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TWO NEW ADVANCED FORMS OF SPECTROMETRY
FOR
SPACE AND COMMERCIAL APPLICATIONS

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ABSTRACT

Reagentless ultraviolet absorption spectrometry (UVAS) and Liquid Atomic Emission Spectrometry (LAES) represent new forms of spectrometry with extensive potential in both space and commercial applications. Originally developed under NASA Kennedy Space Center sponsorship for monitoring nutrient solutions for the Controlled Ecological Life Support System (CELSS), both UVAS and LAES have extensive analytical capabilities for both organic and inorganic chemical compounds. Both forms of instrumentation involve the use of remote fiber optic probes and real-time measurements for on-line process monitoring. Commercial applications exist primarily in environmental analysis and for process control in the chemical, pulp and paper, food processing, metal plating and water/wastewater treatment industries.

REAGENTLESS ULTRAVIOLET ABSORPTION SPECTROMETRY

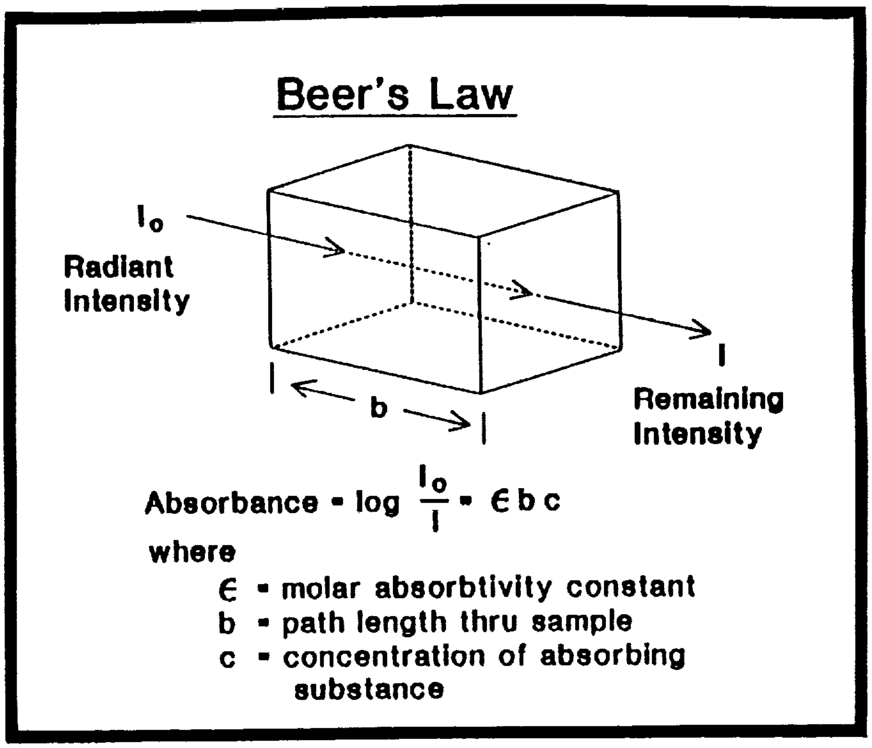
Traditional ultraviolet absorption spectrometry requires the use of chemical reagents that produce chemical reactions that result in strongly absorbing solutions with light absorbances proportional to the target analyte concentration. These reactions often extend their effects into the visible range producing color changes in the sample solutions. The use of such reagents allows for specific measurements because the regent is usually specific to the analyte of interest. Reagent-based ultraviolet-visible absorption spectrometry while quite suitable for off-line laboratory use is not well adapted to on-line, real-time monitoring. The need for a continuous supply of reagents complicates the instrument design and usually results in unreliable measurements.

Many organic compounds absorb light energy in the ultraviolet region and produce characteristic "fingerprint" spectra unique to each compound. Inorganic ions, particularly the transition metals, join with other chemicals called ligands to form complexes in solution known as coordination compounds. These coordination compounds also are characterized by significant ultraviolet spectra. These ultraviolet spectra, which occur naturally without the use of chemical reagents, provide the basis for chemical analysis in combination with mathematical techniques of multicomponent chemical analysis. The specificity provided by the reagent in traditional ultraviolet spectrometry is replaced by the specificity possible with mathematical/statistical analysis.

