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IN-SITU FIBER-OPTIC ABSORPTION AND EMISSION SPECTROMETRY
FOR SIMULTANEOUS MULTIPLE COMPONENT ANALYSIS IN GROUNDWATER

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ABSTRACT

Results from initial laboratory experiments for an absorption spectrometer that can be used to simultaneously monitor numerous chemical constituents in groundwater are reviewed. This system uses an uncoated fiber-optic probe to detect the combined absorption spectra from chemicals in the groundwater. The system then processes the spectral data using sophisticated pattern recognition algorithms in order to extract qualitative and quantitative information about the specific chemicals of interest.

A progress report with results from additional laboratory testing is presented, demonstrating the capability of the ultraviolet-visible absorption spectrometry (UVAS) system to detect specific chemicals such as nitrates, metals and certain organic compounds. Additional information documenting the ability of the system to detect deviations in the spectral signature of groundwater caused by the intrusion of contaminants is also shown.

A variation of the absorption spectrometry system is being developed for NASA and will also be discussed. This variation uses an arc discharge to energize liquid materials in contact with the probe, so that the resulting emission spectra can be conveyed through a fiber-optic cable to an instrument located at the surface. This allows the atomic emission spectra for chemical elements that are present in groundwater to be detected and recognized in-situ.

I. Introduction

Fiber-optic chemical sensors are frequently mentioned as a technology with enormous potential for the detection and measurement of various

contaminants in groundwater [Eccles 1988, Poziomek 1990]. Much attention has been given to the types of fiber-optic sensors that use immobilized reagents on the fiber surface or at the tip of the fiber [Angel 1990, Vo-Dinh 1990]. Once the fiber is inserted into a monitoring well, specific wavelengths of light at a known intensity can be conveyed through the optical cable to the tip of the probe. This permits a measurement to be made of the amount of light absorbed by the complex formed from reactions between the reagent and the target chemical of interest. The resulting sensor is highly specific to this one particular contaminant or chemical but is of little use in the detection of other chemical constituents present in the same matrix. While this type of sensor can be very useful in screening applications, the limited life of the reagent and the need to detect multiple contaminants make this type of sensor less attractive for long term monitoring applications.

A more versatile approach also uses fiber-optic probes, but without the use of reagents to assist in the identification or quantification of specific chemicals. This approach relies upon the natural light absorbing characteristics of contaminants or other chemicals present in the water to be analyzed. In this approach, a broad wavelength range of light is transmitted through a sample. Measurements are made of the amount of light absorbed by the sample at each specific wavelength in the range. This results in the detection of an absorption "signature" for the liquid. The shape and position of this signature is a function of all of the chemical constituents in the water that possess the necessary physical characteristics (free electrons and bond structures) to contribute to light absorption within the wavelength range of interest. If the absorption signature is a result of contributions from more than one chemical, sophisticated mathematical algorithms are used to extract information about the presence and concentration of the specific chemicals of interest [Schlager 1991-a].

The use of ultraviolet-visible absorption spectrometry (UVAS) for direct chemical analysis requires some initial information about the absorption signatures of the individual target chemicals and the background absorption characteristics from other chemicals in the solution to be analyzed. This is not an overwhelming burden for long term monitoring applications where the initial costs to prepare and process a group of samples used as an algorithm training set (also called a learning set or calibration set) are modest when compared to the recurring costs of sample extraction, transport and laboratory analysis. Although the costs of sampling and laboratory analysis will differ from application to application, it is clear that in monitoring applications where the issue is the reappearance of a known contaminant or the detection of known indicators, any technology that can automatically detect the specific target chemicals in question will enjoy an economic advantage.

II. Initial UVAS Tests

Chemicals that possess absorption spectra in the ultraviolet - visible wavelength range theoretically include heavy metals, nitrates, unsaturated hydrocarbons, and aromatics.

Initial tests were performed under NASA sponsorship to demonstrate the feasibility of using chemometric algorithms for direct analysis of complex liquids from the natural absorption spectra of the chemical components [Schlager 1990]. Solutions that contained variable concentrations of fifteen different chemical components were processed to demonstrate the technique. In these solutions, iron was detected over a range of 0 to 10 ppm with an error rate of less than 0.1 ppm and nitrate was detected over a range of 10 to 500 ppm, both with an error rate of less than 1 ppm. The algorithm used for this feasibility test was based on stepwise regression of raw spectral values. This is one of the least sophisticated forms of chemometric analysis, but still powerful enough to produce dependable results. More powerful techniques including principal components analysis or neural networks have produced superior results in other applications when compared to results obtained using these less sophisticated algorithms [Schlager 1991-b]. The feasibility test for NASA confirmed that absorption spectrometry was capable of being used for analysis of certain chemical components in complex liquids.

