

92 **Haz Mat**TM **NORTH-AM**

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September 15-17, 1992
Cobo Convention Center
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A HYBRID ABSORPTION/EMISSION SPECTROMETER FOR IN-SITU DETECTION OF TOXIC CHEMICALS IN WATER AND WASTEWATER

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ABSTRACT

A new spectrometer design uses a common spectrograph to detect ultraviolet - visible absorption spectra and atomic emission spectra directly in liquid media. The light source for absorption analysis is a flash lamp located within the analyzer that introduces light to a submerged optical probe or flow cell through a fiber optic cable. Emission excitation is produced by an arc discharge within in the liquid contents of the optical probe or flow cell with the resulting emission spectra returned to the analyzer through the fiber optic cable. This system is currently being evaluated for several aerospace, industrial and environmental applications since numerous metals and nonmetals can be simultaneously analyzed on-line with this new technology.

REQUIREMENTS FOR ON-LINE ANALYSIS

Toxic substances in water or wastewater are most commonly encountered as individual components of a multiple component chemical matrix. Groundwater that has been contaminated by leachate from poorly contained landfills and mixed waste effluent from industrial operations are examples of the typical multiple component chemical matrix that can contain toxic constituents.

Analysis of a multiple component chemical matrix has typically been performed in a laboratory, where an extracted sample can be physically and chemically manipulated to isolate the individual constituents that are present, one by one. However, there are numerous applications such as quality monitoring or process control where remote analysis of an extracted sample simply will not suffice. These applications require the use of automated analytical systems that can detect an analyte of interest either directly in a flow stream or process tank (in-situ analysis) or in a fractional sample continuously drawn from the main flow or process reservoir (on-line analysis). These applications may require that one or more contaminants or control parameters be detected at trace concentration.

Several techniques are currently available to detect specific chemical constituents in monitoring or control applications. Techniques such as flow injection spectrometry, while capable of detecting a wide range of analytes, are limited in practice to the detection of a single specific analyte for a given configuration of the analyzer. A new injection column and detector (or a second instrument) is needed to detect a second analyte. Since these analytical techniques require that a reagent be introduced, the resulting on-line samples must be discharged to waste and cannot be returned to a process tank. Other techniques that are theoretically capable of multiple constituent analysis in the laboratory such as mass spectrometry or ion chromatography are difficult to operate on-line, and are therefore poor choices for monitoring or control applications.

The ideal analytical technique for these applications would be capable of simultaneously detecting a wide variety of molecular and ionic substances at trace concentrations in liquids. No reagents would need to be used. An operator would not be required for collection or interpretation of the analytical information. Instrumentation would be capable of operation in hostile environments. And, the ideal

technique would also be able to detect and measure varied concentrations of the analytes of interest in the presence of reasonable variations in non-analyte chemical backgrounds within the chemical matrix to be analyzed.

A new generation of hybrid instruments is emerging that is capable of meeting these demanding requirements for on-line and in-situ monitoring of complex liquids. These instruments rely upon a combination of absorption spectrometry and emission spectrometry techniques.

CONVENTIONAL ABSORPTION AND EMISSION SPECTROMETRY

ABSORPTION SPECTROMETRY

Absorption and emission spectrometry are both well accepted laboratory analysis techniques. Absorption spectrometry in the ultraviolet and visible wavelength range is a common technique for detection of analytes following alteration of a sample using chemical reagents, chromatographic separation or some other form of sample preparation. Ultraviolet - visible absorption spectrometry is not often considered a viable technique for the direct analysis of complex liquids (even though direct on-line detection of chemical spectra in the near infrared region is becoming well established). Therefore, on-line applications in the ultraviolet-visible wavelength range have typically been limited to detection of specific analytes after reaction with immobilized or injected reagents.

