Ground Water Management
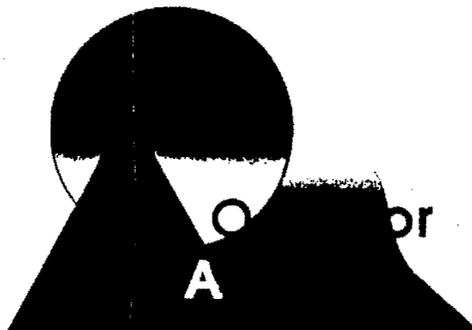
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In-situ Ultraviolet-Visible Absorption Spectroscopy: A New Tool for Groundwater Monitoring

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ABSTRACT: This paper will introduce the reader to the use of absorption spectroscopy in the ultraviolet and visible region for analysis of multiple constituents in groundwater, without the use of reagents, made possible through the use of fiber optics, photodetector arrays and chemometric analysis.

Although present techniques of sampling and laboratory analysis are appropriate for the characterization of a site, there is a need for more economical alternatives if periodic monitoring is to be performed. The trend is toward technologies that can identify and measure a large number of chemical substances in the field, without the need to transport samples elsewhere for analysis at a later time. The ideal would be for the technology to permit analysis of monitoring parameters at or in the monitoring well.

Many chemical substances of interest for groundwater monitoring are known to absorb in the ultraviolet or visible region. For this to be of practical use, a system capable of detecting, recognizing, and quantifying specific target impurities in groundwater based on their absorption spectra is needed. The system must also include software that is able to recognize the absorption signature of a substance against a background of overlaps and interference from other substances.

Recent improvements in technology allow absorption spectroscopy to be used for on-line analysis of groundwater. A specially designed optical probe can be inserted into a monitoring well and linked through fiber optics to an analyzer located on the surface. Improvements in analytical techniques, known as chemometrics, use multivariate analysis and pattern recognition techniques to solve the problem of overlap and interference in multiple component chemical monitoring.

Demonstration of the simultaneous analysis of metal ions and nitrates using ultraviolet-visible absorption spectroscopy (UVAS) has been performed under a NASA contract. Laboratory experiments using this technology to detect several organic compounds and aromatics have been conducted. In addition, an analysis of the theoretical capability of UVAS methods to detect various drinking water quality parameters and groundwater monitoring indicator substances has been made.

I. Absorption Spectroscopy Applications and Apparatus

Absorption spectroscopy is not a new method for chemical analysis but is a familiar and well accepted method for analysis in the laboratory. Many types of instruments for chemical analysis make use of the basic principles of absorption spectroscopy by measuring the attenuation of radiant beams of energy in various portions of the electromagnetic spectrum. Such instrumentation is classified according to the type of electromagnetic radiation employed (x-ray, ultraviolet, visible, infrared, microwave, radio frequency, etc.). Instrumentation is also occasionally classified by the type of energy transition that results from the absorption of energy by atomic or molecular structures (such as magnetic spin resonance, nuclear magnetic resonance, etc.) Figure 1 shows the major divisions of the electromagnetic spectrum and the type of electron transitions resulting from absorption of energy at the various portions of the spectrum.

Figure 1. Absorption transitions

The type of absorption spectroscopy discussed in this paper uses the ultraviolet and visible portions of the electromagnetic spectrum, with wavelengths from 200 to 800 nm. The absorption of energy in this wavelength range results in energy level shifts within the outer electrons of certain atoms and molecules. Since the outer electrons of elements are the ones that are most often involved in the formation of chemical bonds, the bond structures of molecular and ionic substances tend to be good predictors of their ability to absorb energy in the ultraviolet-visible wavelength range. Unbonded electrons and electrons that participate in double bonds or coordinate bonds can often be found in the structure of substances with significant ultraviolet-visible absorption spectra, such as formaldehyde shown in Figure 2. The non-bonded and double bond electrons undergo an increase in energy when exposed to an appropriate frequency of light as illustrated in Figure 3. Also, certain functional groups containing these structures such as those shown on Table 1 can confer color within a substance when attached to the parent molecule (chromophores), or can shift the absorption spectrum of a substance from lower wavelengths into the ultraviolet-visible range (auxochromes).
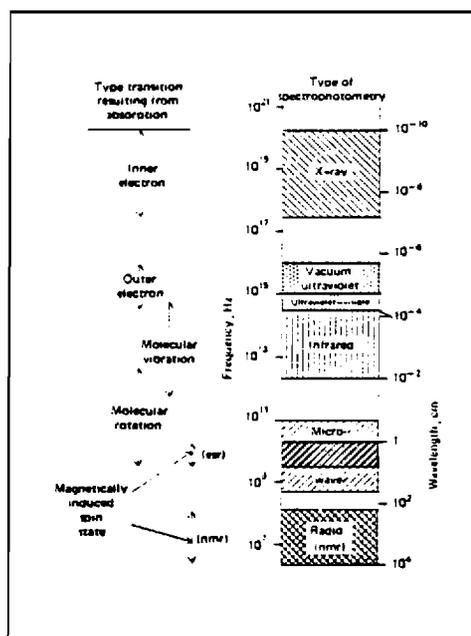

