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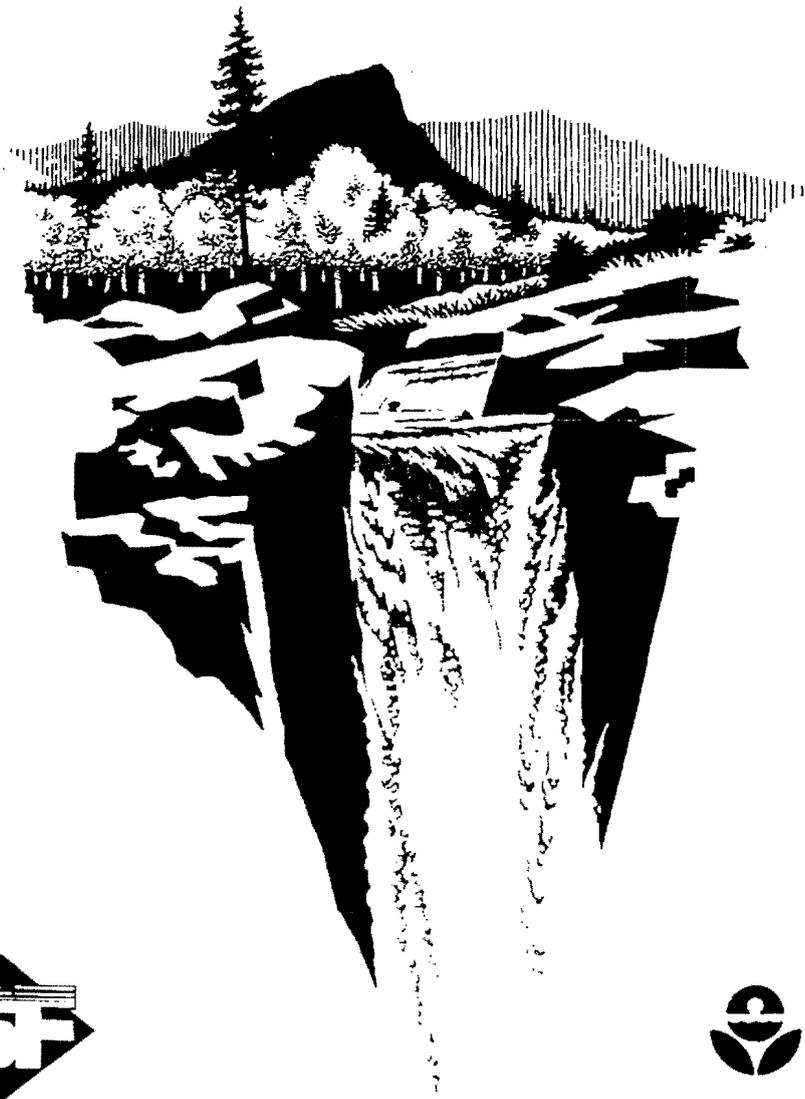
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# TWO EMERGING TECHNIQUES FOR ON-LINE AND IN-SITU MONITORING OF METALS IN ELECTROPLATING WASTES

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## Abstract

Two techniques with potential for continuous real time analysis of heavy metals in electroplating wastewater and other aqueous solutions have recently been demonstrated.

Absorption Spectrometry in the ultraviolet-visible wavelength range (UVAS) has been shown to be capable of detecting absorption signatures for complex solutions without the use of reagents. The use of fiber optic probes permits contact between a source of light and the solution. The use of chemometric algorithms enables individual chemical components in the solution to be identified and quantified.

The second technique, Liquid Atomic Emission Spectrometry (LAES), uses a high energy arc discharge as a source of excitation directly in the liquid to be analyzed. The arc generates atomic emission spectra that can be detected using apparatus similar to that used for UVAS.

## Existing Absorption Spectrometry Methods

Metals in electroplating waste streams are commonly analyzed using absorption spectrometry. All previous techniques require extraction of samples which are processed chemically or physically prior to the detection and measurement of the chemical in question (the "analyte").

Traditional absorption spectrometry requires the use of reagents to selectively combine with a target analyte producing a chemical compound with known absorption characteristics. These characteristics include a predictable absorption peak with an intensity that is proportionate to the concentration of the target analyte. Many colorimetric tests use this basic technique for detection of an analyte in a liquid solution. In order to eliminate possible interference from other chemicals that may also be present in the solution, additional reagents or sample processing procedures must be used. In a mixed waste stream it may not be possible to fully eliminate interference from other metals and chemical constituents.