Additional experiments using UVAS without reagents have demonstrated the feasibility of using the technique for direct analysis of metals such as copper, iron, mercury, zinc, and chromium [Schlager 1990, Schlager 1991-a] in water or wastewater solutions. An example of selected spectra from these experiments is shown in Figure 1.

Recently, prototype instruments capable of on-line and in-situ absorption spectrometry analysis using fiber-optic probes have been built and tested under laboratory conditions. These instruments contain a source of light, the fiber-optic probe, a spectrograph with an array detector and an internal microcomputer for the processing of chemometric algorithms. The basic arrangement of these components is shown in Figure 2.

III. Additional UVAS Experiments

Starting in early 1991, experiments have been conducted to demonstrate the ability of UVAS techniques to monitor the normal absorption signature of the water in a monitoring well and to detect deviations from this signature that may be attributable to the appearance of contaminants.

A previously reported series of experiments compared the spectral signature of uncontaminated groundwater with the signature from the same groundwater that had been intentionally spiked with contaminants such as toluene, 1,2-dichloroethane and iron to simulate the leakage of a landfill liner. Comparison of the contaminated and uncontaminated signatures show a substantial difference resulting from the presence of the contaminants [Beemster 1991]. Spectra from these experiments are shown in Figure 3 and the difference in spectra is shown in Figure 4.

Although the above experiment suggests that UVAS signature deviation has some potential for groundwater monitoring, it was not clear that the technique could distinguish between deviations caused by the intrusion of contaminants versus changes in the natural background chemistry of the groundwater. A related question concerns the sensitivity of the

