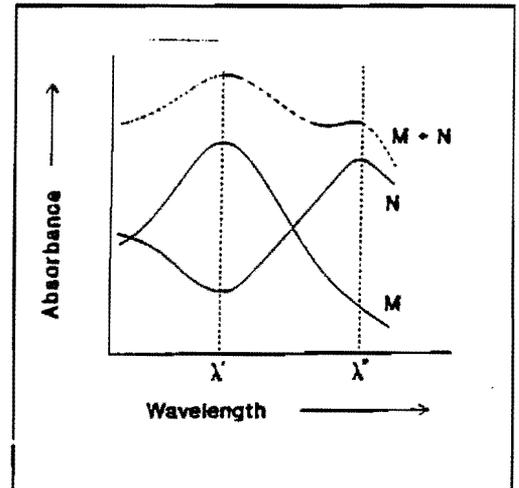
Figure 5

Preprocessing

Preprocessing of emission spectra is often performed for 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.
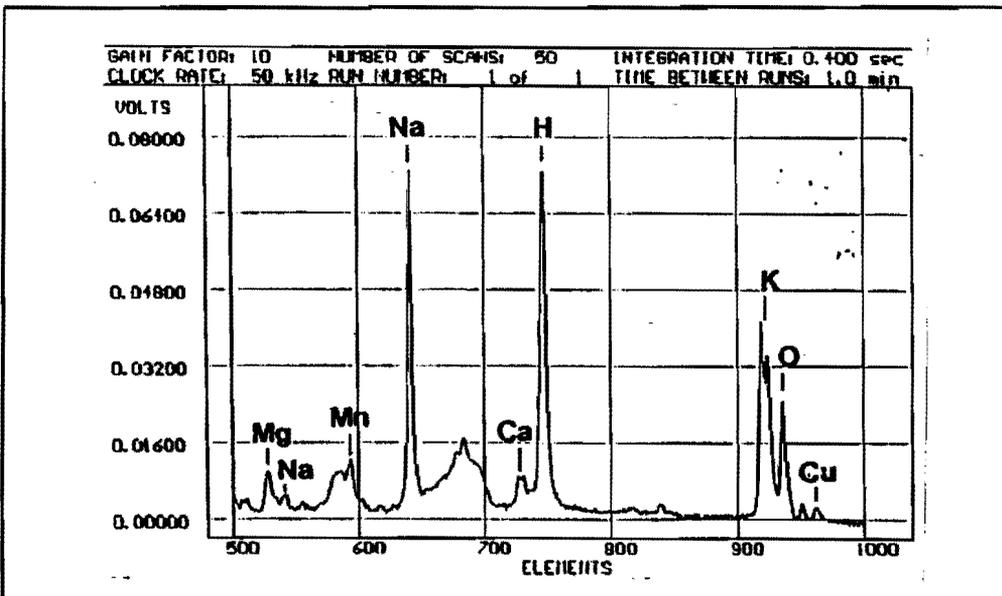
Figure 6

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 emission and absorption problems, often achieving significant improvements in error compared to more conventional methods. Genetic neural networks also have the benefit of being able to process nonlinear cross-coupling problems, such as the matrix effects of multicomponent emission spectra.