Figure 2. Formaldehyde

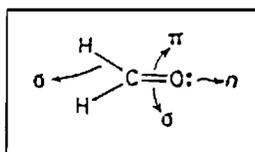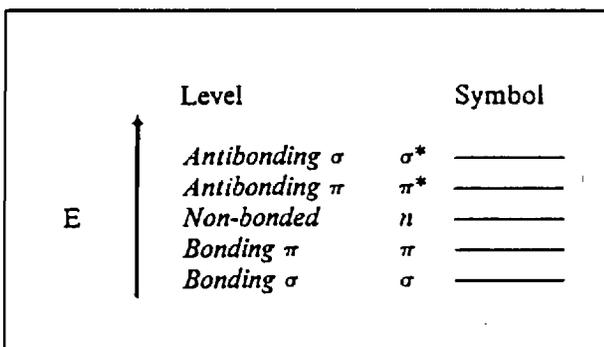|	Level	Symbol	
	Antibonding σ	σ*	
	Antibonding π	π*	
E	Non-bonded	n	
	Bonding π	π	
	Bonding σ	σ	

Figure 3. Energy shifts

Table 1. Chromophores and Auxochromes

Colorimetry is the most familiar application of these principals, where a sample is treated with a reagent selected to result in a color change when combined with the chemical substance to be identified (the analyte). Although visual detection of the color change is sometimes possible, more precise forms of this technique require exposure of a sample to a source of light of a specific wavelength followed by detection and measurement of the intensity of the light remaining after transmission through the sample. The wavelength (or wavelengths) used for analysis are selected based on prior knowledge of the peak wavelength(s) of the absorption spectrum for a specific analyte. Comparison of the transmitted fraction of light with the original intensity of the light at these specific wavelengths permit the analyte to be identified and accurately measured. Given the proper apparatus (light source and detector), similar analysis may be performed for spectra in the ultraviolet portion of the spectrum.

Many chemical substances are able to be detected and analyzed in a transparent solvent without the need for reagents to induce a predictable spectral response, given the proper apparatus for excitation and detection. Metal ions (especially cations formed by transition metals), unsaturated organic structures, and aromatics all tend to possess detectable absorption spectra in the ultraviolet-visible range. Laboratory spectrophotometers are used to detect and analyze the absorption spectrum for a specific substance. Although some instruments are designed for analysis of substances in a vapor state, the type of analyzers of interest for this discussion are those that can be used for the analysis of chemicals in liquids.

The apparatus for analysis of liquid samples consist of a quartz cuvette to hold the sample, a source of ultraviolet-visible light exposed to the sample, and a detector to measure the fraction of light remaining after transmission through the sample as shown in Figure 4. Since analysis is performed over a broad range of wavelengths, the apparatus must include some means of altering the wavelengths at the source or for selecting specific wavelengths for detection after transmission. In either case, the apparatus usually includes optical components that are adjusted to index through a sequence of wavelength intervals so that the spectrum over that range of wavelengths can be detected. The result is an instrument that mechanically steps through a series of wavelengths. These instruments tend to be slow and sensitive to vibration or temperature change, which limits their use to the analysis of static samples in the laboratory.
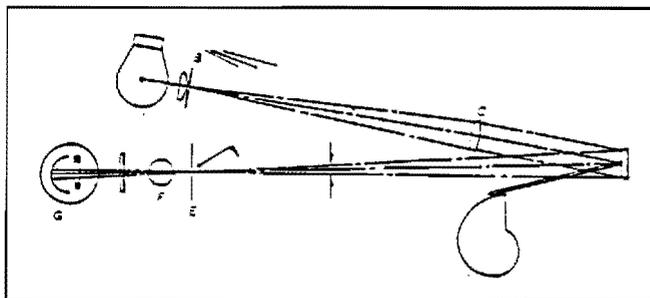

Figure 4. Spectrophotometer apparatus

Analysis models are all based upon application of Beer's Law, which relates the incident light absorbed to the absorbtivity of the media, the path length through the media, and the concentration of absorbing components in the solution. This would normally require knowledge of all absorbing components, which is not feasible for complex solutions. Methods have therefore been developed that define concentration as a function of the absorbances at several wavelengths, called P-Matrix methods. This method allows the concentrations of several analytes to be solved for independently.

II. Requirements for Chemical Analysis in the Field

Chemical analysis for detection of environmental contaminants in groundwater may be performed for three basic purposes:

> SCREENING of samples at a site to determine the presence or absence of a specific chemical or compound. Field methods should be capable of providing rapid and reliable analysis for a specific chemical substance at a specific level of sensitivity and should not be adversely affected by variations in site conditions or water chemistry.

