

Technical Publication

Title: On-line Spectroscopic Monitoring of Plant Nutrients in Hydroponic Space Applications Using Photodiode Array Absorption and Emission Spectrometry

ASA Publication Number: 4

Presented at: International Symposium on
Sweet Potato Technology
for the 21st Century
Tuskegee, Alabama
June 2-6, 1991

Note: This document was originally published by Biotronics Technologies, Inc. in conjunction with the ChemScan Process Analyzer technology base, now owned by Applied Spectrometry Associates, Inc. Please direct all inquiries and correspondence to:

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On-Line Spectroscopic Monitoring of Plant Nutrients
in Hydroponic Space Applications
Using Photodiode Array Absorption and Emission Spectrometry

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ABSTRACT

Significant needs exist for on-line real-time monitoring of plant nutrients in hydroponic space applications. Primary and micro-level nutrients including nitrate, potassium, phosphate, iron, copper, magnesium and molybdenum are of major interest and are more often effectively controlled by on-line monitoring. In the NASA Space Station and other long duration space missions, hydroponic food grown in space could benefit significantly from on-line monitoring of plant nutrients in order to maximize crop yields and allow for close control of the plant production system.

A new on-line fiber optic ultraviolet-visible photodiode array spectrometer provides a very effective instrument for absorbance and atomic emission measurements of metal and non-metal ion solutions for chemical concentration analysis. Problems created by interfering and overlapping spectra are solved through the use of statistical and pattern recognition methods of multicomponent chemical analysis.

THE NEED FOR ON-LINE MONITORING OF PLANT NUTRIENTS

Hydroponic Plant production systems are critically dependent on the chemical composition of nutrient solutions for effective yields. Although innovative concepts in open-loop nutrient feeder and blender systems have been implemented in recent years, the need still exists for close loop control of hydroponic nutrient systems. Such close loop control requires the use of an analytical instrument able to provide on-line, real-time measurements of nutrient chemical concentrations.

Although atomic absorption spectrometry and gas chromatography are the typical methods of analysis for most of the nutrient components, these methods are not practical for continuous on-line monitoring in multi-constituent media due to sample preparation requirements and apparatus that can handle only a limited number of samples. Another limitation is the need to change lamps if more than one nutrient metal is to be analyzed. Multiple instruments would be required for analysis of more than one nutrient constituent. These methods are also impractical for remote automated analysis due to their need for a controlled operating environment and peripheral equipment for sample processing. The power requirements, optical stability, weight, envelope dimensions, special gasses required and operator skills demanded are also factors that preclude use of conventional instruments for this application.

However, another form of optical spectrometry, ultraviolet absorption spectrometry, is ideally suited to the needs of on-line nutrient analysis in space. Traditionally, ultraviolet-visible absorption measurements such as colorimetry have required the use of chemical reagents specific to a particular analyte (nutrient component) to react with the analyte and produce a

color change proportional to the concentration of the analyte. Recent advances in spectrometry now make it possible to determine chemical concentrations in liquids based on ultraviolet light measurements without the need for reagents of any kind. It is now possible to mathematically transform an ultraviolet light spectra into an estimation of the chemical composition of a particular solution using pattern recognition techniques. A number of plant nutrients such as nitrate, iron and copper produce strong spectra in the ultraviolet region. These spectra can be measured on-line and then mathematically transformed into estimates of nutrient concentrations. This paper will briefly review the principles that make this analysis possible.

