

ON-LINE ANALYSIS OF NITRATE AND IRON IN DRINKING WATER

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ABSTRACT

A new instrument is available for on-line monitoring of nitrate and/or iron in water. This instrument uses absorbance spectrometry and highly advanced analytical algorithms to determine the presence and concentration of certain chemical components in solutions. The analytical technique uses the natural absorbance characteristics of a sample stream over a range of wavelengths without the need to physically alter the sample or the need to introduce any reagents into the sample line. The technology is capable of simultaneously analyzing several chemical constituents and of monitoring multiple sample lines.

Although this technology was originally developed for use by NASA, it has since been demonstrated for use in water and wastewater applications, including the monitoring and control of several important water treatment processes. Information will be presented which will compare on-line analytical results obtained using this instrument with analytical results obtained using standard laboratory methods.

REQUIREMENTS FOR ON-LINE ANALYSIS

The ideal analytical technique for water treatment applications would be capable of simultaneously detecting a wide variety of molecular and ionic substances at trace concentrations in liquids. No reagents would need to be used. An operator would not be required for collection or interpretation of the analytical information. Instrumentation would be capable of operation in hostile environments. And, the ideal technique would also be able to detect and measure varied concentrations of the analytes of interest in the presence of reasonable variations in non-analyte chemical backgrounds within the chemical matrix to be analyzed.

A new generation of instruments is emerging that is capable of meeting these demanding requirements for on-line and in-situ monitoring of complex liquids. These instruments rely upon a combination of absorption spectrometry and multivariate pattern recognition techniques.

CONVENTIONAL ABSORPTION SPECTROMETRY

ABSORPTION SPECTROMETRY

Absorption spectrometry is a well accepted laboratory analysis technique. Absorption spectrometry in the ultraviolet and visible wavelength range is a common technique for detection of analytes following alteration of a sample using chemical reagents, chromatographic separation or some other form of sample preparation. Ultraviolet - visible absorption spectrometry is not often considered a viable technique for the direct analysis of complex liquids (even though direct on-line detection of

chemical spectra in the near infrared region is becoming well established). Therefore, on-line applications in the ultraviolet-visible wavelength range have typically been limited to detection of specific analytes after reaction with immobilized or injected reagents.

There is a strong perception that because so many substances absorb light in the uv-visible range, there is no practical or reliable way to capture any meaningful information concerning the individual chemical constituents without use of reagents to selectively combine with a target analyte and/or suppress interferences. When physical/chemical sample preparation techniques are used in conjunction with absorption spectrometry it is possible to obtain qualitative and quantitative information for a single analyte at one significant (usually peak) wavelength, thus simplifying detector design for that analyte at the expense of increased complexity ahead of the detection step.

Absorption spectra from multiple component liquids will be a combined function resulting from all absorbing components in the matrix. If no manipulation of samples is performed, analysis of a specific component is only possible if the contribution from the spectra of the component to the overall spectra of the solution can be quantified and detected. Special instrumentation and analytical techniques are required for this task.

ON-LINE SPECTROMETRY TECHNOLOGY

Three technologies make on-line spectrometric analysis of multiple component chemical solutions possible. These technologies are fiber optic probes, linear photodiode detector arrays, and chemometric analysis algorithms.

FIBER OPTIC PROBES

Fiber optic cables permit substantial distance between the analyzer and the solution to be analyzed while providing the means for continuous analysis of the solution. The analyzer can be located either

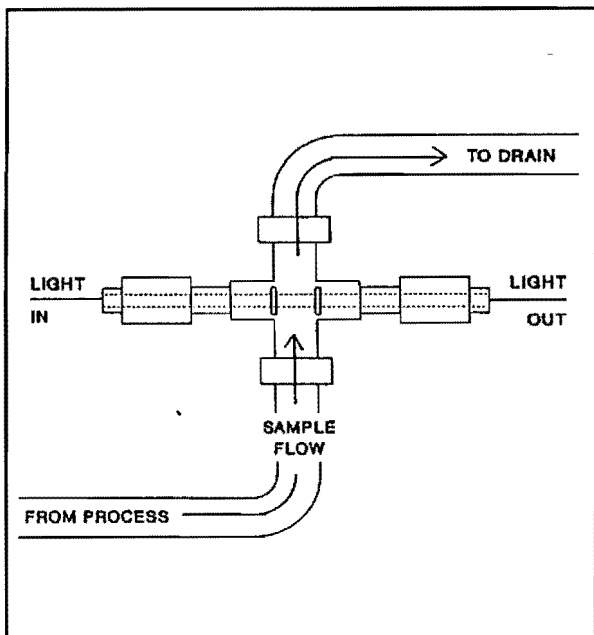


Figure 1. On-Line Probe.