> CHARACTERIZATION of a sample to determine the exact concentrations of specific chemicals and compounds. These results often have liability consequences, and must therefore be performed using standardized methods that can be legally defended. Thus, the precision and repeatability of the method are as important as the sensitivity. Characterization is rarely performed in the field. Laboratory methods performed by skilled operators are the usual technique employed.

> MONITORING of a site to detect the presence of contaminants. This requires periodic analysis, usually for a group of chemicals and compounds that are considered to be reliable indicators of the presence of contamination at a site. Indicators may be mandated by regulation or may be selected based upon the history of a specific site.

Analytical methods that are appropriate for one purpose may be inappropriate for other purposes. For example, screening methods that are specific for a particular analyte or group of analytes may not be capable of the precision required for characterization purposes. Conversely, laboratory methods that are well suited to characterization may not be economical for use in screening and monitoring.

According to EPA officials, more than 90% of the groundwater samples analyzed for screening or monitoring purposes show no detectable levels of contamination. The typical cost to collect, transport and analyze samples using characterization techniques has been estimated to be between $500 and $1000 for each sampling event in each well. This application of expensive resources merely to confirm the continued absence of contamination at a site uses scarce analytical and skilled labor capacity that could otherwise be focused on the remediation of problem sites, research, or other more productive uses. Furthermore, the absence of economical analytical techniques for field use may reduce the willingness or ability of involved parties at potentially endangered sites to engage in voluntary preventative monitoring of groundwater.

A recent article co-authored by the Manager of EPA's Advanced Field Monitoring Methods Program and the former Research Director at the U.S Army Chemical Research, Development and Engineering Center defines several desirable characteristics for field screening methods.[8] Many of these characteristics, which are listed in Table 2, could also be applied to monitoring systems.

Table 2. Desirable Characteristics for Screening Methods

Low Cost	Small	Rapid
Specific	Rugged	Sensitive
User-Friendly	Lightweight	Reliable

The one possible exception as a characteristic for monitoring systems is the specificity of sensors. Sensors for screening systems are often specific to a particular analyte or group of analytes in order to be tolerant of the many variations that can be expected in site conditions and water chemistry. But these same systems may be inappropriate for periodic monitoring at a specific site, especially for in-situ (down the well) monitoring, due to the number of different sensors that would be required to obtain a comprehensive analysis.

This distinction is consistent with the general trends occurring within the sensor industry, where technology has diverged into two distinct classes. One class consists of sensors that are dedicated to the detection of a specific analyte or group of analytes, while the other includes sensors that detect general physical characteristics and must therefore contain fairly sophisticated analytical routines to extract information corresponding to a specific analyte. The relationship between sensor specificity and the capability of the analytical models needed to interpret detected information can be seen in Figure 5.

Although general purpose sensors may be able to be used for both screening and monitoring applications, the analytical models used with these systems usually require a "learning set" consisting of a large number of site specific samples with known analyte concentrations, which may not be feasible for screening applications.
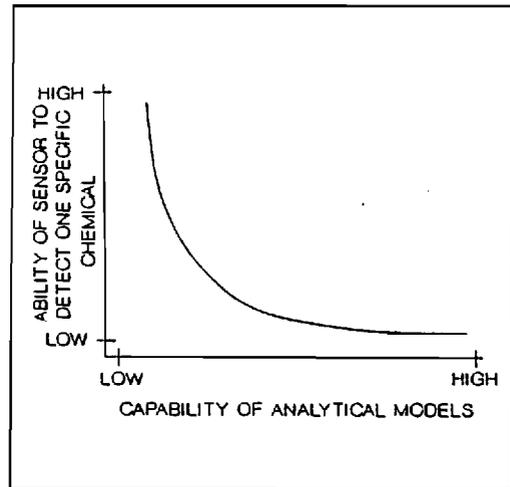

Figure 5. Sensor relationships

III. Feasibility of Absorption Spectroscopy for Field Use

Groundwater monitoring is a classic case of multicomponent chemical analysis since many naturally occurring chemical constituents contribute to the background chemistry of a groundwater sample. An "uncontaminated" water sample will not consist of pure water but may also contain measurable amounts of calcium, magnesium, iron, manganese, sodium, potassium, bicarbonate, sulfate, chloride, nitrate, silica and other chemical constituents that reflect the chemistry of the adjacent geology. Technically, anything in the water matrix that is not H_2O is a contaminant. One purpose of groundwater monitoring, therefore, is to distinguish between contaminants in the water that can be explained by the natural chemical characteristics of the site and those contaminants that do not have a natural explanation. The identification of each constituent, natural and otherwise, must be done in a matrix that contains a background of many other chemical constituents and the possibility of many inter-component chemical reactions.