DETECTION OF ABSORPTION SPECTRA

Absorption in the ultraviolet and visible region of the spectrum is a result of the changes in energy levels that occur in the bond structures and valence electrons of atoms when in contact with a source of ultraviolet-visible light. The energy changes occur in the outermost orbital, which consists of two high energy levels and three lower energy levels. Electrons will normally be found in the lowest energy level, but can become "excited" from absorption of a photon of electromagnetic energy from light in the proper frequency, causing the electron to temporarily occupy one of the higher energy levels. [Rao, 1967; Thompson, 1974; Silverstein, 1981] Many heavy metals have strong absorption spectra in the ultraviolet-visible region due to the formation of ion complexes and ligands in water. It is well known that many of the heavy metals classified as transition elements possess the characteristic of forming complexes that are highly colored, that is, they absorb light in the visible wavelength range which is one reason why they are often used in pigments and dyes. [Hopp, 1983]

The term "absorption" refers to the characteristic of allowing only some fraction of light at certain wavelengths to pass through an otherwise transparent substance (or be reflected off of a solid), the balance being "absorbed" by the substance. Thus, absorption is the inverse of transmittance, and solutions that are fully transmissive within a certain wavelength range will not absorb any light within that range. Conversely, solutions that fully absorb within a certain wavelength range will not permit any light within that range to be transmitted through the solution. [Thompson, 1974]

Chemical analysis using ultraviolet-visible absorption spectra relies upon the same basic principals used for color analysis, but with far more attention to relative absorption characteristics at many specific wavelengths over the entire ultraviolet and visible range. It is possible to analyze solutions qualitatively and quantitatively based on the pattern of absorption observed for the solution across this wide range of wavelengths, but special apparatus is required to detect the spectra and interpret the information. The absorption observed

will be a function of all of the absorbing components within the solution, which complicates the problem of analysis.

APPARATUS REQUIRED FOR DETECTION OF ABSORPTION SPECTRA

The pattern of absorption (or transmittance) across a range of wavelengths defines an absorption spectrum for the substance being analyzed. If the substance is an element dissolved in a transparent solvent, such as pure water, the absorption spectrum that can be observed using the appropriate equipment defines the absorption spectra for that element (in that solvent).

Figure 1 shows several spectra for iron in pure water, each for a different concentration ranging from .1 ppm to 2 ppm. Two observations can be made. First, no matter what the concentration is, the absorption spectra for iron has features that form a distinct pattern. (The graphics and scale used result in some loss in visual feature detail which can only hint at the extensive feature detail that is available for analysis in the form of numerical values for each spectra.) It is possible to define the common aspects of the spectral patterns in mathematical terms, so that any spectra that conforms to the resulting mathematical model will be recognized as "iron". If an analyzer can detect the spectra of an unknown substance (in the same solvent), the pattern can be evaluated in terms of iron by observing significant features of the absorption pattern for the unknown substance, then comparing these features to the model that was developed to describe iron.

Furthermore, it is possible to approximate the concentration of the unknown substance if it has been recognized as iron. If information is available that defines the relative position (intensity) that has been previously observed for the iron patterns at known levels of concentration, an interpolation can be made for a similar pattern falling between two known patterns in order to accurately calculate an estimated concentration value for the newly recognized substance. In this manner, recognition and measurement of a substance requires prior qualitative (pattern) and quantitative (intensity) calibration using known concentrations of the substance to be recognized.

The apparatus required to accomplish analytical tasks in absorption spectroscopy is well known to analytical chemists, but may not be evident to others who do not regularly work in the analytical or research sciences. Basic elements of any system include a source of light in the wavelength range of interest, a transparent cell to hold the sample and permit the light to be transmitted through the sample for a specific distance, a detector to measure the amount of light that has been transmitted through the sample and convert this information into numbers, and finally a means to process and interpret the information detected from the sample. The instruments currently in use range from the simple to the sublime.

Simple absorption spectroscopy systems have a limited (or single) wavelength range, and very simple fixed computational capabilities built into the instrument. These systems recognize only one substance (or family of substances) and usually require that the samples be processed or chemically altered to yield an indicator color prior to analysis. Systems with a broader range of capabilities are designed to permit analysis of a greater amount of information by detecting absorption at several (or many) wavelengths. This is accomplished by either altering the wavelength at the light source and using a fixed detector, or using a broad band light source and then selecting wavelengths for detection after transmission through the sample. In either case, the instrument must mechanically step through a sequence of wavelengths in order to collect information from the entire range of interest. This makes the instrument slow, fragile, and mechanically complicated, none of which are qualities that are suitable for use in field or space environments for real time/on-line analysis of unaltered flowing samples.