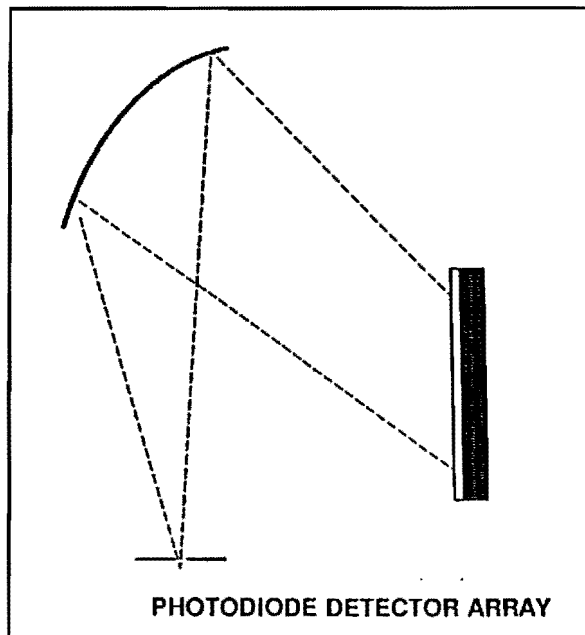


Figure 2. Array Detector.

in a benign environment remote from the solution being analyzed or can be located adjacent to the solution but in a sealed enclosure. An on-line probe can be linked to the analyzer using fiber optics, as illustrated in Figure 1.

LINEAR PHOTODIODE DETECTOR ARRAYS

The development of linear photodiode detector arrays has made it possible to rapidly scan an entire wavelength range and thus detect absorption signatures in real time, even in a flowing sample. These detectors eliminate the need to mechanically index through wavelength intervals with adjustable optics, thus eliminating the moving parts that would otherwise compromise use of the instrument in field or factory environments. In absorption spectrometry applications, the light to be analyzed is projected onto a fixed diffraction grating, where it is separated into discrete wavelengths and reflected onto the array detector. This basic arrangement is illustrated in Figure 2. Each element in the detector array is matched with a dedicated integrating capacitor that can be rapidly scanned to record the intensity detected by a specific segment of the array.

CHEMOMETRIC ANALYSIS ALGORITHMS

Chemical solutions contain numerous components resulting in overlapping or closely grouped spectra. Chemometrics is a term used to describe the application of statistical methods, mathematical methods and methods based on mathematical logic to problems in analytical chemistry. This includes analysis of the effects from multiple chemical constituents on the observed spectral pattern for a solution. Although different techniques are used for absorption spectrometry and emission spectrometry, there are three basic steps involved in any process using chemometric techniques for analysis of spectra. These steps are illustrated in Figure 3.

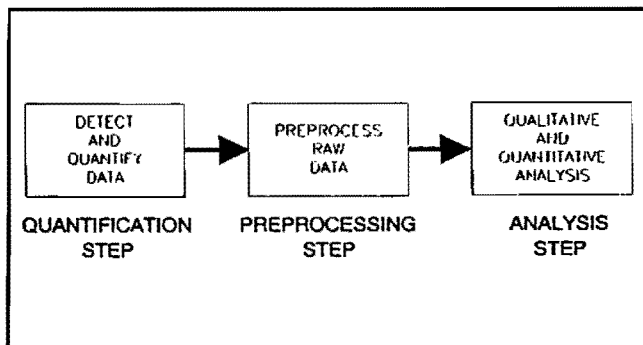


Figure 3. Analysis Steps.

QUANTIFICATION involves converting detected spectra for calibration solutions and unknowns into numerical values that can be processed using mathematical and statistical procedures.

PREPROCESSING of raw data reduces the effects of noise and transforms spectral information into forms that permit more efficient analysis.

ANALYSIS of information at multiple wavelengths identifies individual components and calculates an estimate of their concentrations in the solution.

A source of light is located within the analyzer and has a known output across a broad wavelength range. The light is conveyed from the analyzer to the optical probe through a fiber optic cable. The light remaining after transmission through the media being analyzed is returned to the analyzer through a companion fiber optic cable, where it enters the spectrograph for separation and detection.