There is a strong perception that because so many substances absorb light in the uv-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. When physical/chemical sample preparation techniques are used in conjunction with absorption spectrometry it is possible to obtain qualitative and quantitative information for a single analyte at one significant (usually peak) wavelength, thus simplifying detector design for that analyte at the expense of increased complexity ahead of the detection step.

Absorption spectra from multiple component liquids will be a combined function resulting from all absorbing components in the matrix. If no manipulation of samples is performed, analysis of a specific component is only possible if the contribution from the spectra of the component to the overall spectra of the solution can be quantified and detected. Special instrumentation and analytical techniques are required for this task.

EMISSION SPECTROMETRY

More than 70 elements may be detected using optical emission spectrochemical analysis techniques. In emission spectrometry, absorption of energy from an electrical discharge is used to excite atoms in a sample. Absorbed radiation is emitted when the atoms revert from an unstable excited state back to their stable states. Since the emissions from specific atoms occur at known wavelengths for each atom under a given set of excitation conditions, spectrometric analysis of multiple components is possible at the atomic level. And, since many of these emissions occur in the ultraviolet - visible wavelength range a dispersive uv-visible spectrometer can be used for the parallel detection of numerous elements.

Despite the above capabilities current generation emission spectrometers are rarely used outside of the laboratory due to the difficulty of controlling excitation conditions, the need for samples to be properly vaporized or ablated and the requirements for environmental stability in the detection system. The form of the sample is also an important constraint for repeatable excitation control in current

generation technology which favors solids and vapors over liquids.

If a matrix to be analyzed contains multiple chemical components the spectra detected will be a function of several components. If emission spectrometry is to be performed in real time, hardware and software techniques that are capable of rapidly detecting and interpreting parallel atomic spectra will be needed. This implies that the analysis system has the benefit of information concerning the location and intensity of spectra for each element over a range of concentrations so that possible intercomponent effects can be calculated.

ON-LINE SPECTROMETRY TECHNOLOGY

Three technologies make on-line spectrometric analysis of multiple component chemical solutions possible. These technologies are fiber optic probes, linear photodiode detector arrays, and chemometric analysis algorithms.

FIBER OPTIC PROBES

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 be located either in a benign environment remote from the solution being analyzed or can be located adjacent to the solution but in a sealed enclosure. Either an in-situ or an on-line probe can be linked to the analyzer using fiber optics, as illustrated in Figures 1 and 2. The figures show probes that are typical for absorption spectrometry. A emission spectrometry probe would eliminate the incoming optical fiber, but contain electrodes for excitation of the liquid using a controlled arc discharge.

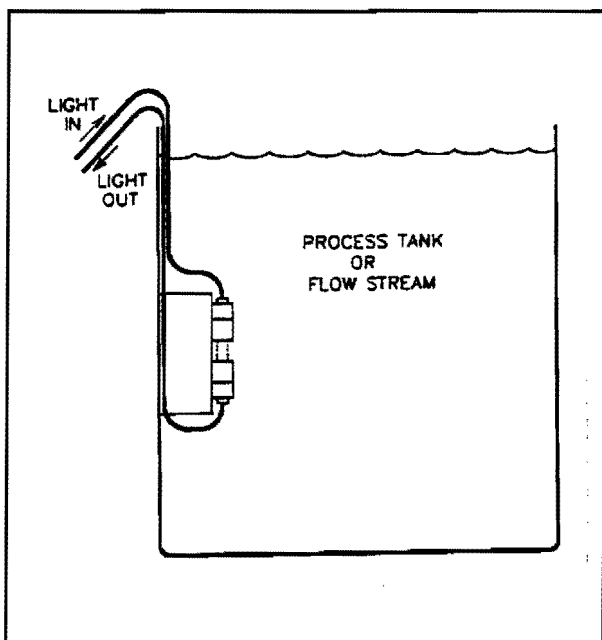


Figure 1. In-Situ Probe.