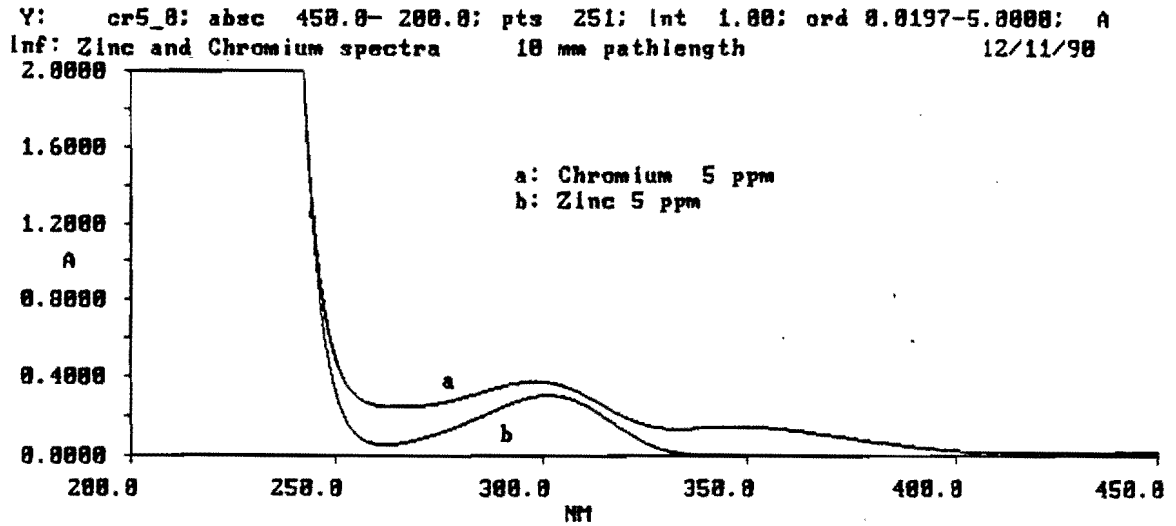


Figure 1. Spectra of zinc and chromium in water

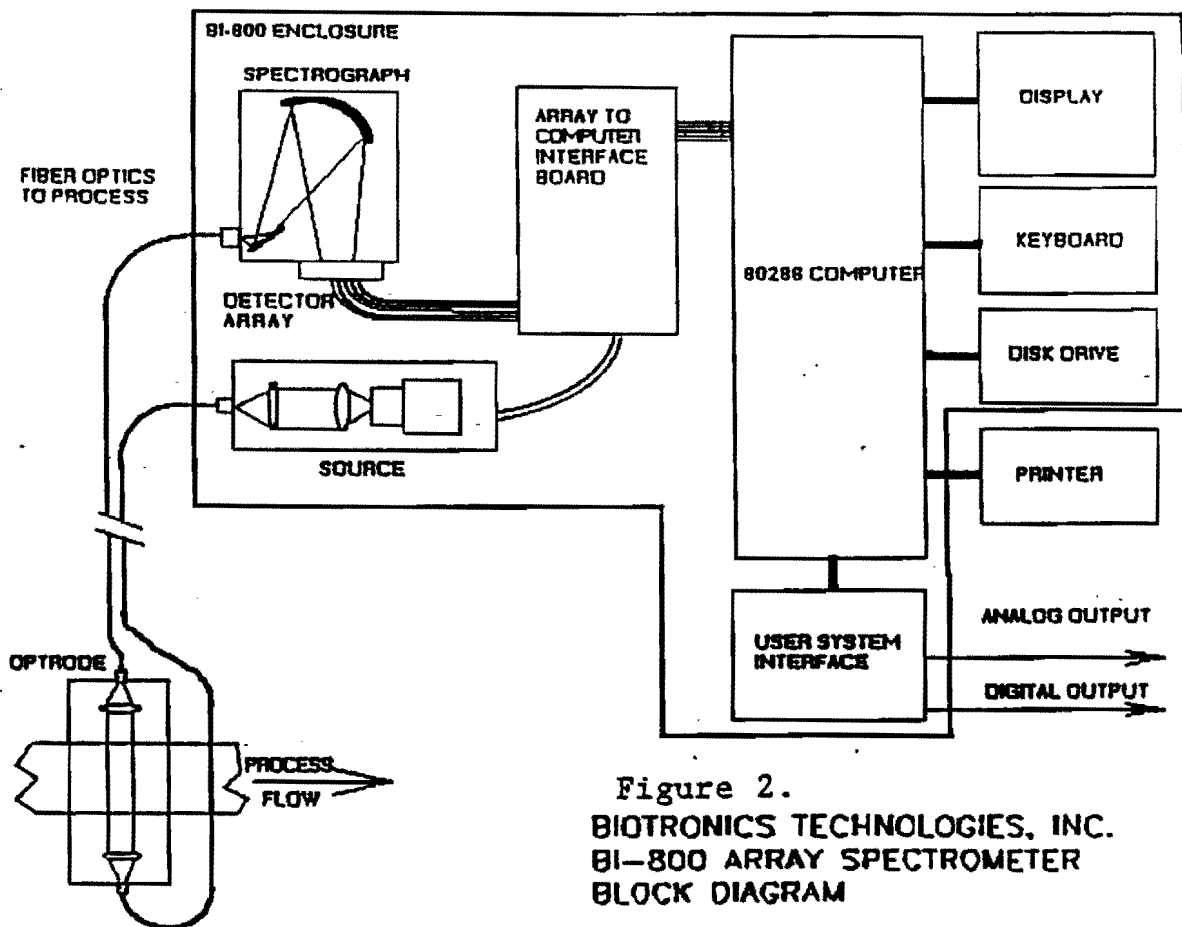


Figure 2.
 BIOTRONICS TECHNOLOGIES, INC.
 BI-800 ARRAY SPECTROMETER
 BLOCK DIAGRAM

Y: WSPK2: absc 450.0- 200.0; pts 251; int 1.00; ord 0.0050-0.4184; A
inf: WELL SPIKE 10 MM PATH 2/4/91

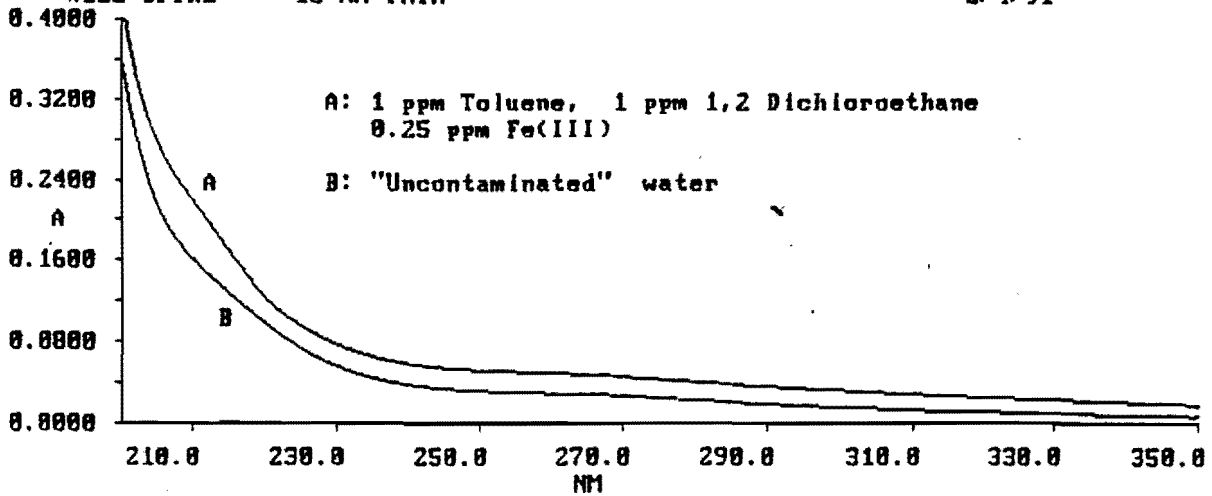


Figure 3.