The absorption spectrum for a particular multiple component chemical solution will be a function of the individual absorbing components in the solution and the spectral interaction of these compounds across a selected wavelength range. Several of the chemical components in nutrient hydroponic solutions (including nitrates and transition metals) are known to absorb light in the ultraviolet-visible wavelength range.

Single Component Chemical Analysis

The absorption of light in the ultraviolet-visible range is a result of shifts in the electronic energy of an atom or molecule caused by excitation from the appropriate wavelengths of light. Absorption spectrometry is based on Beer's Law which states that absorption through a liquid medium is a function of the absorptivity of the medium, the path length through the medium and the concentration of the absorbing components in the medium. These relationships can be restated to solve for concentration of an absorbing component if the absorption of a known path length through the liquid can be measured. Figure 1 illustrates the basic relationships defined in Beer's Law.



Absorbance = $\log \frac{I_o}{I} = \epsilon b c$

where

ϵ = molar absorbtivity constant
b = path length thru sample
c = concentration of absorbing substance

Figure 1. Beer's Law

Absorption at a specific wavelength can be thought of as the ratio of the incident intensity value of light at a specific wavelength before passing through the liquid to the value of the remaining light intensity at that same wavelength after passing through the liquid. Measurement of absorption at several wavelengths over a range will result in an absorption spectrum or "signature" for the liquid over the wavelength range with smaller intervals between wavelengths resulting in better resolution of the absorption signature.

Multicomponent Chemical Analysis

In the case of a solution with only one absorbing component, concentration can be related directly to the absorption measurements, often using a single (peak) wavelength. In more complex solutions, however, absorption at any one wavelength may be the result of the combined effects of several absorbing components. Each absorbing component has its own unique signature that remains constant in relative shape but changes in intensity as concentration changes. If this signature and the signature of the other absorbing components can be characterized, their influence on the composite absorption signature for the solution can be calculated using pattern recognition algorithms. These algorithms, frequently referred to as "chemometric models," permit absorption spectrometry to be used for multicomponent analysis.

Because specific absorbing components may contribute significantly to the absorption measurement at one specific wavelength but little or nothing to the absorption at another wavelength, multicomponent chemical analysis using absorption spectrometry will usually require measurements of absorption at several different wavelengths. If the analysis is to be performed "on-line" such as on a flowing sample, special instrumentation is needed that is capable of capturing information for a range of wavelengths and for immediate interpretation using chemometric models.

Instrumentation for Ultraviolet Absorption Spectrometry

A spectrometric instrument for ultraviolet-visible absorption spectrometry (UVAS) is shown in Figure 2. This same instrument also operates in the atomic emission mode, a form of spectrometry that is discussed in the latter part of this paper. In the absorption mode, the spectrometer transmits broad band light from a xenon flash lamp through a fiber optic cable to an optrode in a process pipe or tank. Light passes through the process fluid with selective light absorption that is dependent on the chemical composition of this same process fluid. Light surviving passage through the optrode is then returned via fiber cable to a spectrograph that disperses the light across a 200 - 800 nm spectrum. A silicon photodiode array of 1,024 elements detects light at each of 1,024 wavelengths and converts it to electrical form for subsequent processing. The 1,024 signals are sequentially converted to digital form and stored in computer memory. Spectral data is then processed through a series of signal processing and pattern recognition algorithms to estimate the chemical composition of the process. All of these measurement and processing operations are carried out in real time for on-line chemical monitoring of the process fluid.

On-line, real-time ultraviolet-visible spectrometric process analysis provides a strong capability for product improvement and cost reduction in many areas of the process industries. Some of these applications will now be discussed.

On-Line Ultraviolet-Visible Absorption Spectrometry Applications

On-line ultraviolet-visible absorption spectrometry may be applied in environmental analysis and a wide variety of process industry markets including the following:

1. The chemical industry
2. The food processing industry
3. The petroleum and petrochemical industries
4. The pulp and paper industry
5. The metal plating industry
6. The electronics industry
7. The water and wastewater treatment industry

Specific applications for UVAS can be identified in each of these industries, but emphasis here will be on one specific market within the water and wastewater treatment industry: the industrial water treatment market. This market is important not only because of its specific nature but because it is a market application that is currently being field tested with Biotronics' UVAS analyzer and with production scheduled for 1992. Three primary segments exist in the industrial water treatment market:

1. In-process
2. Boiler feed
3. Cooling

UVAS at Biotronics has found its first application in the cooling water market. Chemicals are used in this market to prevent corrosion and scale (from calcium and magnesium salts) and the growth of bacteria and algae. Corrosion, scale deposition and microbiological growth can significantly reduce operating efficiency and increase plant maintenance costs. Phosphonates, azoles and molybdates are typical chemicals used in cooling water treatment. The Biotronics BI-800 UVAS instrument provides for on-line analysis of these treatment chemicals for cost economy and optimal control of corrosion and scale.