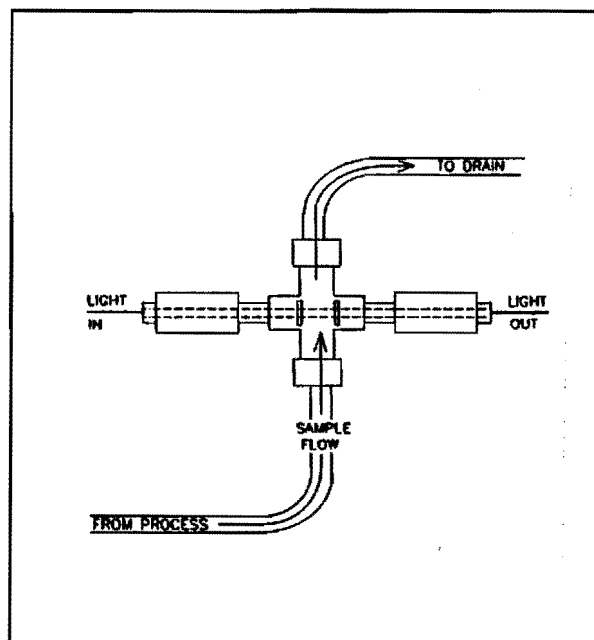


Figure 2. On-Line Probe.

LINEAR PHOTODIODE DETECTOR ARRAYS

The development of linear photodiode detector arrays has made it possible to rapidly scan an entire wavelength range and thus detect absorption or emission 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 the 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 Hybrid Spectrometer described in this paper detects spectral features in the 200 nm to 800 nm wavelength range using a 1024 element array.

CHEMOMETRIC ANALYSIS ALGORITHMS

Chemical solutions 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 analysis of the effects from multiple chemical constituents on the observed spectral pattern for a solution. Although different techniques are used for absorption spectrometry and emission spectrometry, there are three basic steps involved in any process using chemometric techniques for analysis of spectra. These steps are illustrated in Figure 4.

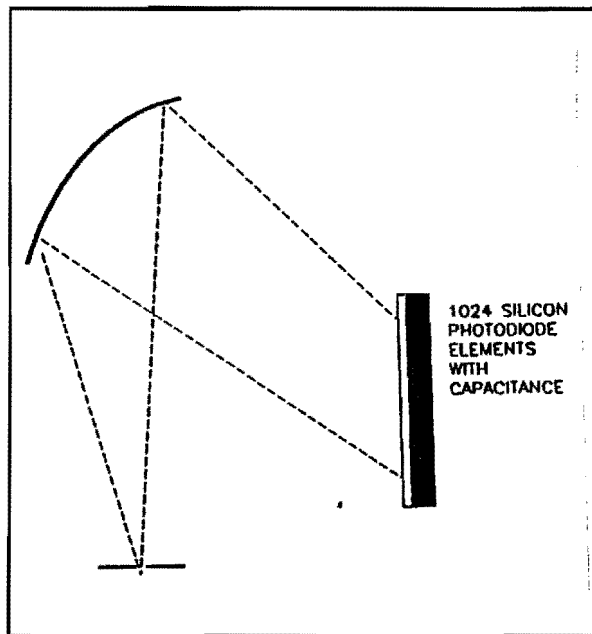


Figure 3. Spectrograph Arrangement.

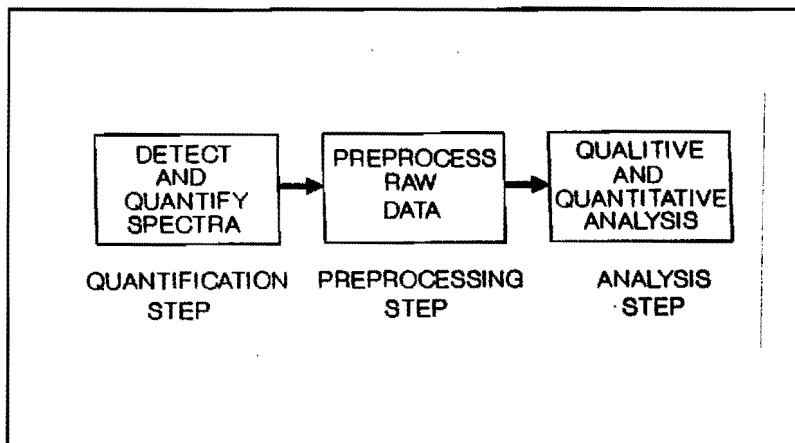


Figure 4. Chemometric Analysis Steps.