The usual solution to this problem is to extract a sample in sufficient volume to permit an analysis for each analyte of interest. If the purpose of the analysis is to confirm the absence of unnatural contaminants, individual tests must be performed to confirm the presence or absence of each individual contaminant, which can rapidly multiply analysis costs. For this reason, EPA is conducting research into indicator parameters for industry specific monitoring, so that a short list of reliable and inexpensive parameters on an industry by industry basis can be used to provide an indication of subsurface leakage.

One approach to more economical monitoring would be to use general purpose sensors to detect the physical characteristics present in a variety of chemical constituents. Absorption spectroscopy in the ultraviolet-visible wavelength range is an excellent candidate for this task. Many natural and unnatural water contaminants are known to have ultraviolet-visible absorption spectra. This includes ions of heavy metals; nitrates and sulfates; organic molecules containing bromine, iodine and chlorine; unsaturated organic molecules or molecules containing unsaturated functional groups (alkenes, alkynes, carbonyls, carboxyls, amidos, azos, conjugated dienes); and most aromatic compounds. Many potential indicators of unnatural contaminants will therefore have a unique ultraviolet-visible absorption spectrum.

In order for the ultraviolet-visible absorption spectrum of a chemical substance to be of use for analysis, it must be able to be detected against the background of all other components in the matrix. Since many absorbing components can be expected to be present in the matrix, the absorption spectra will be closely grouped or overlapped with one another, as illustrated in Figure 6.
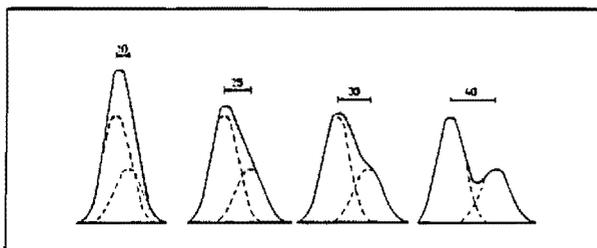
The detection of spectra in liquids results in a smooth continuous structure over a range of wavelengths which is a result of contributions from all of the absorbing components in the matrix. An example of a typical multi-component signature is shown in Figure 7. Although the structure may appear to be featureless (compared to the strong peaks typical of single component analysis in the vapor state), there is considerable information present if only it can be detected and interpreted.
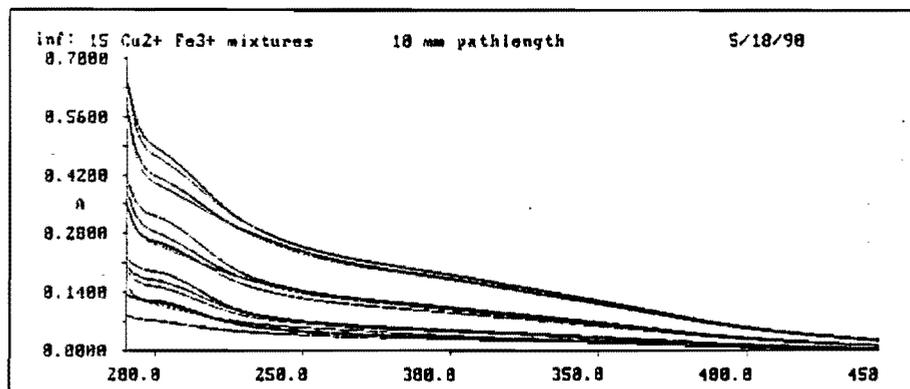

Figure 6. Overlap of spectra

Figure 7. Multi-component absorption spectra

Thus, if Ultraviolet-Visible Absorption Spectroscopy (UVAS) is to be used to monitor for the presence of contamination indicators in the field, the system must be capable of:

1. detecting the overall spectral signature for the groundwater sample being monitored, resulting from both natural and unnatural contaminants.

2. determining the contribution to this spectrum from specific indicators of unnatural contamination and make quantitative determinations of these constituents if required.

3. performing this task using sensors that can either be immersed in the monitoring well (in-situ analysis), fed by a sample pump (on-line analysis), or manually fed with a bailed or pumped sample (on-site analysis).

It would be ideal if this analysis could be performed on the raw water sample without the use of any reagents or sample processing. Recent advances in the technology discussed in section IV make it possible to meet all of these requirements.

There are two basic approaches to the use of UVAS techniques for groundwater monitoring, with the only differences between the two being in the software used for analysis. The first approach, called SIGNATURE RECOGNITION, uses detection and interpretation of ultraviolet-visible absorption signatures to identify and quantify one or more individual chemical constituents in the groundwater matrix. Signature recognition requires that the UVAS system be taught to recognize signature contributions using a learning set of known analyte concentrations against a random background of the other constituents in the matrix. For multiple analytes, this learning phase is a necessary but tedious investment at the front end of a monitoring project. Even so, the overall savings at a site with long term monitoring needs is usually worth the effort.