The cooling water treatment industry represents a market in excess of $2 billion annually with an estimated 1,500,000 customer sites worldwide. Biotronics' Fortune 100 chemical industry corporate partner estimates that it currently supplies 47,000 of the estimated 280,000 major sites that will have use for a water analysis instrument. The corporate partner expects to increase its market share as a result of the proprietary position offered by the new analytical instrumentation. Even without such an increase in market share, however, the cooling water instrument market represents a market potential of $235 million. Other water treatment markets such as boiler feedwater and wastewater represent future markets of equivalent size. With pending production orders scheduled for 1992, ultraviolet spectrometry has moved from a Phase I NASA SBIR in 1990 to quantity production in less than two years time.

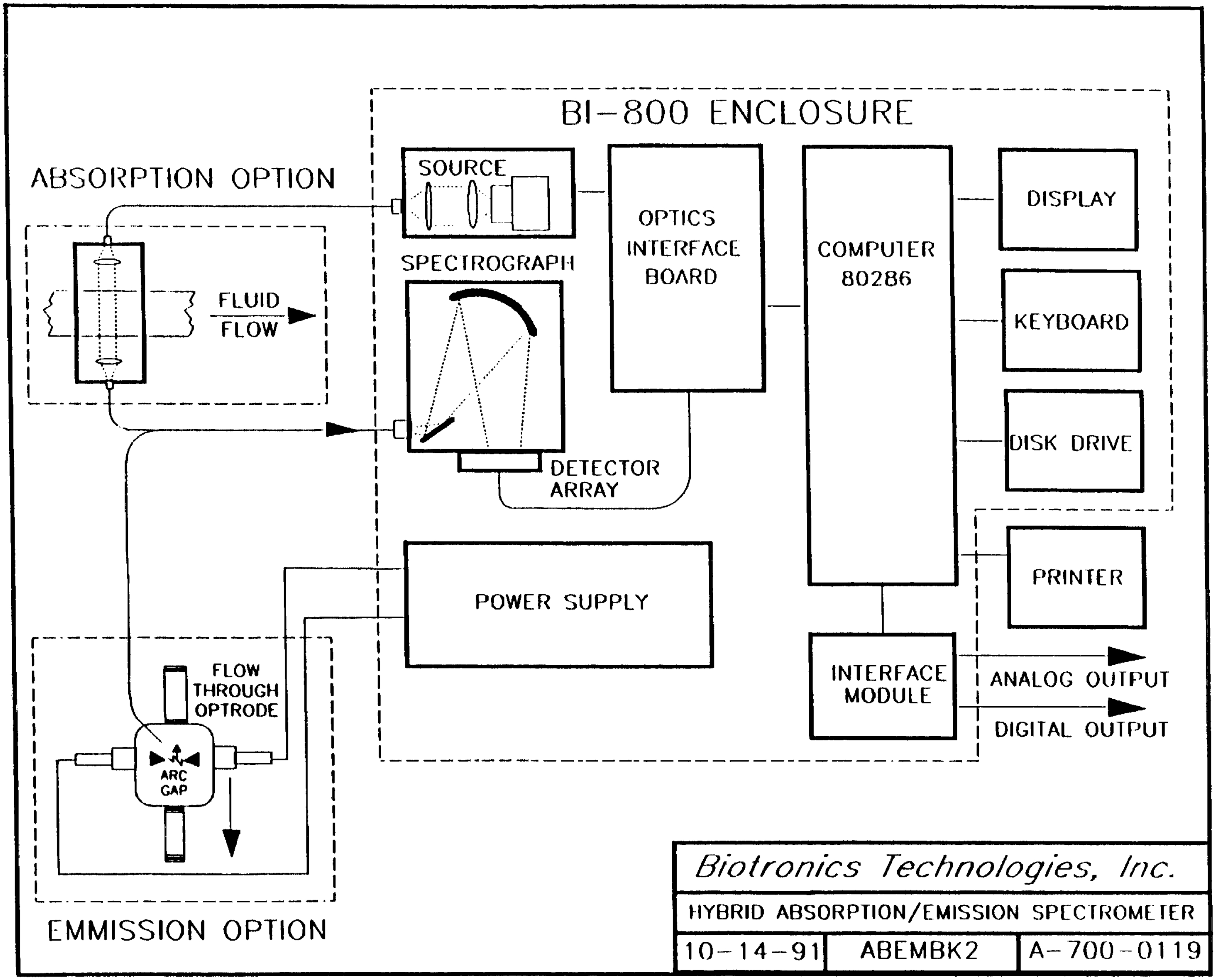

BI−800 ENCLOSURE
ABSORPTION OPTION
SOURCE
SPECTROGRAPH
OPTICS INTERFACE BOARD
COMPUTER 80286
DISPLAY
KEYBOARD
DISK DRIVE
FLUID
FLOW
DETECTOR ARRAY
POWER SUPPLY
PRINTER
INTERFACE MODULE
ANALOG OUTPUT
DIGITAL OUTPUT
FLOW THROUGH OPTRODE
ARC GAP
EMMISSION OPTION
Biotronics Technologies, Inc.
HYBRID ABSORPTION/EMISSION SPECTROMETER
10−14−91
ABEMBK2
A−700−0119

Figure 2.

LIQUID ATOMIC EMISSION SPECTROMETRY

Fourteen different primary and trace nutrients comprised the original set of CELSS requirements. With the addition of pH and dissolved oxygen, sixteen analytes were candidates for on-line measurement. These analytes are listed in Table 1. Only five of these analytes were strong candidates for effective measurement using ultraviolet-visible absorption:

1. Nitrate (NO_3)
2. Iron (Fe)
3. Manganese (Mn)
4. Copper (Cu)
5. Zinc (Zn)

Two other analytes, phosphate (H_2PO_4) and sulfate (SO_4), were weak absorbers and marginal prospects for UVAS spectrometry.

ALTERNATIVE TECHNIQUES FOR UV-VISIBLE ABSORPTION ANALYSIS

ORIGINAL STUDY OBJECTIVES			EXPANDED STUDY OBJECTIVES		
	ABSORBANCE			ABSORBANCE	