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 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.

HYBRID SPECTROMETER DESIGN FEATURES

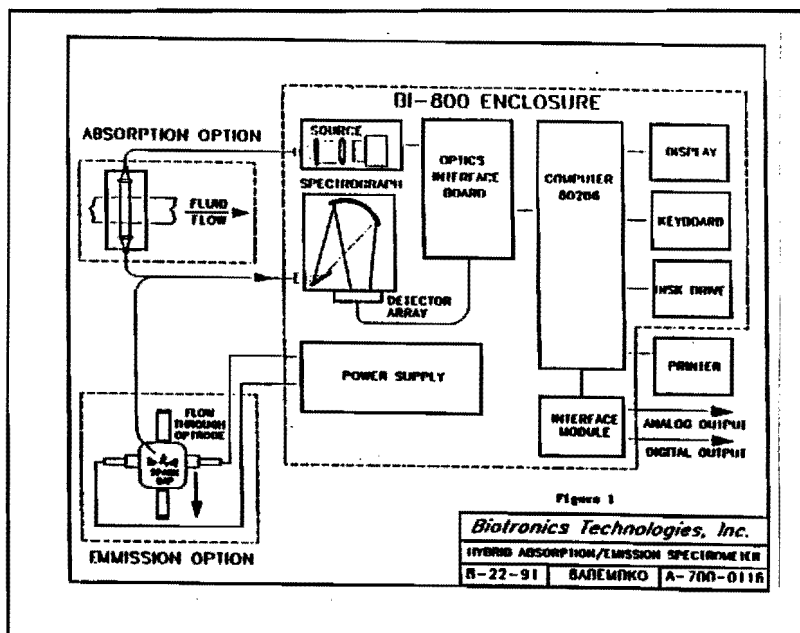


Figure 5. HAES Block Diagram.

In the absorption mode, a xenon flashlamp 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.

The foregoing principles have been incorporated into the design of a Hybrid Absorption/Emission Spectrometer (HAES) system for real time chemical analysis. A block diagram of this analyzer is shown as Figure 5. The design incorporates a fiber optic link to an optical probe, a spectrograph with a stationary diffraction grating and a 1024 element photodiode detector array, and internal processors for execution of chemometric algorithms, operator interface routines and communications tasks.

In the absorption mode, a xenon flashlamp located within the analyzer is used as a source of light with a known output across a broad

CURRENT USES OF HYBRID ABSORPTION/EMISSION SPECTROMETRY

The potential of hybrid absorption/emission spectrometry to perform multi-component chemical analysis is being demonstrated under current NASA and US Navy contracts. The objective of the NASA 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 this analysis. The Navy contract is demonstrating the use of these hybrid techniques to perform analysis of toxic metals and sea water constituents in oceanographic applications. Independent research is also being performed to demonstrate the use of hybrid absorption/emission techniques to detect contaminants and toxic materials in water and wastewater flow streams.