Z: : absc 450.0- 200.0; pts 251; int 1.00; ord 0.0035-0.0622; A
inf: DIFFERENCE BETWEEN CONTAMINATED AND UNCONTAMINATED SPECTRA 2/4/91

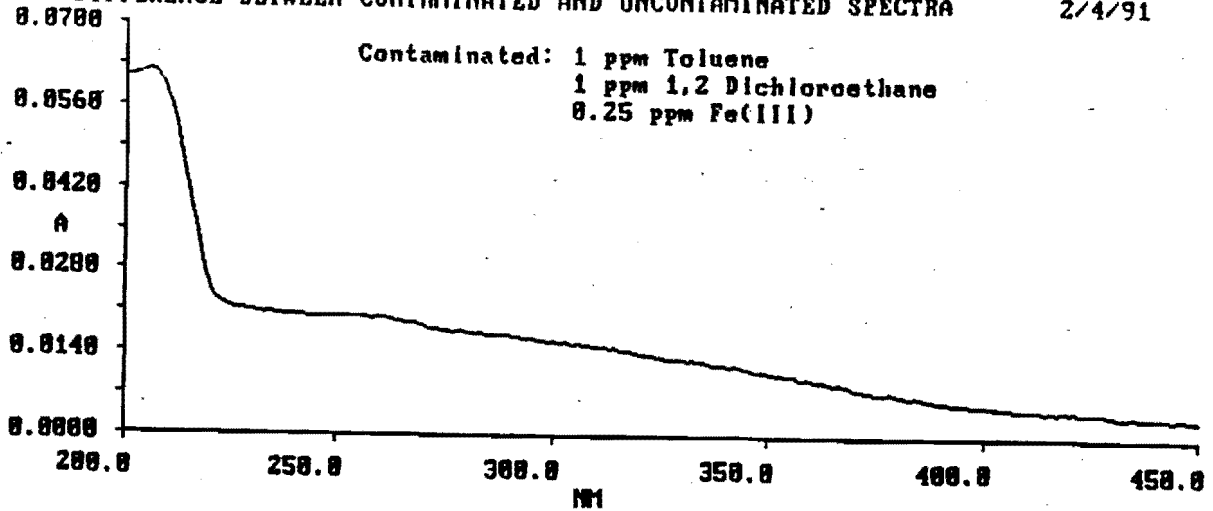


Figure 4.

technique to trace concentrations of specific contaminants. A series of experiments were organized to begin to address these issues.

Groundwater that is considered to be uncontaminated is not necessarily free of chemical constituents. Even uncontaminated groundwater contains measurable amounts of dissolved minerals, nutrients and other chemical constituents, such as those listed in Table 1.

One initial question relating to the absorption signature of groundwater was the amount of deviation that could be expected from seasonal changes in the background chemistry of the water. Samples were periodically extracted from a drinking water well in southeast Wisconsin over a one year period. Samples were scanned for absorption spectra in increments of 1 nm over the range of 200 to 800 nm using a Perkin Elmer Lambda 9 laboratory spectrometer set for a 10 mm path length. Deviation data for the spectra at two individual wavelengths are presented in Figures 5 and 6.

Figure 5 shows seasonal variation at 220 nm, with a low point of 0.040 absorbance units in the 8/91 sample and a high point of 0.150 absorbance units in the 2/92 sample, a difference of 0.110 absorbance units at this wavelength.

Figure 6 shows seasonal variation at 300 nm, with a low point of around 0.011 absorbance units in the 12/91 sample and a high point of 0.065 absorbance units in the 9/91 sample. The difference is 0.054 absorbance units at this wavelength.

Table 1. Chemicals Found in "Uncontaminated" Groundwater

Calcium
Magnesium
Iron
Manganese
Sodium
Potassium
Bicarbonate
Sulfate
Chloride
Nitrate
Silica

The preceding experiments attempted to establish some predictable range of deviation for groundwater absorption spectra from a specific well location. After recording the background absorption signature the 2/92 sample was intentionally contaminated with 10 ppm of trichloroethylene