NITRATE AND IRON ANALYSIS USING ON-LINE ABSORPTION SPECTROMETRY

Numerous experiments have been conducted at Biotronics to use on-line absorbance spectrometry to detect iron in water solutions including deionized water, boiler feed water, untreated well water and treated municipal wastewater. An example of absorbance spectra obtained from boiler feed water samples spiked with several concentrations of iron ranging from 0.5 to 10.0 ppm can be seen in Figure 4. This experiment was part of a project to demonstrate the ability of an on-line analyzer to detect both copper and iron in the feedwater system of a power utility. In this experiment, iron was analyzed over the Figure 4 range with an average error of 0.13 ppm. Copper was analyzed over a range of 1.0 to 5.0 ppm with an average error of 0.007 ppm.

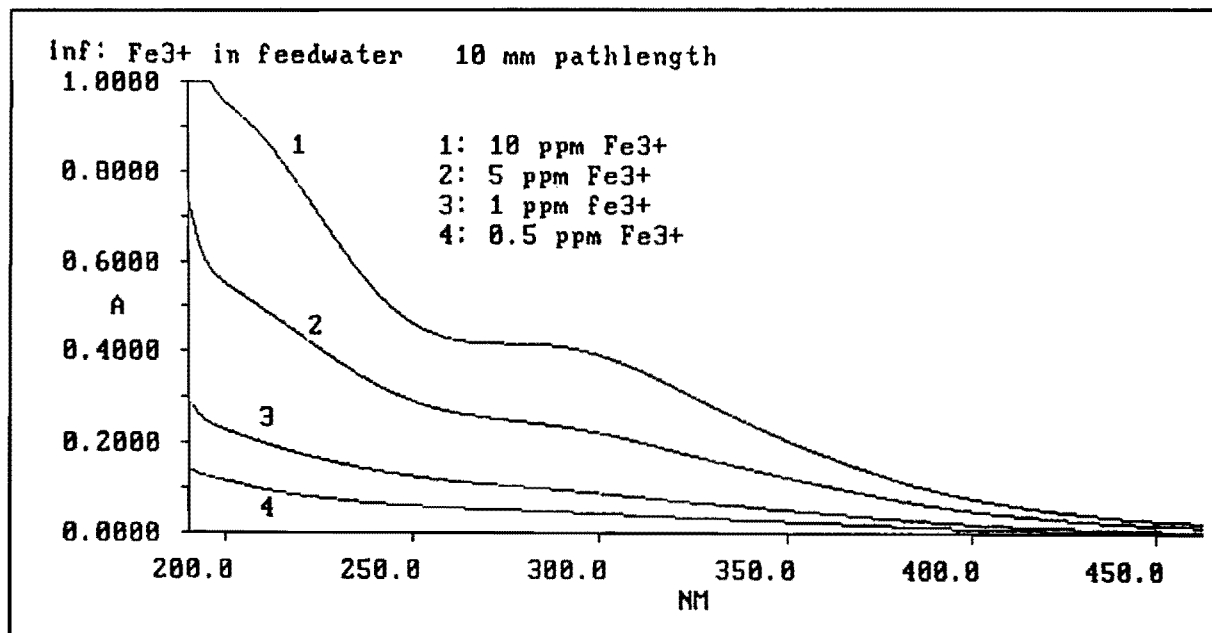


Figure 4. Iron in Feedwater.

The potential of on-line absorption spectrometry to perform multi-component chemical analysis was originally demonstrated under several NASA contracts. The objective of the NASA project is to use either on-line absorption spectrometry or on-line emission spectrometry to identify and measure each of fifteen chemical components in a hydroponic plant growth nutrient solution. A hybrid analyzer absorption/emission analyzer has been fabricated and is being used for this analysis, although the absorption portion of the analyzer operates in a similar manner to the commercial process analyzer.

The NASA work has demonstrated that ultraviolet/visible absorption spectrometry is capable of detecting random concentrations of nitrate and iron in nutrient solutions which also contain numerous other absorbing constituents.