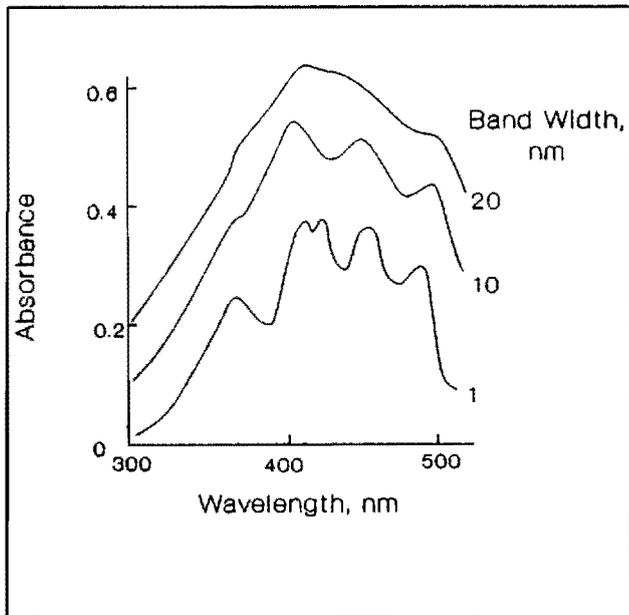
Other spectrometric techniques such as flame or furnace atomic absorption spectrometry are also used for the analysis of metals in wastewater, particularly if the measurement must be reported to an enforcement agency and must therefore be made using a recognized method. In a typical flame technique for analysis of a metal, the sample is aspirated and directly atomized in an acetylene flame. At the same time, a light beam from a hollow lamp with a cathode made of the same element being measured is directed through the flame onto a monochromator that is tuned to a specific wavelength. The light energy absorbed by the flame is a measure of the

concentration of the element in the sample. When the furnace technique is used, an aliquot of the sample is placed in a graphite tube, evaporated to dryness, charred and then atomized.<sup>[1]</sup>

Although flame or furnace atomic absorption spectrometry are the required methods for periodic enforcement testing, other techniques that are able to provide real time information may be more useful for the day to day needs of electroplating and treatment facility operators for control or monitoring purposes. Simplified but reliable automated analysis techniques may be of use at any point in the waste stream from the plating bath itself to the discharge point for treated effluent. These techniques should be able to be operated on-line (without transport of a bottled sample to a laboratory) or in-situ (with a probe located directly within the process tank or flow stream).

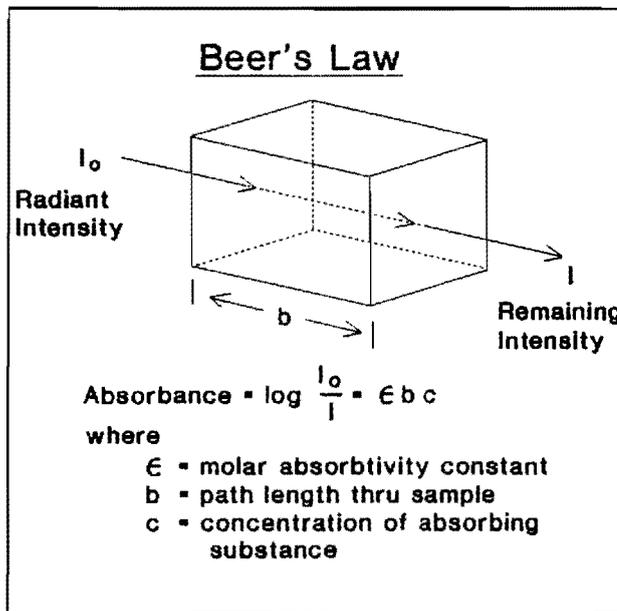
### On-line Absorption Spectrometry

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.



**Figure 2. Resolution of Spectral Signatures**

(including nitrates and transition metals) are known to absorb light in the ultraviolet-visible wavelength range.



**Figure 1. Beer's Law**

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, as illustrated in Figure 1. These relationships can be restated to solve for concentration of an absorbing component if the absorption at a known path length through the liquid can be measured.

One approach to the problem of continuous analysis of metals in electroplating wastewater is to monitor the natural absorption spectra of the solution. The spectral signature for a mixture will be a function of the individual absorbing components in the solution and the interaction of their spectral overlaps and interferences across a certain selected wavelength range. Many of the chemical components in a mixed waste solution

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 "signature" for the liquid over the wavelength range, with smaller intervals between wavelengths resulting in better resolution of the absorption signature, as illustrated in Figure 2.

Many chemical substances that possess certain electron characteristics are able to absorb energy in the ultraviolet or visible wavelength range (200 to 800 nm). Each substance yields a characteristic signature that is unique for each compound. Many inorganic ions, particularly the heavy metals, are able to join with ligands to form coordination compounds that are possess characteristic ultraviolet-visible absorption signatures. In electroplating solutions, water acts as the ligand to form a coordination compound with a metal ion similar to that illustrated in Figure 3.