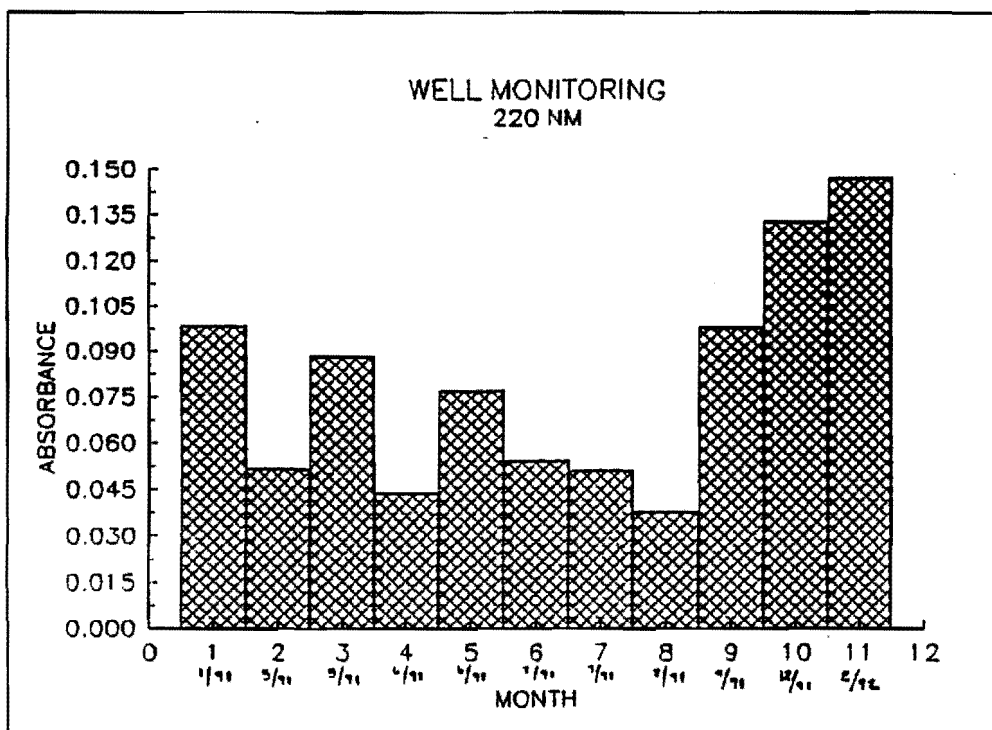


Figure 5. Seasonal variation at 220 nm

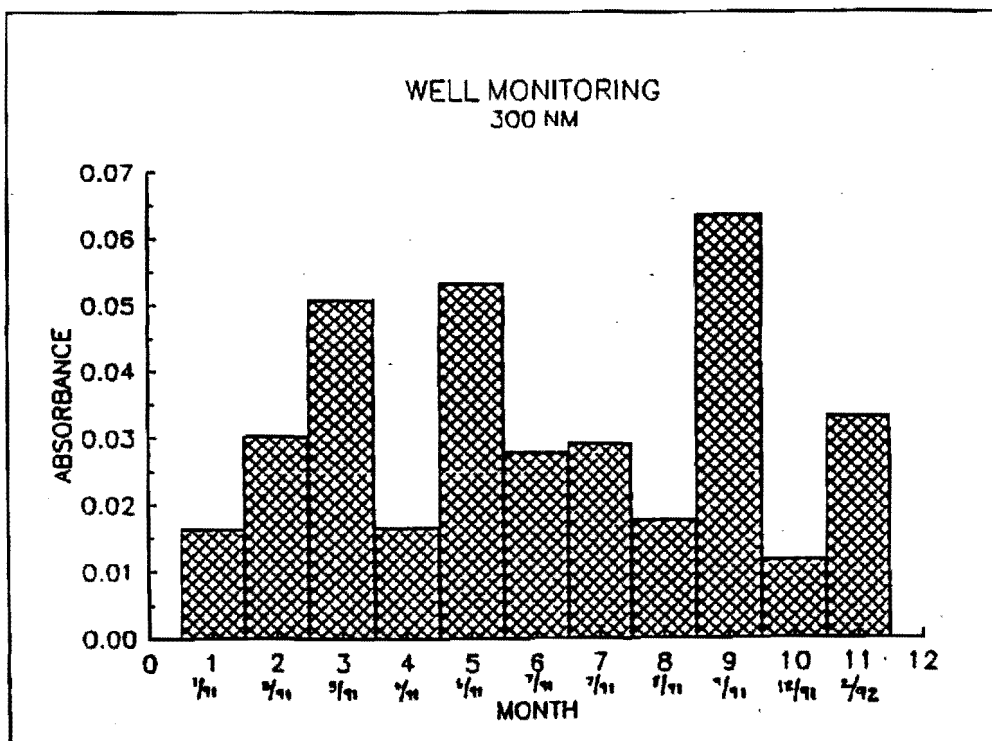


Figure 6. Seasonal variation at 300 nm

and scanned for any changes in absorption spectra. Figure 7 shows a comparison of the absorbance at 220 nm for the contaminated sample to the previous high points for uncontaminated samples during winter and summer periods. While the deviation in absorbance spectra for uncontaminated samples was previously denominated in tenths of an absorbance unit, the new absorbance for the contaminated sample is now a full 2.75 units more than the previous high point, an enormous deviation in absorbance at this wavelength.