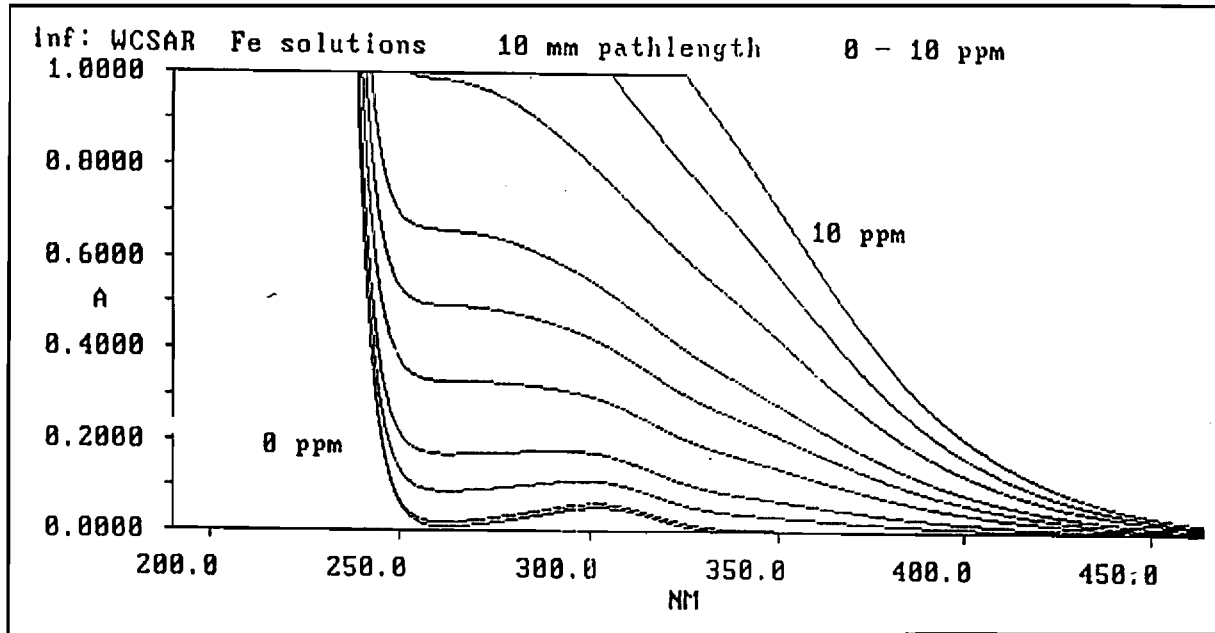


Figure 5. Nutrient Solution Absorbance Spectra.

Figure 5 shows a plot of absorbance spectra from several nutrient solutions that contain random distributions of nutrient components and known concentrations of iron ranging from 0 to 10 ppm. When this information was used to build a calibration file to predict iron concentration, a modest size learning set was able to produce predictions that correlated to within 0.03 ppm. In later stages of the project, a more elaborate calibration file was produced with twenty members. This file also produced

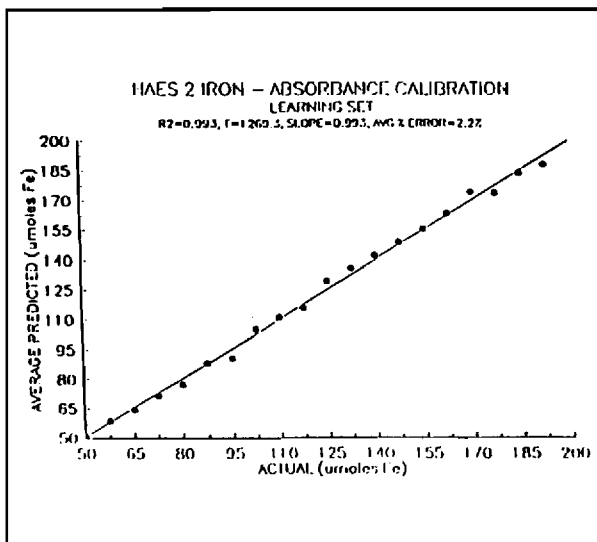


Figure 6. Iron Calibration.

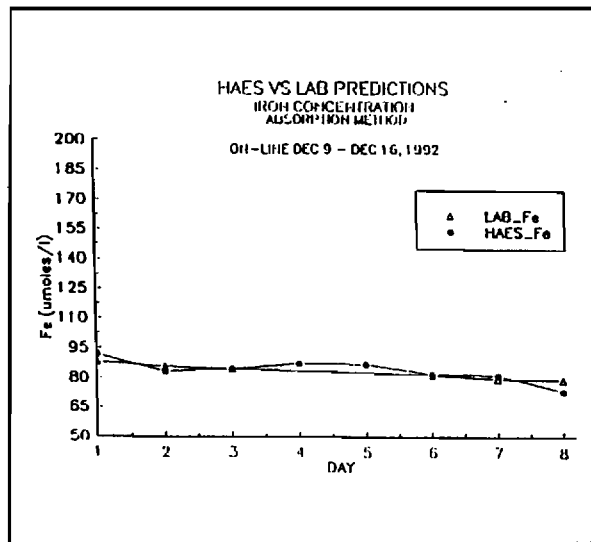


Figure 7. Iron On-line vs. Lab Analysis.