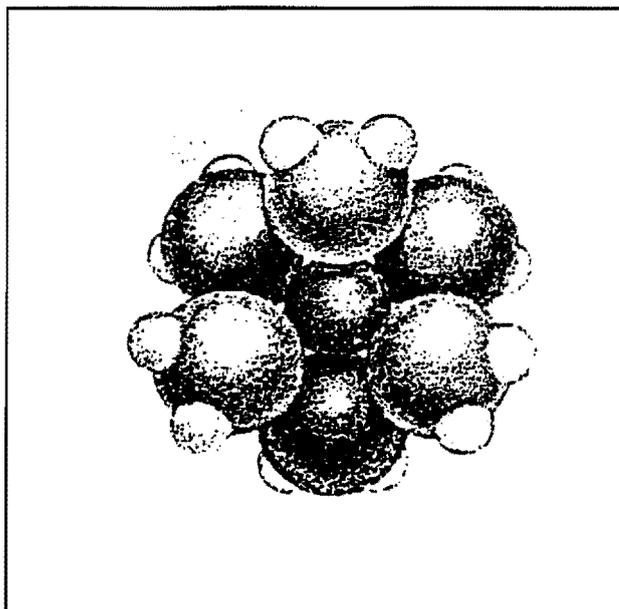


Figure 3. Coordination Compounds

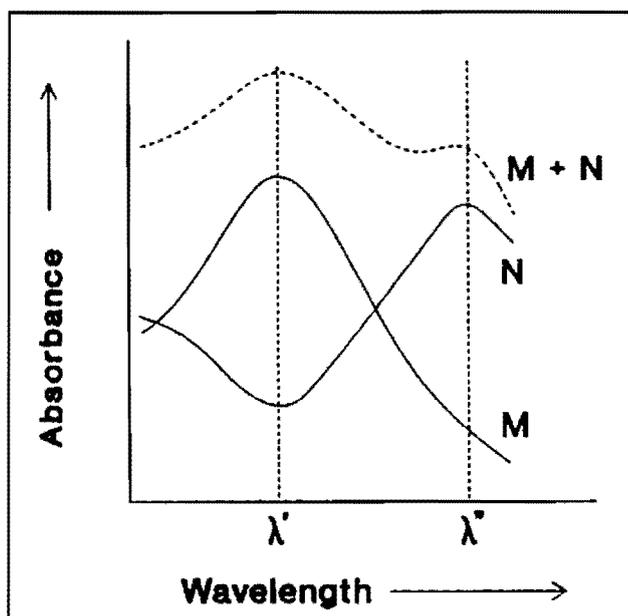


Figure 4. Multiple Component Spectra

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In the case of a solution with only one absorbing component, the absorption signature can be used to perform concentration 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, as illustrated in Figure 4. 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", are the major breakthrough that has enabled absorption spectrometry to be used for real time multi-component chemical analysis.

Since a given absorbing component may contribute significantly to the absorption measured at one specific wavelength but little or nothing to the absorption at another wavelength, multiple component chemical analysis using absorption spectrometry will 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 simultaneously capturing information for a range of wavelengths so that interpretation using chemometric models can be performed.