The second approach, called SIGNATURE DEVIATION, establishes a baseline ultraviolet-visible absorption signature for groundwater at a particular site or in a particular monitoring well and makes an allowance for the contaminants that are naturally occurring. Deviations in the groundwater absorption signature that result from the presence of unnatural contaminants can be detected and used to signal the need for further action.

Signature deviation methods can be used for SERIAL monitoring, where the signature from a specific well is compared to a baseline signature at intervals over a period of time. Some allowances must be made for changes in the natural water chemistry resulting from seasonal or geological factors, without losing the ability to detect deviations caused by the appearance of an unnatural contaminant in the matrix.

PARALLEL monitoring with the signature deviation method can be used to compare the upgradient and downgradient wells at a particular site, with the upgradient well being used as the baseline. Some allowance must be made for naturally explainable deviations caused be geological differences between wells.

Combinations of methods can easily be used since the differences in methods are only in the techniques used to process the detected information. For example, the monitoring scheme at a site may call for quarterly detection events, during which the serial signature deviations of upgradient wells are analyzed to assure that no significant change in the baseline has occurred. All downgradient wells can then be analyzed using parallel signature deviation methods.

By way of example, Figures 8 shows a comparison for the signatures of the same well water before and after the addition of trace concentrations of unnatural contaminants such as toluene and 1,2-dichloroethane and a higher than normal concentration of a natural contaminant such as iron. While the differences in signature may not appear to be dramatic when presented in graphic form, the actual differences are detected in rich detail and converted to numerical values by the UVAS system.
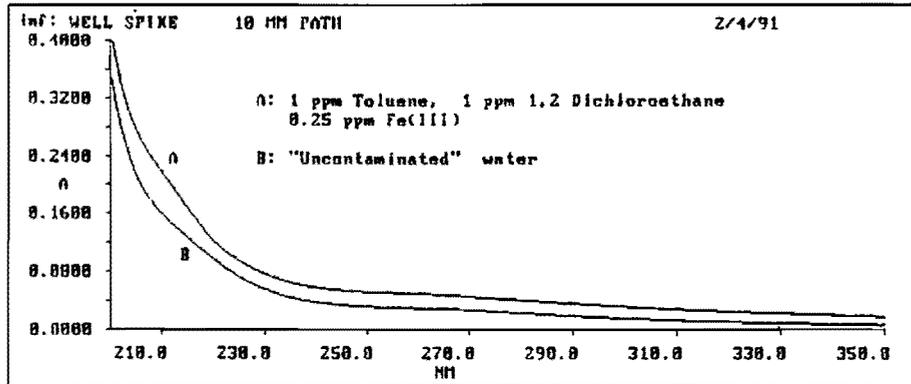
Figure 8. Well water before and after contamination

These differences are significant in mathematical terms and are easily able to be recognized by the UVAS software as a deviation resulting from the presence of unnatural contaminants. Figure 9 shows an expanded scale plot of the differences between the signatures before and after the addition of contamination, which is an indication that a substantial difference has been detected.
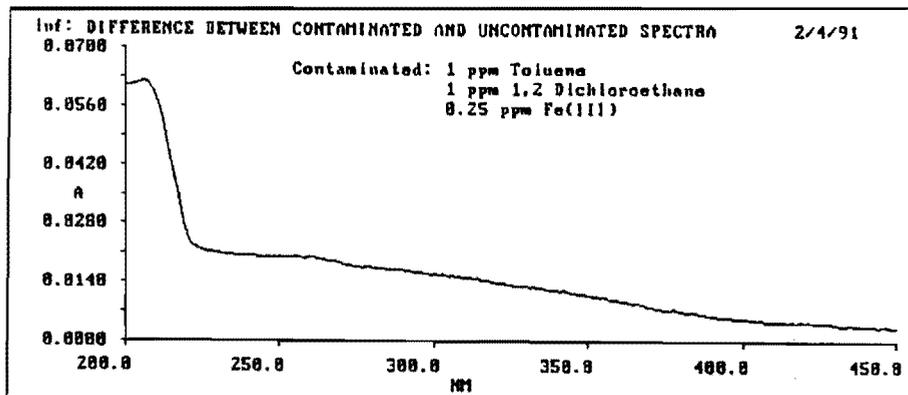

Figure 9. Signature difference before and after contamination

IV. Technology for Real Time Absorption Spectroscopy

There are three technical advances that have converted ultraviolet-visible absorption spectroscopy from a laboratory technology to one that can be used for real time analysis of groundwater. These advances are:

> FIBER OPTICS which permit substantial distance between the analyzer and the water to be analyzed. The light source, detector and electronic components can be housed in the analyzer and connected by fiber optic cables to an OPTICAL PROBE which permits light to be transmitted through the groundwater, then collected and returned to the analyzer. Optical probes can be designed to accommodate several types of field analysis systems, as summarized on Table

3. IN-SITU analysis can be performed with either removable or dedicated probes that are immersed directly in the monitoring well. The capability to extract samples may also be present in the well, but is only required if the well is to be purged prior to analysis of if samples are to be extracted upon detection of an alarm condition. ON-SITE analysis uses manual methods to extract samples from the well and introduce them into the optical probe. ON-LINE analysis makes use of a flow through cell that is connected to a dedicated or removable sampling pump in the well. Figures 10 and 11 illustrate optical probes for in-situ and on-line use.