ANALYTE	PRIMARY	SECOND'Y	ANALYTE	PRIMARY	SECOND'Y
Fe	YES	YES	Na	NO	YES
K	NO	YES	Cl	NO	YES
Mg	NO	YES	Mn	YES	YES
Ca	NO	YES	Cu	YES	YES
pH	NO	YES	Zn	YES	YES
NO_3	YES	NO	MoO_4	YES	YES
H_2PO_4	YES	YES	BO_3	YES	YES
SO_4	YES	YES	O_2	NO	NO

Table 1.

An alternate approach to absorption measurements, designated as secondary absorption spectrometry, makes use of immobilized reagents on fiber optrodes. These reagents react reversibly with the analyte of interest to produce a change in absorption. This approach was demonstrated for magnesium using 8-hydroxyquinoline as the immobilized reagent and for pH with a number of reagents. Secondary absorption methods, however, raise major questions regarding the long term permanency and stability of such reagents in space or industrial environments. These questions provided a strong incentive to search for a new method of spectrometric analysis that could measure the remaining analytes of interest for NASA CELSS. This new method was discovered in a new form of emission spectrometry, Liquid Atomic Emission Spectrometry (LAES).

Atomic spectrometry is a long established technology for the analysis of gases and solids. All forms of atomic spectrometry require the application of energy to break the molecular bonds and reduce the substance to atomic form prior to analysis. Flame photometry is a traditional form of this technology still used for less demanding applications. Other forms of atomic spectrometry make use of electric arcs and sparks, graphite furnaces and radio frequency plasmas. Either light emission or light absorption techniques are used to quantify the concentrations of target analytes.

All of the above spectrometric technologies convert the material under analysis to a gaseous state or plasma prior to analysis. This state allows individual atomic elements to produce emission or absorption lines at specific wavelengths that are predictable for each element for a specific form of excitation and detection. This technique, however, requires that a sample of the substance being investigated be extracted from the source.