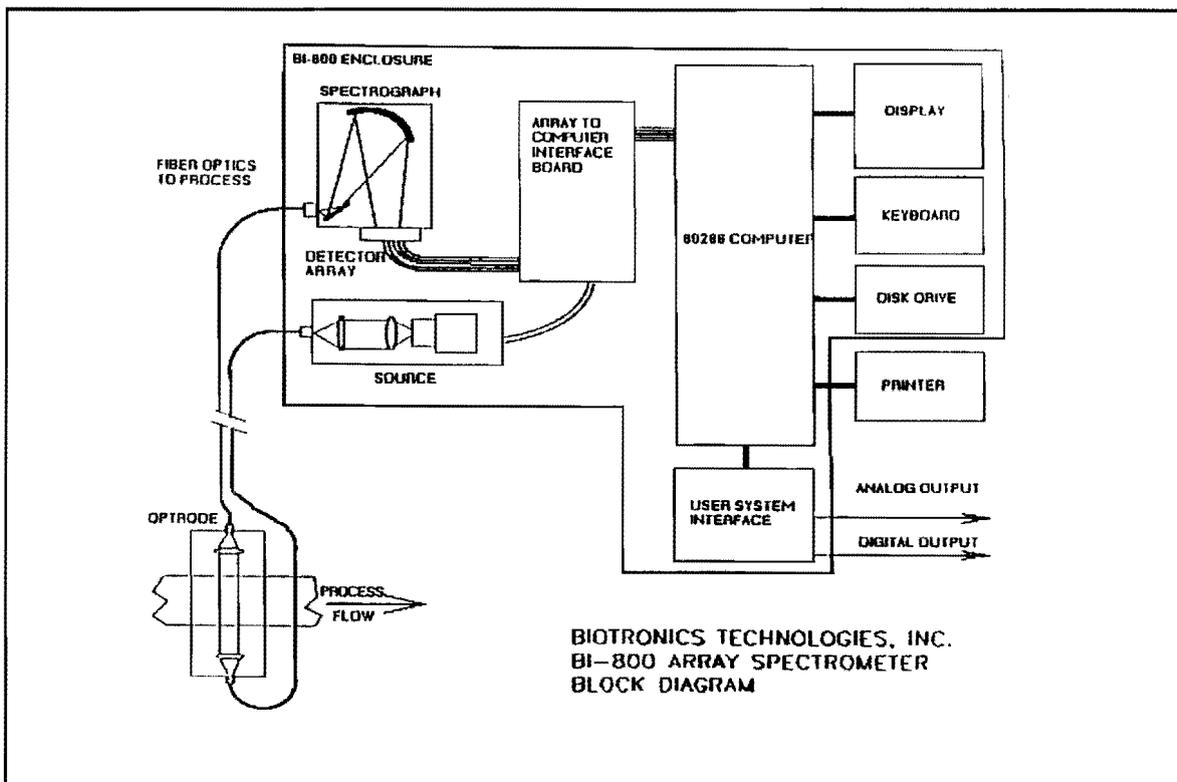
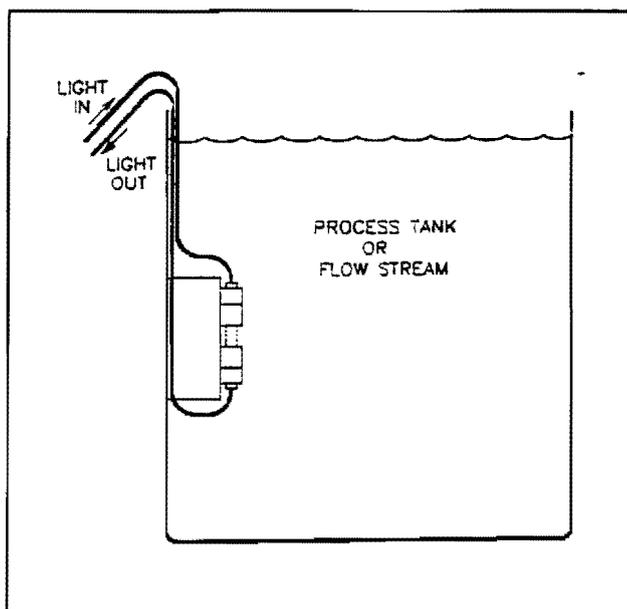


Figure 5. On-Line Spectrometer

### Instrumentation for Real Time Absorption Spectrometry.

One instrument that is capable of performing real time absorption spectrometry is illustrated in Figure 5. The instrument features an optical probe connected to a central analyzer using fiber optic cables. The central analyzer contains a xenon flash lamp light source for excitation at wavelengths from 220 to 800 nm. This light is conveyed to the optical probe through one branch of the fiber optic cable.

The analyzer also contains a fixed diffraction grating and a linear photodiode detector array for separation and measurement of light returned from the optical probe. The light is returned through a companion fiber optic cable after transmission through the liquid under investigation. Detection of the absorption signature using a multiple element array, such as the 1024 element detector used in the Figure 5 instrument, permits the entire ultraviolet-visible absorption spectrum for the solution to be simultaneously detected to increments of less than a nanometer. This provides excellent resolution of spectral features. A microcomputer, contained within the instrument,



**Figure 6. In-Situ Optical Probe**

analytes do not possess natural absorption spectra in the ultraviolet-visible wavelength range, or possess only weak spectra. If UVAS techniques are to be used for analysis, secondary methods must be employed. These methods require the use of a reagent that has been immobilized so that a reversible reaction occurs with the analyte, producing a compound with detectable absorption spectra. It is very difficult to identify reagents that are selective, reversible and able to be immobilized onto a substrate.