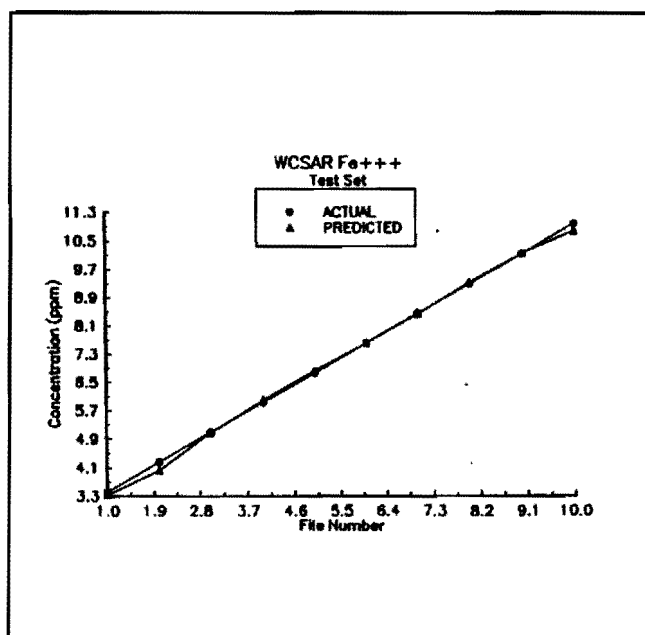


Figure 6. Predicted vs. Actual Iron Concentrations.

On-line absorption spectrometry has already been demonstrated capable of detecting nitrates, metals (Iron, copper, zinc) and organic compounds (aromatics, unsaturated hydrocarbons) in complex solutions. Figure 6 shows a plot of actual and predicted iron concentrations in multiple component nutrient solution samples using on-line absorption spectrometry.

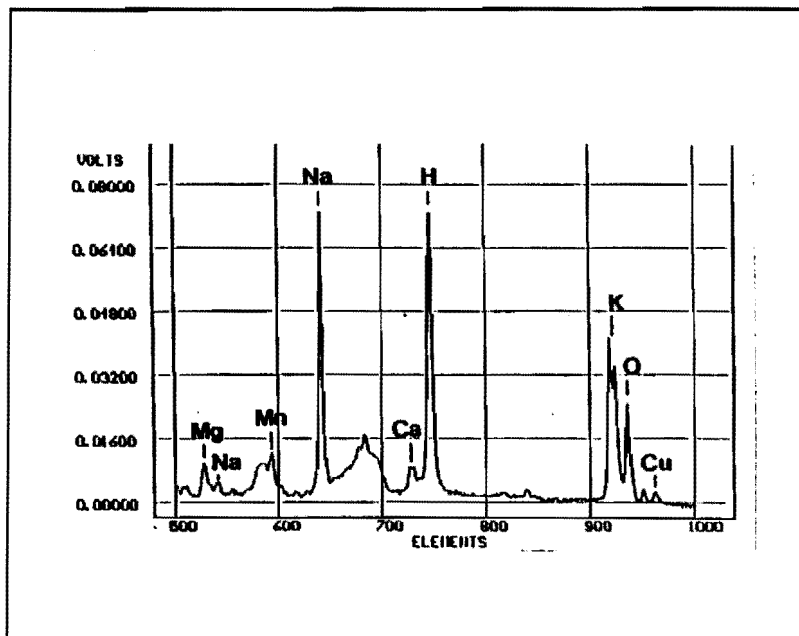


Figure 7. Liquid Atomic Emission Spectra.

Liquid Atomic Emission Spectrometry (LAES) has been shown to be capable of detecting numerous elements in water including alkali metals (sodium, potassium), alkaline earth metals (calcium, magnesium), heavy metals (iron, copper, zinc, molybdenum, lead, mercury, chromium, nickel, cadmium), and dissolved gases (oxygen, hydrogen). Figure 7 shows a portion of the emission spectra from the same multiple component nutrient solution used in the iron experiments discussed above. Note the variety of components that can be identified using the LAES technique.

CONCLUSION

Hybrid absorption/emission spectrometers that are capable of parallel analysis of a wide variety of chemicals and elements, including many toxic substances, are being demonstrated in several important aerospace, industrial and environmental applications. This technology will make it possible to perform on-line analysis of multiple chemical constituents in water and wastewater.