For on-line analysis of liquids, an analytical technique that will permit simultaneous analysis of many elements directly in the flow stream is required. Liquid Atomic Emission Spectrometry (LAES) is a new form of atomic spectrometry in which an arc or spark discharge is used to generate atomic light emission directly in the liquid medium. The light emission not only occurs directly in the liquid, but is also detected directly in the liquid using special apparatus that will permit in-situ simultaneous analysis for a spectrum of multiple elements.

Instrumentation

The instrumentation required for Liquid Atomic Emission Spectrometry is similar to the instrumentation used for UVAS. In fact, one of the principal advantages of LAES is that the same 1,024 element photodiode array detector can be used for both LAES and UVAS analysis.

The LAES instrument, originally used for experimental analysis of NASA nutrient solutions, used a beaker to hold a sample of the liquid. A flow through cell, illustrated in Figure 2, has now been developed for on-line analysis. An arc was created in the beaker using electrodes immersed in the nutrient solution and separated by an electrode gap. A fiber optic cable linked the analyzer and the beaker with the termination of the cable located in close proximity to the arc gap. This arrangement provided the energy necessary to accomplish molecular breakdown of the elements in the solution, as well as the energy necessary to stimulate atomic light emission from these elements.

The spectrometer used for the original LAES experiments was identical to that used for the ultraviolet-visible absorption experiments discussed above. The fiber optic cable was connected to a spectrograph containing a diffraction grating that separates light returned to the analyzer through the cable into discrete wavelengths from 200 - 800 nm and projects these wavelengths onto a 1,024 element linear photodiode detector array. Each element in the array is matched with a dedicated capacitor which stores spectral values that can be rapidly scanned to accumulate information and convert the information into digital values. This information can then be processed by pattern recognition software implemented in an 80286 computer built into the instrument. A block diagram of an instrument designed for both absorption and emission spectrometry is shown in Figure 2.

A series of experiments were conducted near the end of the Phase I program to explore the capability of the LAES concept and its potential as an on-line monitoring technology. Solutions were prepared using distilled water and a single compound that contained an analyte of interest. Several individual test solution were made containing known concentrations of each analyte. Each individual solution was subjected to an arc-induced excitation, and the resulting light emission was captured and recorded using the instrumentation described above. Because customized pattern recognition software was not available for this new technology, standard conventional atomic emission spectra tables were used to help identify the emission peaks observed during the experiments.

Following experimentation with the individual analyte solutions, a multicomponent nutrient solution with known components was tested, and the results were recorded.

Test Results

Individual Analyte Solutions. All of the solutions tested exhibited prominent peaks at or near the wavelengths predicted for the element under investigation when liquid atomic emission results were compared to the known emission lines from conventional atomic emission techniques. An example can be seen with sodium, shown in Figure 3, which would conventionally be expected to show peak emissions at 589 nm. The LAES experiments showed strong peaks at photodiode element number 644, which translates into a wavelength of approximately 589 nm. Furthermore, results show that the relative intensity of the peak is consistent with the relative concentration of the sodium contained in each of the test solutions. Similar results were obtained for magnesium, calcium, potassium, copper, and zinc.

Nutrient Solutions. Additional experiments were performed with a multicomponent nutrient solution in order to illustrate the ability of the LAES technique to simultaneously capture multiple element emission peaks. Although some peaks were not identified, the emission information detected was able to be matched with expected peaks for calcium, copper, zinc, hydrogen, sulfur, magnesium, molybdenum, manganese, potassium and oxygen, as shown in Figure 4. No attempt was made to quantify these elements due to the lack of sufficient information to establish adequate calibration models.

Liquid Atomic Emission Applications

Because Liquid Atomic Emission Spectrometry is still in the development stage, it is not yet possible to speak of demonstrated applications ready for commercial production. Nevertheless, two major applications should be in the field testing stage by the middle of 1992: environmental monitoring of toxic metals and process monitoring and control in the metal plating and electronics industries.

Toxic metals such as lead, chromium, nickel and cadmium are a recognized environmental health threat. There is a pressing need for on-line monitoring of these metal analytes in drinking water, wastewater and in on-site soil surveys. Biotronics is currently working with the U.S. Army Corps of Engineers in developing an on-site system for direct detection and quantification of toxic metals in soils. As an augmentation of the Army Corps of Engineers SCAPS (Site Characterization and Analysis Penetrometer System), this system would provide on-site three-dimensional mapping of toxic metals in survey areas at depths of up to 150 feet. This same LAES should find an extensive market in municipal and industrial wastewater treatment.