A technology was discovered in the later stages of a NASA research project that offered the potential of direct simultaneous analysis of many chemical elements. This technology was named "Liquid Atomic Emission Spectrometry (LAES)".<sup>[5]</sup>

**Basic Principles of Liquid Atomic Emission Spectrometry**<sup>[6,7]</sup>

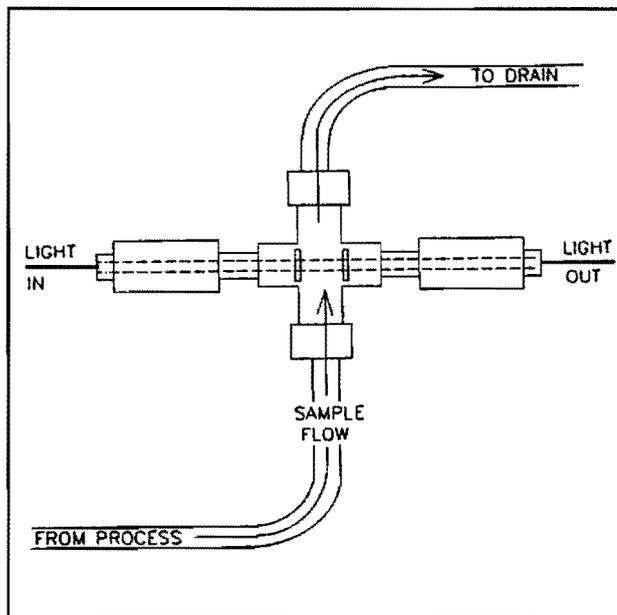
Several technologies are presently used for analysis of elements in their atomic form were discussed earlier in this manuscript. Because the elements to be analyzed are usually presented for analysis bound in molecules, energy must be applied to rupture the molecular bonds and reduce the substance to atomic form prior to analysis. The various forms of energy used to break molecular bonds differentiate several different forms of atomic spectrometry presently in use. These include flame atomic emission, electrothermal

permits rapid interpretation of this absorption information using a processing algorithm that includes the specific chemometric routines that are most appropriate for a particular analytical problem.

The optical probes are specially designed to operate within a process tank or flow stream, as illustrated in Figure 6. An alternative design permits a fractional side stream to flow through the optical probe with light transmitted through the flow as illustrated in Figure 7.

**Liquid Atomic Emission Spectrometry**

Absorption spectrometry was demonstrated to be capable of providing the means for on-line analysis of many chemical substances in several studies.<sup>[2,3,4]</sup> Absorption spectrometry, however, does have some limitations. Some



**Figure 7. On-Line Optical Probe**

(furnace) atomic emission, and emissions from other energy sources such as electric arc, electric spark, or radio frequency inductive coupling.

Once a substance has been reduced to atomic form, several techniques can be used to extract qualitative and quantitative information. Specific wavelengths of light can be transmitted through an energized cell and the amount of light absorbed by the atomic element under investigation can be measured (atomic absorption spectrometry). Another alternative is to measure the wavelength and intensity of light emitted from a cell that contains atomic matter following excitation of the cell with a burst of energy.

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 with 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 detection 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 emissions directly in the liquid medium. The light emission not only occurs directly in the liquid, but is also detected directly from the liquid using special apparatus.

#### Instrumentation for Liquid Atomic Emission Spectrometry. [6,7]

The instrumentation used for Liquid Atomic Emission Spectrometry is similar to the instrumentation used for Ultraviolet-Visible Absorption Spectrometry. In fact, one of the principal advantages of LAES is that the same 1024 element photodiode array detector can be used for both LAES and UVAS analysis, as illustrated in Figure 8.

The LAES instrument used in the original experimental analysis for NASA used a beaker to hold a sample of the liquid. (A flow through cell was subsequently developed for on-line analysis applications.) A spark was created in the beaker using electrodes immersed in the nutrient solution and separated by an electrode gap. A fiber optic cable was fitted between the analyzer and the beaker with the termination of the cable located in close proximity to the spark gap. This arrangement provided the energy necessary to accomplish atomic separation of the elements in the solution, as well as the energy pulse necessary to stimulate atomic light emissions from these elements.

The spectrometer used for LAES analysis is identical to that used for the ultraviolet-visible absorption spectrometry. A fiber optic cable conveys the emission spectra to the spectrograph where the diffraction grating separates the emission spectra into discrete wavelengths from 200 to 800 nm and projects these wavelengths onto the 1024 element linear photodiode detector array. Each element in the array is matched with dedicated capacitance 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 contained on the 80286 computer built into the instrument.