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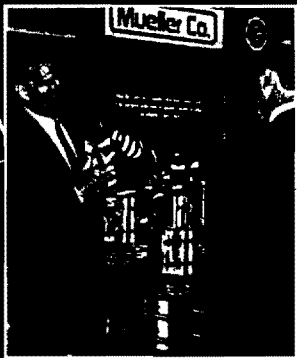
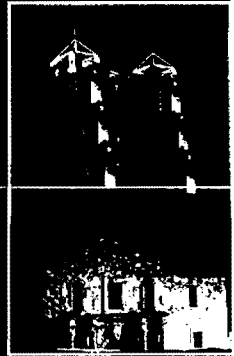
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excellent results with a correlation above 0.99 as seen in Figure 6. This calibration file was used to monitor iron concentrations on-line in nutrient solutions. Periodic samples were extracted and subjected to laboratory analysis using atomic absorbance techniques. Figure 7 shows the comparison between the laboratory analysis of iron and the analysis using the on-line analyzer.

Numerous nitrate analysis experiments were also conducted for NASA, culminating in a series of on-line demonstrations. Figure 8 shows a twenty member calibration set for nitrate in nutrient solutions, with nearly perfect correlation. Figure 9 documents the results from an initial on-line demonstration of nitrate analysis in nutrient solution compared to periodic grab samples. Some difference in the results can be explained by pointing out that there was some delay prior to laboratory analysis of these biologically active samples.

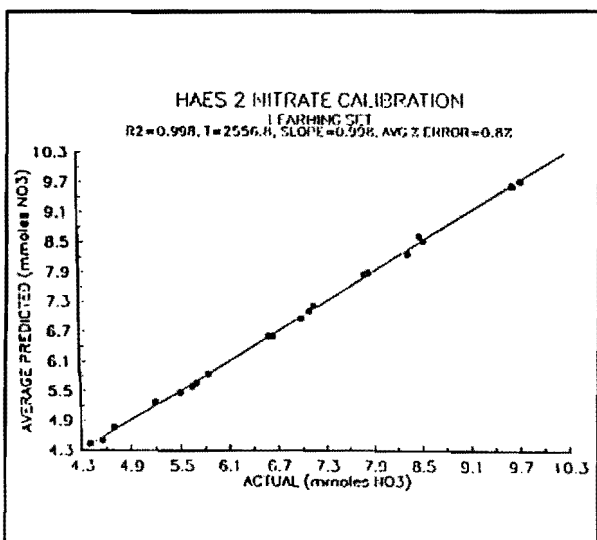


Figure 8. Nitrate Calibration.

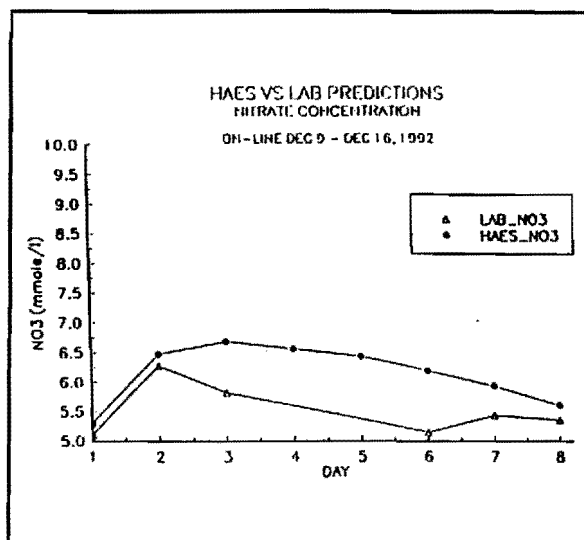


Figure 9. Nitrate On-line vs. Lab Analysis.