The above experiment documented that a significant deviation could be detected for a substantial (10 ppm) concentration of trichloroethylene. This raises an issue of sensitivity for this particular analyte. An experiment was conducted to provide an indication of the relative sensitivity of natural absorbance for this contaminant. The path length through the samples was increased to 100 mm in an effort to improve the sensitivity of detection. The same groundwater source was used as in the prior experiment. Samples were contaminated with 20 ppm, 10 ppm and 2 ppm concentrations of the contaminant. Results of this analysis are shown in Figure 8. Note that the uncontaminated sample now has an absorbance of almost 1.5 absorbance units at the 100 mm path length compared to a maximum of 0.15 absorbance units at the 10 mm path length used in the previous experiments.

The analysis suggests that contaminant sensitivity in the low ppm range could be achieved at 220 nm with a 100 mm path length, but that detection of this particular contaminant in water at lower concentration levels may be difficult to achieve. The spectrum for 0.2 ppm contamination (not shown) was virtually indistinguishable from the uncontaminated spectrum at this wavelength and all others. Nevertheless, these are encouraging results for an analyte that is not particularly soluble in water. (It should be noted that no effort was made to use multiple wavelengths and pattern recognition algorithms for this analysis. These techniques can usually provide substantial improvements in accuracy and sensitivity over visual methods.)

IV. Liquid Atomic Emission Spectrometry

A related technique, also being developed for NASA, has potential application for groundwater monitoring. This technique uses an arc discharge directly in the liquid being analyzed to energize the liquid in the vicinity of the electrodes. This energy pulse is sufficient to rupture molecular bonds and convert chemical substances in the liquid into their atomic components. Many of these atomic components will emit spectra at one or more ultraviolet or visible wavelengths as a result of this excitation. These spectra can be collected in a fiber-optic probe, separated by wavelength and projected onto a detector identical to that used for the UVAS analyzer. The result is an emission profile for the solution similar to that shown in Figure 9. Special deconvolution and pattern recognition algorithms are used to analyze this information.

This technique has the advantage of being sensitive to a wide variety of elements including calcium, carbon, chlorine, hydrogen, oxygen,