Metal plating is a process used in a variety of industries from jewelry and automobiles to electronics (integrated circuits and printed circuit boards) and aerospace. Both quality and cost control of metal plating processes could significantly benefit from on-line monitoring and control metal concentrations in plating baths. This multi-billion dollar market is an ideal one for LAES because the new spectrometric technology is capable of direct plating bath measurement of metal concentrations. Biotronics has previous experience in this industry and is already working with a major supplier of plating solutions to develop this market application.

Phase I SBIR to Market in Two Years

Biotronics' on-line BI-800 ultraviolet/visible spectrometer represents a NASA success story in technology transfer. The compressed time period of the transition from research concept to volume production is evidenced from the following timetable of events:

Phase I SBIR Completed - July 3, 1990
Corporate Partner Development Agreement Executed - September 12, 1990
First Prototypes Delivered to Corporate Partner - June, 1991
First Production Spectrometers Delivered - March, 1992

It is important to emphasize that the above development scenario includes only the UVAS portion of the NASA SBIR program. A Phase II contract to develop the more experimental Liquid Atomic Emission Spectrometer (LAES) was concluded in May, 1991. Market implementation of this technology is approximately two years away. Nevertheless, the fact remains that a NASA sponsored Phase I SBIR has resulted in a commercial product in less than two years from the completion of the Phase I feasibility study.