Development of Algorithms

A process is performed at the beginning of each project 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 hybrid ultraviolet-visible absorption/emission spectrometer for real-time chemical analysis. A block diagram of this analyzer is shown as Figure 7. 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.
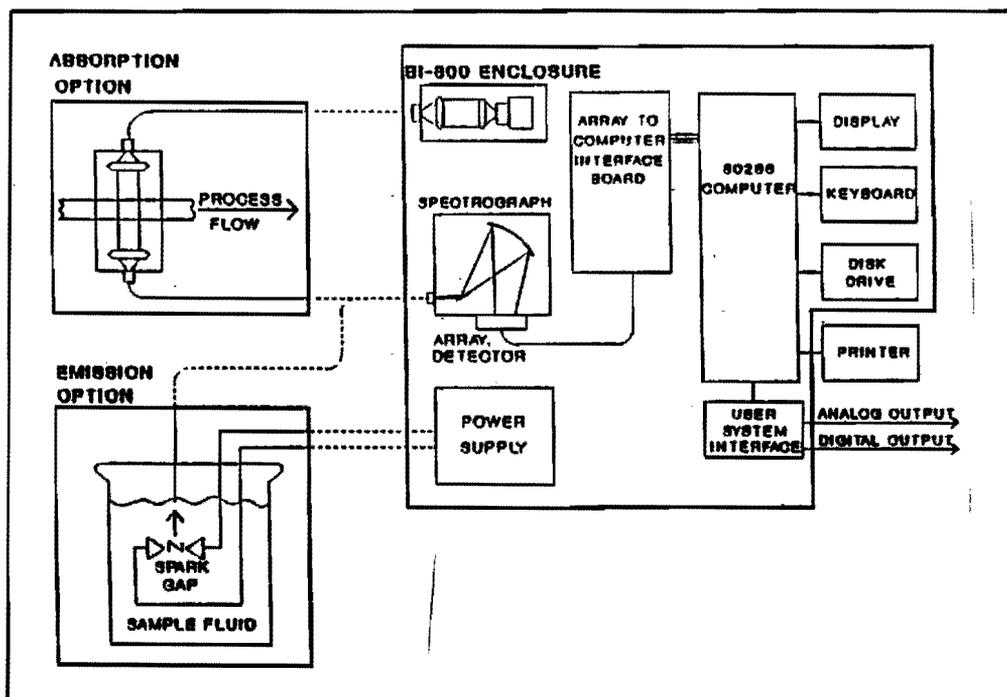

Figure 7

In the absorption mode, a xenon flash lamp located within the analyzer is used as 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 a 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.

In the emission mode, light excitation is replaced by an arc discharge directly in the liquid media. The arc is generated using a power supply located in the analyzer and connected by wire to electrodes located within the optical probe. Following arc excitation of the sample, the resulting emission spectra is collected by an adjacent fiber optic cable and conveyed to the analyzer for detection. Note that the same spectrograph is used for detection of both emission spectra and absorption spectra.

This design invites the possibility that absorption and emission information can be coprocessed to provide a better analysis of the chemical composition of a solution than would be possible through the use of either technique by itself.

CURRENT USES

The potential of a HAES system to perform multi-component chemical analysis is being demonstrated under a current NASA contract. The objective of this project is to use either absorption spectrometry or emission spectrometry to identify and measure each of fifteen chemical components in a hydroponic plant growth nutrient solution. A hybrid analyzer has been fabricated and is being used for the analysis. Thus far, all of the analytes shown in Table I have been identified using either absorption or emission spectrometry.

Table I

Atomic Spectral Lines for Various Elements

Element	Wavelengths (nm)	Intensity
Sodium	589.0, 589.5	2000, 1000
Potassium	766.5, 769.9	1800, 900
Calcium	393.3, 396.8	4200, 2200
Magnesium	285.2, 383.8	6000, 500
Hydrogen	656.3	3000
Iron	373.5	700
Manganese	403.1, 403.3	2060, 1400
Copper	324.7, 521.8	5000, 100
Zinc	636.2	500
Molybdenum	379.8, 386.4	3200, 2800
Oxygen	777.1	1000
Boron	249.8	500
Sulfur	469.5	500
Phosphorous	253.5	80
Nitrogen	411.0	1000
Lead	405.8	2000
Mercury	435.8	3000
Chromium	425.4	5000
Nickel	352.4	1000
Cadmium	643.8	2000

During an earlier phase of this 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. Nitrates were measured with errors of less than 1.0 ppm over a range of 10.0 to 500.0 ppm. Methods that were developed for quantitative analysis of nutrient elements using on-line emission spectra are currently under evaluation by NASA.

Another application of this technology is for groundwater monitoring. Absorption spectrometry is being evaluated for the detection of certain aromatics and unsaturated hydrocarbons, while emission spectrometry has been studied for detection of heavy metals and other indicators of contamination. Hybrid techniques have the potential to provide rapid characterization of possible contamination in groundwater samples without the need for expensive, time consuming laboratory analysis.

CONCLUSION

New technology is converting ultraviolet-visible absorption spectrometry and emission 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 algorithms.

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