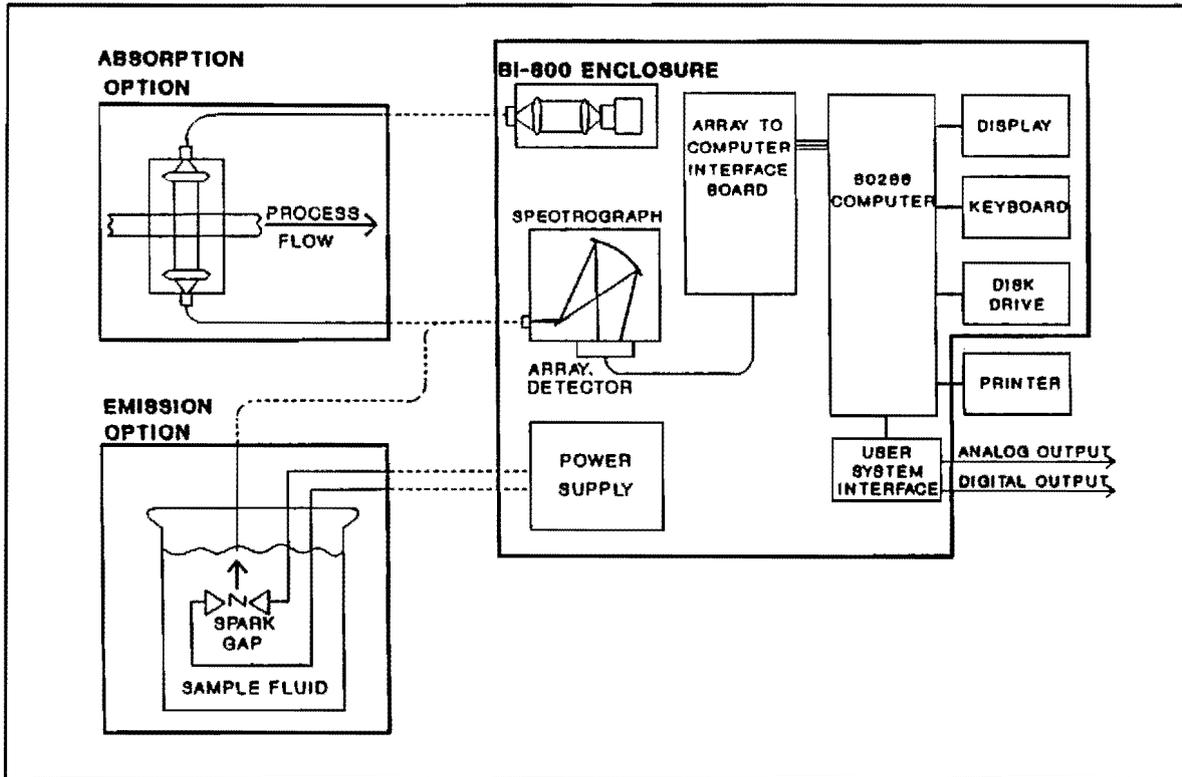


Figure 8. Combined UVAS and LAES Spectrometer

### UVAS Experiments and Test Results

The results of several experiments that verify the ability of ultraviolet-visible absorption spectrometry (UVAS) to be used for analysis of metals in multiple component chemical solutions using naturally occurring absorption spectra have been reported in previously published manuscripts. This includes the use of UVAS for the analysis of iron,<sup>[3,5,6,8,9]</sup> copper,<sup>[3,5,8,9]</sup> chromium,<sup>[3,9]</sup> mercury,<sup>[3,9]</sup> and zinc.<sup>[3,5,9]</sup> Tests to verify the ability of UVAS to detect chromium and zinc at trace levels in a mixed industrial effluent, including wastes from electroplating operations, have been conducted.<sup>[9]</sup>

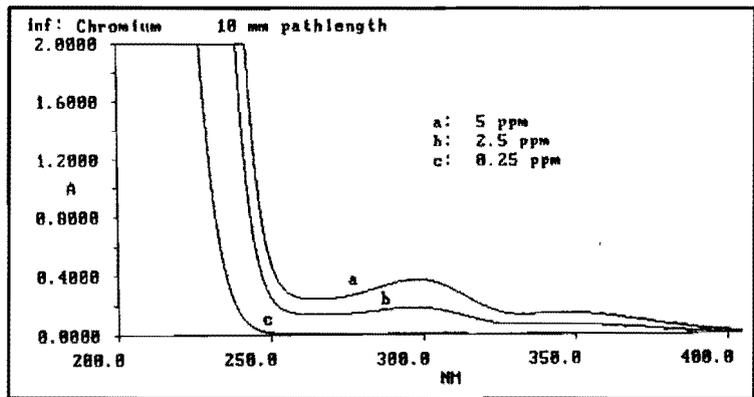


Figure 9. Chromium Absorption Spectra

The sensitivity of analysis using UVAS has also been demonstrated. Iron, for example, has been detected in multiple component solutions at concentrations as low as 0.1 ppm. The range of detection for iron has been demonstrated from 0.1 to 100 ppm, although researchers believe that