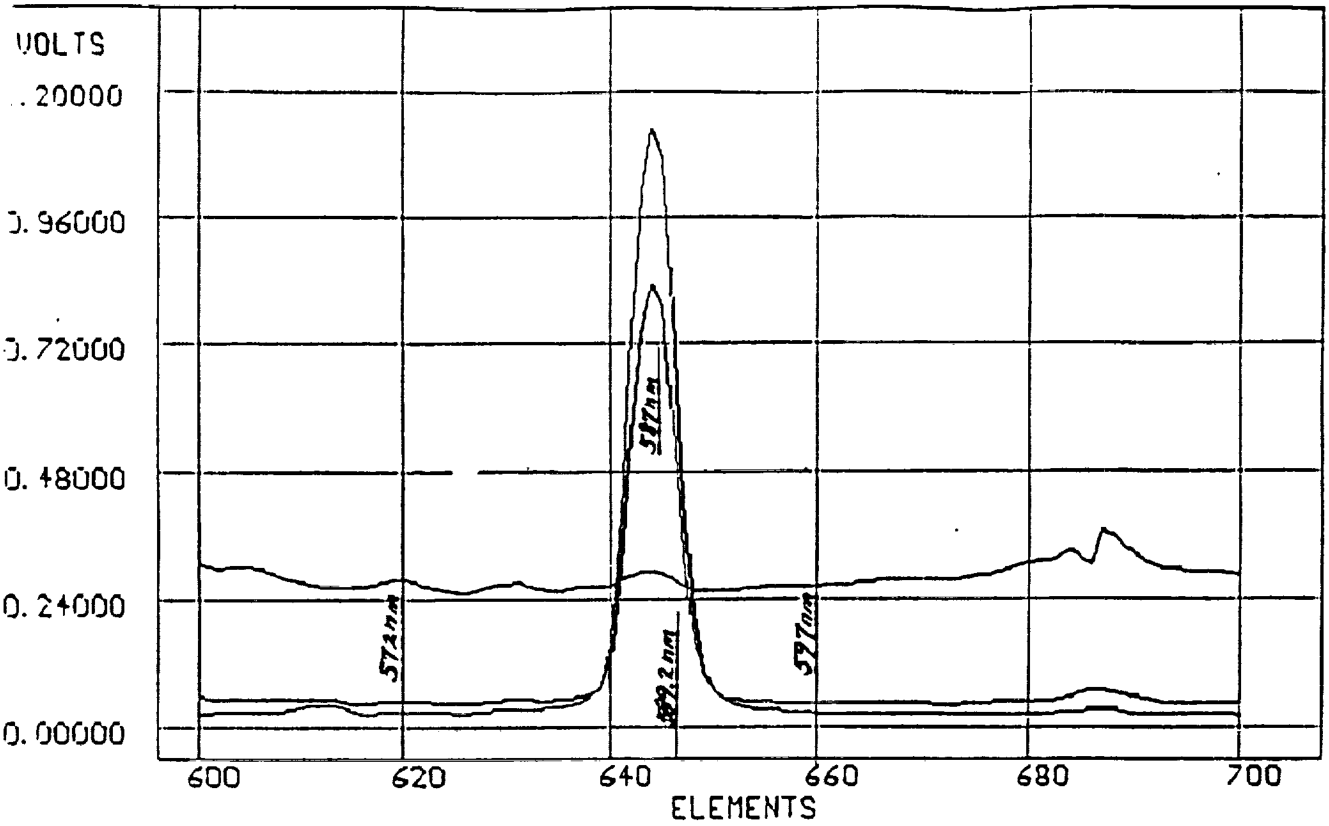


Figure 3. Atomic Emission Spectra for Sodium

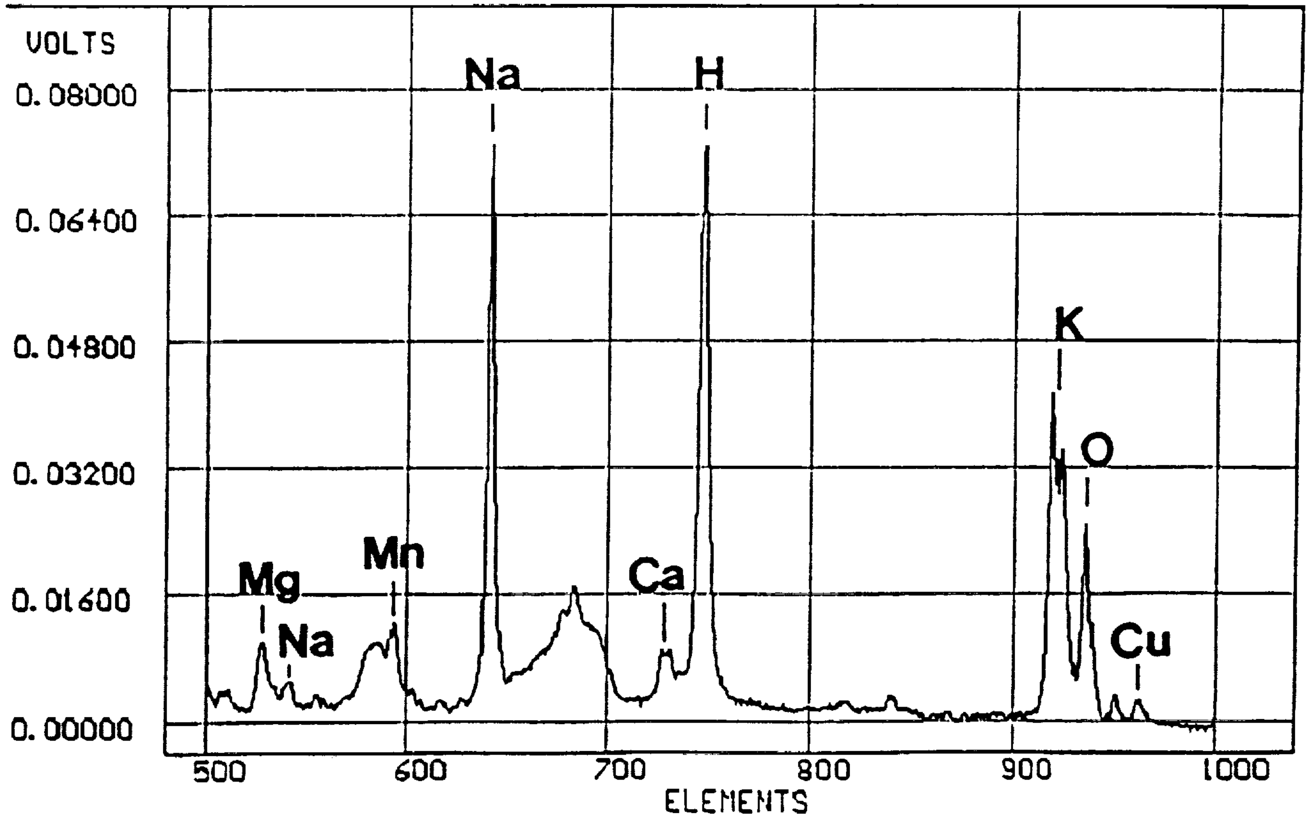


Figure 4. Atomic Emission Spectrum for a Nutrient Solution