Table 3. Real Time Analysis Systems

SAMPLE COLLECTION	ANALYSIS TYPE	PROBE TYPE
NO EXTRACTION	IN-SITU	REMOVABLE
PARALLEL EXTRACTION		DEDICATED
MANUAL EXTRACTION	ON-SITE	POUR THROUGH
REMOVABLE PUMP	ON-LINE	FLOW THROUGH
DEDICATED PUMP		
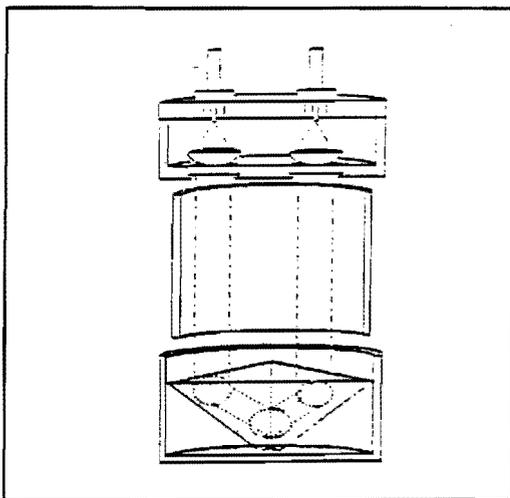
Figure 10. In-situ optical probe
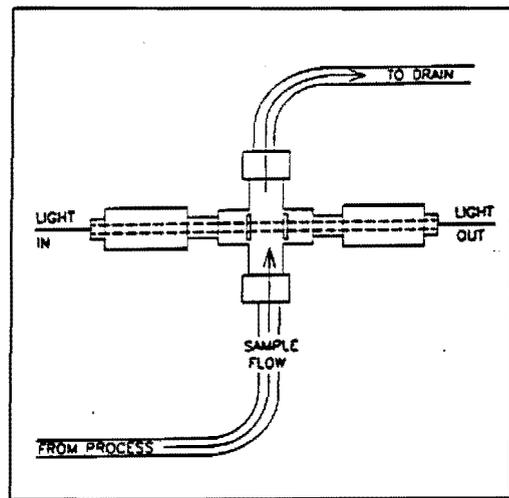
Figure 11. Flow through cell

PHOTODETECTOR ARRAYS permit a broad wavelength range to be simultaneously detected at discrete intervals. These arrays eliminate the need to mechanically create wavelength intervals by the use of movable gratings or mirrors. Instead, the full wavelength range from a broad source of ultraviolet-visible light can be used, such as a Xenon lamp with an output of 200 nm to 800 nm. The light returned to the analyzer is projected onto a fixed grating where it is separated into wavelengths and projected onto a detector consisting of 1024 discrete elements, as illustrated in Figure 12. The intensity of the returned light for each interval can be compared to an intensity at a refrence wavelength in order to establish an absorption spectrum over the range. Wavelength intervals that do not contain information needed for the analysis can be ignored, although some wavelengths that are not affected by the matrix under analysis are used for zeroing by the analyzer.

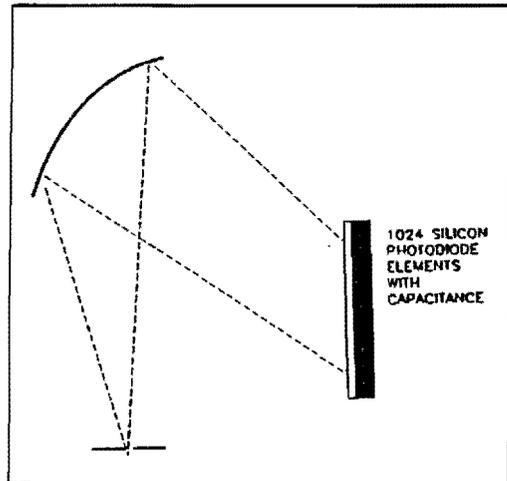1024 SILICON PHOTODIODE ELEMENTS WITH CAPACITANCE

Figure 12. Photodetector array

CHEMOMETRICS is the most meaningful advance making real time analysis possible. General purpose sensors require high capability analytical models to extract analyte specific information, as shown earlier in this discussion. Chemometrics can generally be described as the application of statistical and mathematical analysis techniques to analytical chemistry problems. These include methods to identify unknowns by using information from calibrated learning sets or contained within stored data bases. Specific techniques employed can be grouped into three basic steps, as shown on Figure 13. As previously discussed, concentrations for analytes can be defined in terms of the absorbance values at several wavelengths. It should be noted that an absorbance vector of multiple dimensions is defined, thus complicating any subsequent analysis.