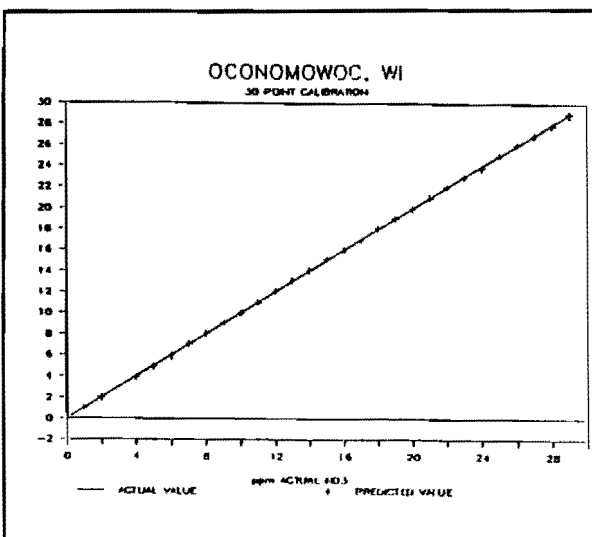


Figure 10. Wastewater Nitrate Calibration.

A better example of on-line nitrate detection in multicomponent solutions is from a long term test conducted at a municipal wastewater treatment facility in Wisconsin. A disinfected and filtered secondary treatment effluent was continuously monitored for nitrate using a commercial version of the on-line analyzer. The analyzer was calibrated for nitrate using a thirty member calibration file, which yielded nearly perfect correlation as seen in Figure 10. Periodic grab samples were extracted and subjected to analysis at Biotronics and at a third party laboratory, both using a cadmium reduction method for nitrate analysis. A comparison between these results can be seen in Figures 11 and 12. Not only can good relative accuracy be seen, but the tracking between analyzer and laboratory values is excellent.

As with iron, numerous experiments have been conducted for on-line nitrate analysis in less demanding media such as deionized water and well water, with excellent results.

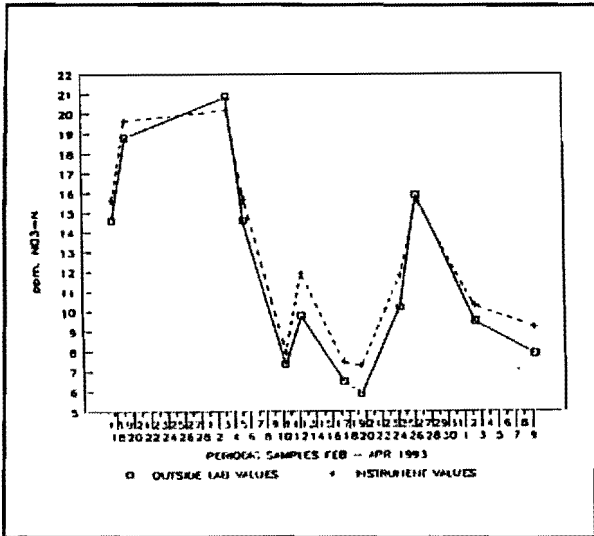


Figure 11. On-line Nitrate vs. BTI Lab.

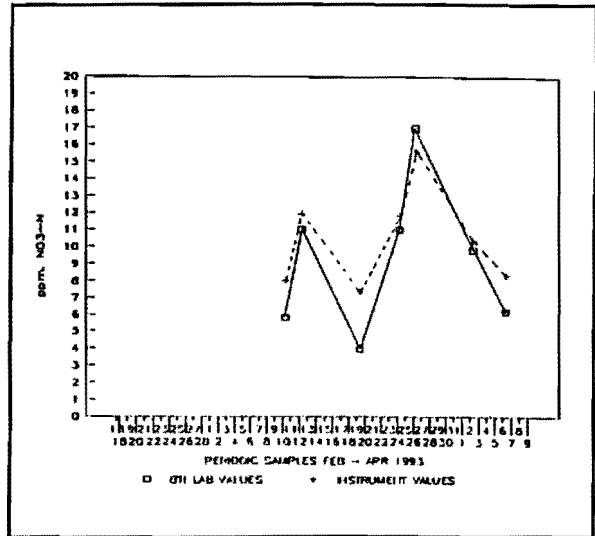


Figure 12. On-line Nitrate vs. Outside Lab.

CONCLUSION

On-line absorbance spectrometry is currently being demonstrated in several important aerospace, industrial and environmental applications. This technology will make it possible to perform on-line analysis of nitrate, iron and other absorbing constituents in water and wastewater, including numerous process monitoring applications for municipal drinking water plants.