TECHNOLOGY ADVANCES FOR ON-LINE ABSORPTION SPECTROMETRY

Several recent developments have made ultraviolet-visible absorption spectroscopy a feasible technology for use in space:

FIBER OPTICS permit substantial distance between the analyzer and the substance to be analyzed. The remote analyzer can house a light source, detector, and electronic components. Fiber optic cables convey the source light to an OPTRODE, where the light is transmitted through the sample, then collected and returned to the detector through a companion cable. Optrodes may be immersed in a process tank or flow stream, then removed after the analysis has been performed, or may be permanently located at the sample point for continuous monitoring. These are two types of IN-SITU analysis. Alternatively, a sample line may be connected to a flow through cell containing the optrode. This is ON-LINE analysis.

PHOTODIODE ARRAY DETECTORS permit a broad wavelength range to be simultaneously detected at discrete intervals. This eliminates the need to create intervals by altering wavelengths at the source or prior to detection. Instead, a broad source can be used and fully detected. An evaluation can be made of wavelengths which contain absorption features relevant for the analysis. Wavelengths and ranges which do not contain information that contribute to the analysis can be ignored, even though the detection will include information from the entire range. If used to detect uv-vis absorption, the original excitation is from a xenon lamp with an output from 200 nm to 800 nm. If used to detect atomic emission spectra, excitation is from an energy pulse (spark) within the liquid. For nutrient analysis, an array detector that segments the detection range into 1024 equal intervals and scans across this entire range is used.

CHEMOMETRICS may be the most meaningful advance in technology that makes on-line analysis possible. The more specific the sensor is to a particular chemical, the less sophisticated the model required to extract meaningful information. Sensors that detect information for multiple constituents in a complex chemical matrix must rely upon very capable analysis algorithms in order to extract information for a specific chemical constituent. Although one trend in analytical chemistry is toward sensors that are ion or chemical specific, a less publicized trend is toward general purpose analyzers that have very sophisticated data analysis capabilities available within the instrument. These chemometric techniques are used to compare unknowns with calibrated standards and data bases, to perform advanced forms of cluster analysis, and to extract features from unknowns that are used as information in statistical and mathematical models.

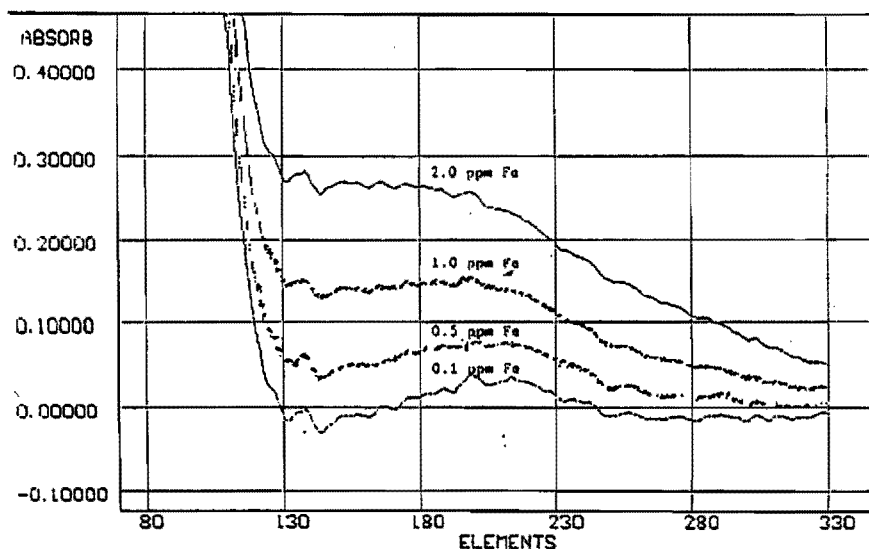


Figure 1. Iron in pure water.

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