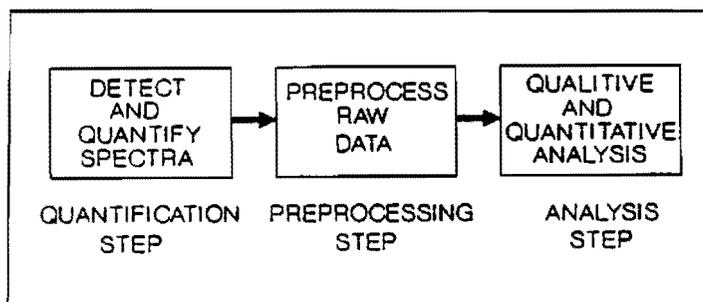| DETECT AND QUANTIFY SPECTRA | PREPROCESS RAW DATA | QUALITIVE AND QUANTITATIVE ANALYSIS |
| QUANTIFICATION STEP | PREPROCESSING STEP | ANALYSIS STEP |

Figure 13. Chemometric analysis steps

Quantification steps include the detection of absorption spectra and the conversion of this information into numerical values that can be processed using statistical and mathematical procedures. The preprocessing step makes use of one or more of several available techniques to reduce noise in the raw data, amplify differences in closely grouped data sets, isolate principal components, or otherwise transform information into a form that results in the most effective analysis possible. The final analysis step uses one of several available techniques, such as regression or discriminant analysis to recognize and quantify the contributions made by individual chemicals to the spectra for a multiple component solution.

When chemometric methods are used for applications similar to the signature recognition method described in a previous section, the three basic steps are optimized at the start of the monitoring project by using a procedure similar to the model described in Figure 14. If the project requires specific chemicals to be recognized and measured during the monitoring program, a "learning set" consisting of several known concentrations of the analytes in the matrix to be monitored are needed. The spectra for the learning set is detected, and wavelengths that appear to contain significant information are identified. These data are transformed using several preprocessing techniques. Various combinations are then processed using the several available analytical models. The combination of wavelengths, transformation techniques and analysis method that produces the lowest error for predicted versus actual values in the learning set is identified. This method is then used to identify and measure the analytes contained in several test sets in order to verify that low error rates can consistently be achieved. Once verified, the method is identified in the software for the system to be used for the monitoring project as the method of choice for a particular analyte. It is possible for different methods to be used for different analytes in the same matrix at a given site.
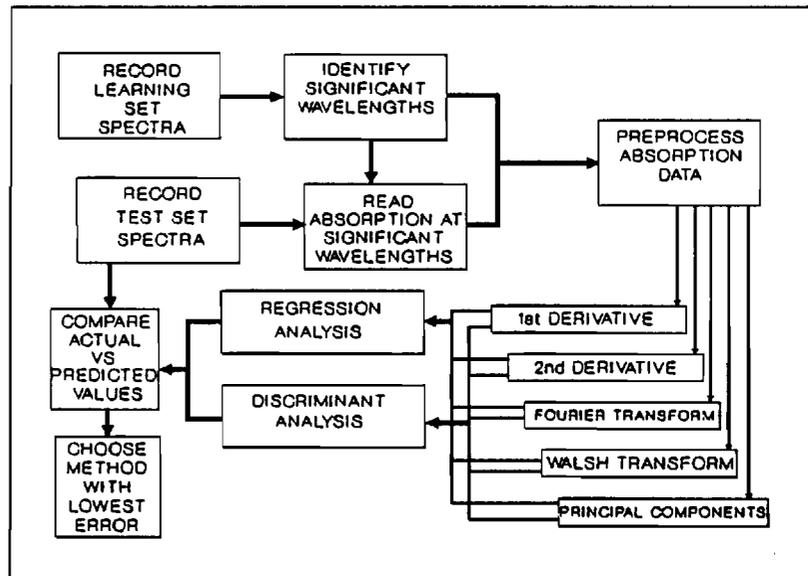