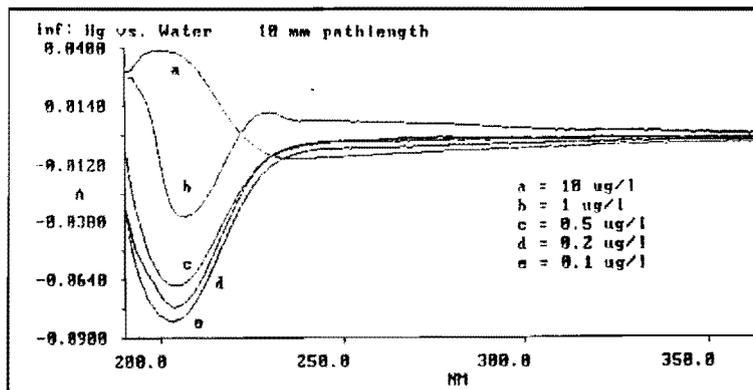


Figure 10. Mercury Absorption Spectra

both higher and lower concentrations are possible. Chromium (VI) has been detected at concentrations of well under 1.0 ppm as illustrated in Figure 9, while mercury has been detected at the microgram per liter concentration level as illustrated in Figure 10.

### Initial LAES Experiments

A series of experiments were conducted for NASA to explore the capability of the LAES concept for use as an on-line monitoring technology. Solutions were made using distilled water and a single compound that contained an analyte of interest. Several individual test solutions 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. Since customized pattern recognition software was not available for this new technology, a standard conventional atomic emission spectra guide was used to help identify the emission peaks observed during the experiments.

Following experimentation with the individual analyte solutions, a multiple component nutrient solutions with known component concentrations were tested and the results were recorded.

All of the solutions tested exhibited prominent emission peaks at or near the wavelengths predicted for the element under investigation when liquid atomic emission results were compared with the known emission lines from conventional arc emission techniques. Encouraging results were obtained for solutions containing sodium, magnesium, calcium, potassium, copper, and zinc.

Several experiments were performed with a multiple component 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. An example of a portion of this information can

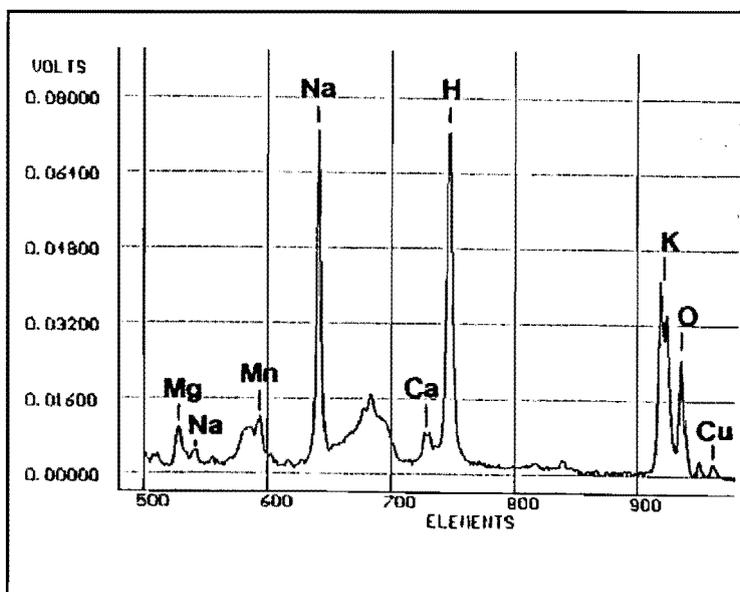


Figure 11. Liquid Atomic Emission Spectra

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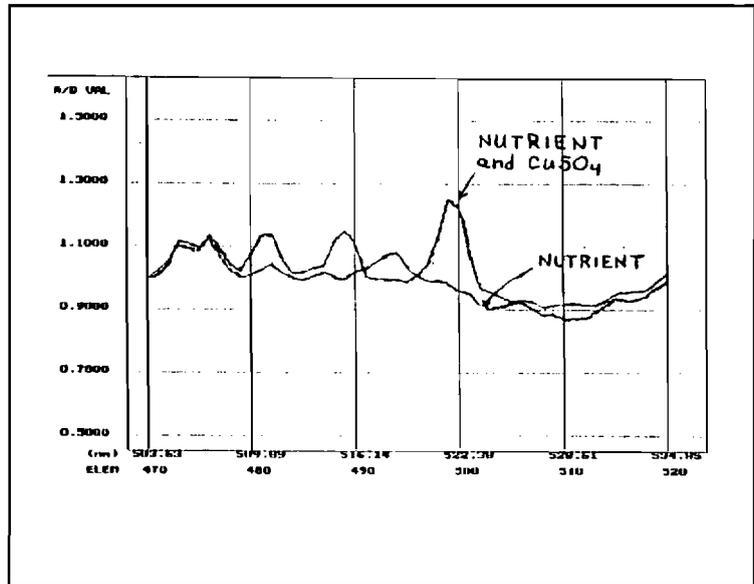
Figure 11. Liquid Atomic Emission Spectra