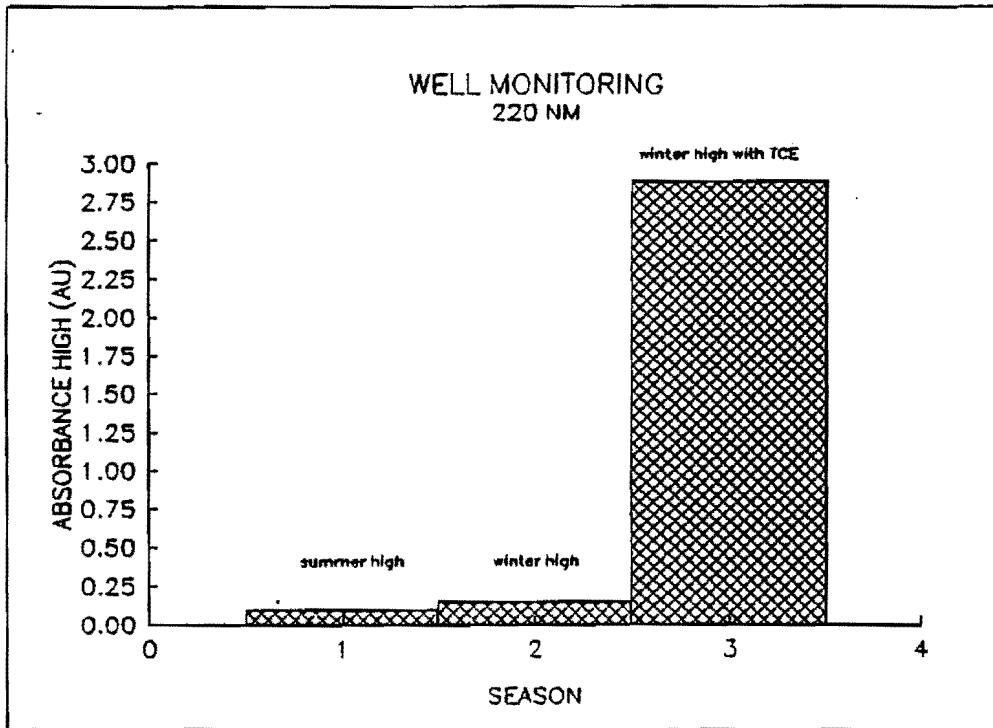


Figure 7. Comparison between contaminated and uncontaminated samples

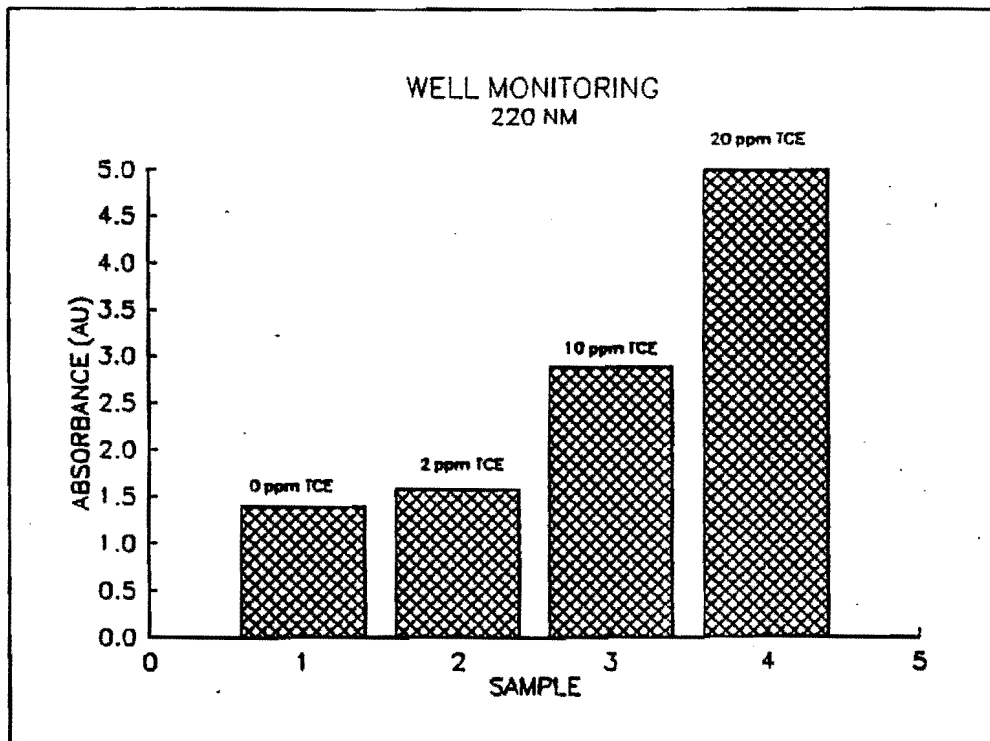


Figure 8. Samples showing different levels of contamination

RUN DESCRIPTION:

FILE NAME: \aen\100sof_3.p

100 ppm 304 in nutrient solution 7 24 90

GAIN FACTOR: 10

NUMBER OF SCANS: 50

INTEGRATION TIME: 0.400 sec

CLOCK RATE: 50 kHz

RUN NUMBER: 1 of 1

TIME BETWEEN RUNS: 1.0 min

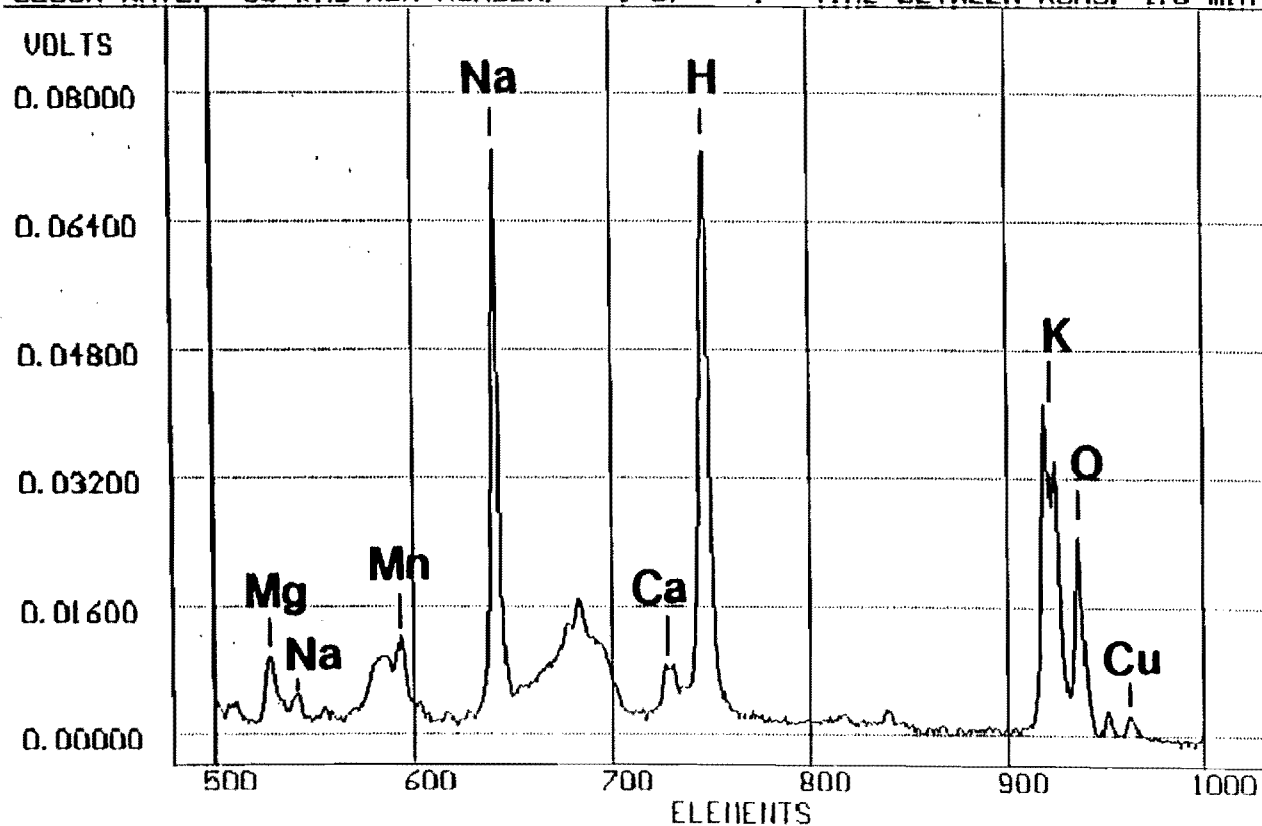


Figure 9. LAES emission profile

phosphorus, potassium, sodium, sulphur and most of the transition elements. Many of these elements cannot be detected directly in water using absorption spectrometry, and could only be detected indirectly if they were contained in a molecule or in an attached group that possessed absorption characteristics.

Liquid atomic emission spectrometry (LAES) is potentially a very powerful technique for simultaneous analysis of the atomic elements contained within a solution. This technique can be operated on-line through a flow cell or in-situ through an optical probe similar to the ways previously suggested for UVAS. Indeed, because the same detector can be used to capture either absorption or emission spectra, it is natural to consider the possibility of a hybrid instrument. This instrument will use absorption spectroscopy for information about certain ionic or molecular components in a solution and use emission techniques for analysis of the atomic elements present. The instrument will have a common detector, computer and operator interface but will use different algorithms for each type of analysis, although the possibility exists for hybrid analysis. For hybrid analysis, information about the molecular content of the solution would help interpret the atomic data while information about the atomic distribution or intensities in the solution may help establish the molecular configuration and concentration of the components. A Hybrid Absorption/Emission Spectrometer (HAES) is currently under development for NASA, the U.S. Navy and others.

IV. Conclusion

The ultraviolet-visible absorption spectrometry (UVAS) and liquid atomic emission spectrometry (LAES) techniques both have significant potential for direct monitoring of multiple chemical components in groundwater.

UVAS has been demonstrated in the laboratory to be capable of being used for detection and analysis of specific chemical constituents that possess absorption spectra in an appropriate wavelength range. UVAS has also been demonstrated in the laboratory for use as a monitoring instrument to detect deviations in the absorption signature of groundwater resulting from the intrusion of certain contaminants. Additional work is needed to demonstrate detection and/or deviation sensitivities for various types of contaminants in a variety of groundwaters inside and outside of the laboratory.

LAES shows potential for simultaneous detection of atomic elements in liquids based upon initial laboratory investigations. Additional work is required to perfect quantitative analysis methods for use with this technique and to build a library of spectra for elements of interest in groundwater monitoring applications.

REFERENCES

Angel, M., "Remote Sensing with Fiber Optics," DOE Real Time Subsurface Monitoring of Groundwater, Houston, April 17-18, 1990.

Beemster, B. and Schlager, K., "In-Situ Ultraviolet-Visible Absorption Spectrometry: A New Tool for Groundwater Monitoring," NWWA/AGWSE, Fifth National Outdoor Action Conference, Las Vegas, May 1991.

Eccles, L. and Eastwood, D., "Rationale for In-Situ Environmental Monitoring with Fiber Optics," SPIE Proceedings, vol. 990: Chemical, Biochemical and Environmental Applications of Fibers, Boston, 1990.

Poziomek, E., "Coating Selection and Evaluation: Weak Links in the Development of In-Situ Reactive Sensors," DOE Real Time Subsurface Monitoring of Groundwater, Houston, April 17-18, 1990.

Schlager, K., "Final Report, Fiber Fluorometry (Spectrometry) for On-Line Chemical Analysis of Nutrient Solutions," NASA, Kennedy Space Center, Contract Number NAS10-11656, July 27, 1990.

Schlager, K. and Beemster, B., "On-Site and On-Line Spectroscopic Monitoring of Toxic Metal Ions Using Ultraviolet Absorption Spectrometry," EPA, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, February 12-14, 1991 (a).

Schlager, K., Schloegel, K., Owens, M. and Beemster, B., "On-Line Monitoring of Nutrients and Microbiological Contaminants in Controlled Plant Growth Environments," Georgia Tech Research Institute, 1991 Food Industry Environmental Conference, Atlanta, November 11-13, 1991 (b).

Vo-Dinh, T. and Griffin, G., "Antibody Based Fiberoptic Sensors for In-Situ Monitoring," DOE Real Time Subsurface Monitoring of Groundwater, Houston, April 17-18, 1990.