Figure 14. Optimization of methods

V. Current Applications of Real-Time UVAS Technology

An example of the potential that exists for multiple component analysis using UVAS was recently shown in conjunction with a NASA project to quantify the components of a nutrient solutions proposed for use in hydroponic systems on future space stations. The solutions contain fourteen components including minerals, nitrates, and phosphates. As a demonstration of feasibility, iron and nitrates were identified in the nutrient solutions using UVAS. Figure 15 shows spectra for several levels of iron with random concentrations of the other nutrient components. Twenty samples were processed as a learning set. An analysis model using multiple regression of untransformed absorbance values produced an error of less than 0.03

ppm over a range of iron concentrations from 0 to 10.0 ppm. Test sets that were processed using the same model produced similar results. Nitrates were also analyzed using a 20 member learning set with errors of less than 1.0 ppm over a range of 10.0 to 500.0 ppm.
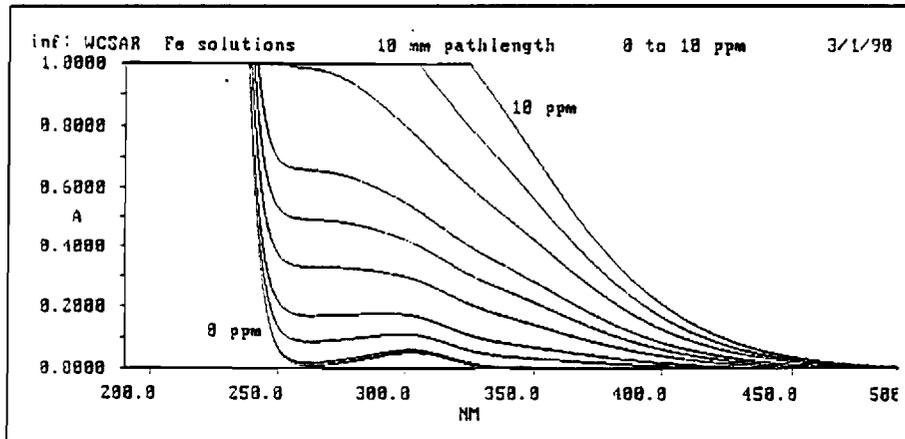

Figure 15. Iron in nutrient solutions

Other applications that demonstrate the capability of UVAS to identify and measure individual chemical components in a multi-component matrix include:

Identification of iron and copper in boiler feed water. Methods used include Walsh transformations and discriminant analysis, which produced errors of 0.13 ppm for iron and 0.007 ppm for copper.

Identification of molybdates, triazoles, phosphonates, iron, copper and other chemical substances in cooling water.

Identification of heavy metals in industrial wastewaters, including mercury at levels as low as 0.0001 ppm, plus zinc and chromium at levels under 1.0 ppm with errors of less than 0.04 ppm.

Some testing of water quality contaminants had also been performed to demonstrate the ability of these contaminants to cause a detectable deviation in the absorption signature of well water. Figure 16 shows the absorption spectra detected for concentrations of toluene, benzene, chloroform, and 1,2-dichloroethane, each in pure water. Figure 8, discussed earlier, shows deviations causes by the introduction of two of these components. Other contaminants tested include gasoline, kerosene, ammonia, and a cleaning solution containing several contamination components.
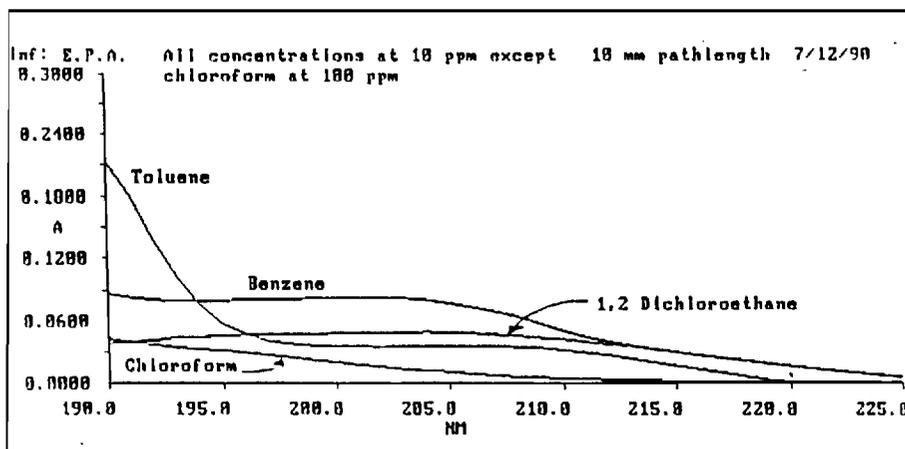

Figure 16. Spectra of water contaminants

VI. Conclusion

Several advances in technology have combined to permit use of ultraviolet-visible absorption spectroscopy in the field for real time analysis of groundwater, including possible use as an in-situ monitoring method. These techniques offer the advantage of not using reagents of any kind. Potential uses of the technology include identification and measurement of specific chemical components that contribute to the absorption spectra of groundwater. Other uses include detection of the presence of certain unnatural contaminants in groundwater by detecting the deviations to the absorption signature for the water caused by the contaminants.

Although actual field testing has not yet been performed, laboratory tests performed on real world samples suggest that both signature recognition and signature deviation techniques could be successfully applied in the field.

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