be seen in Figure 11. No attempt was made to quantify the concentrations these elements due to the lack of sufficient information to establish adequate calibration models at this early stage in the development of the technique.<sup>[5]</sup>

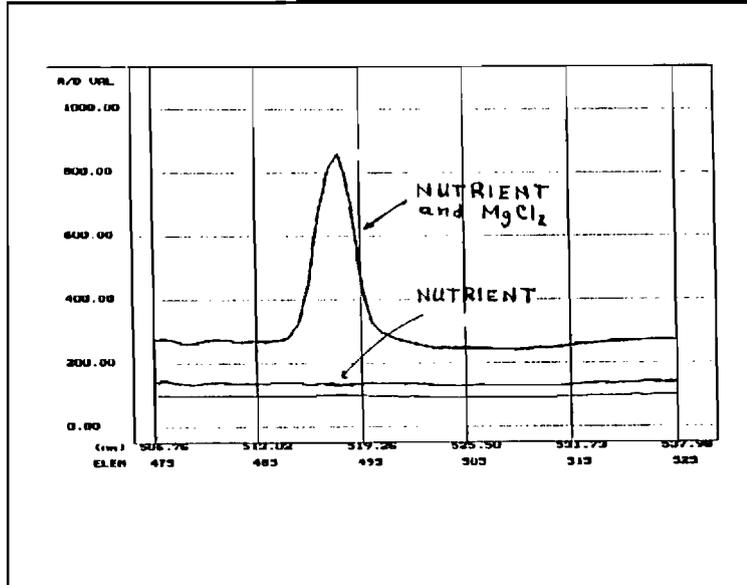
**Additional LAES Experiments**

Some of the initial LAES experiments have also been reported.<sup>[5,6,7]</sup> A new round of experiments and development tests have been conducted starting in the fall of 1991 under an additional NASA contract.<sup>[10]</sup> Some results from these experiments are available and tend to support the conclusion that LAES can be used to detect metals in multiple component solutions such as electroplating rinse tanks and waste streams.

In the typical experiment, a nutrient solution containing 15 chemical components essential for plant growth (including metals such as iron, copper, zinc and molybdenum) is spiked with a known concentration of metal compound. The solution is energized using a specially designed arc source. The emission spectra for the solution containing the metal spike is compared to the emission spectra of the solution without the spike. Differences in the spectra are noted and compared to a standard list of arc emissions for the elements under investigation.



**Figure 12. Nutrient and Copper Spectra**



**Figure 13. Nutrient and Magnesium Spectra**

The solution is energized using a specially designed arc source. The emission spectra for the solution containing the metal spike is compared to the emission spectra of the solution without the spike. Differences in the spectra are noted and compared to a standard list of arc emissions for the elements under investigation.

An example of one experiment can be seen in Figure 12. The nutrient solution was spiked with a 100 ppm concentration of copper sulfate. Emission scans show significant peaks at three different wavelengths. These peaks are at or near the wavelengths where copper is known to possess strong arc emission spectra (510.55 nm, 515.32 nm, and 521.82 nm).

Another very striking example is shown in Figure 13, which illustrates the emission spectra from

506 to 538 nm before and after a 100 ppm spike of magnesium chloride in the nutrient solution. A very large peak is seen just under the 519 nm wavelength interval. Magnesium has expected arc emission spectra at 516.73 nm, 517.27 nm, and 518.36 nm. Since these spectra are very closely grouped and since the analysis is being performed in a liquid media, the researchers believe that the spectra have combined to contribute to the peak that was observed for this experiment. Similar observations for combined close group spectra were also observed for magnesium at 381.00 to 383.83 nm and at 277.98 to 280.27 nm.

## Conclusions

It is believed that both ultraviolet-visible absorption spectrometry (UVAS) and liquid atomic emission spectrometry (LAES) have the potential to be used for real time analysis of electroplating wastewaters and other electroplating waste streams. Additional testing must be performed on actual electroplating waste solutions to support this conclusion, but initial results in complex multiple chemical solutions are very encouraging.

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