ABSTRACT

On-Line Detection of Nitrates in Wastewater Effluents Using Natural Absorption Spectra

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ABSTRACT

Detection and control of nitrates in water supplies is important for protection of the environment and for control of human health. Waste waters that contain nitrates can promote the unnatural growth of blue-green algae. The decay of dead algae causes a reduction in the amount of dissolved oxygen available in the water resulting in an upset of the food chain.[1] Another significant reason for the control of nitrates is the possible occurrence of infantile methemoglobinemia (blue baby syndrome). Nitrites are not commonly ingested directly, but nitrate ions that enter the body in food or water can be reduced in the stomach to nitrite, especially in the stomachs of infants where low acidity allows the growth of nitrate reducing organisms. Drinking water supplies that contain high concentrations of nitrates are therefore considered to be a public health danger. [2]

The contribution of nitrates into the environment from sewage treatment operations is a result of the biological processes used to treat wastewater. These processes convert organic wastes to inorganic forms or to cellular matter. Since nitrogen and phosphorus are essential constituents for cellular activity, wastewater must contain these elements if the biological treatment processes are to be effective.[3] Most of the nitrogen in wastewater originates in the form of ammonia. Discharge of ammonia from wastewater treatment plants will consume oxygen in receiving waters and directly promotes the growth of algae just as effectively as nitrates. Because a major objective for wastewater treatment is to reduce the concentrations of oxygen demanding substances, it is preferable to produce an effluent which has already oxidized ammonia into the form of nitrates. If the receiving streams do not have sufficient hydraulic flow or chemical load carrying capacity to receive a constant flow of nitrates, it may be necessary to provide additional (tertiary) treatment to denitrify the effluent.

Two basic EPA methods are presently used for analysis of nitrates. The first method is based on the reaction of the nitrate ion with brucine sulfate. The color of the resulting complex is measured at 410 nm using a spectrophotometer. Dissolved organic matter, salinity, or the presence of strong oxidizing or reducing agents will cause interferences with this method, resulting in the need for the addition of various reagents prior to analysis. Absolute temperature control is very important to the proper color development when this method is used.[4] The other methods use reagents (hydrazine sulfate or a column of granulated copper-cadmium) to reduce nitrate in the sample to nitrite. The nitrite is then reacted so that the resulting azo complex can be measured at 540 nm using a spectrophotometer. Automated and manual procedures are available for the cadmium reduction method. [5,6,7]

None of these methods are well suited for continuous on-line monitoring of wastewater effluents. On-line analysis requires a method that does not utilize multiple step sample processing, elaborate glassware, carefully prepared reagents or controlled conditions such as temperature stability.

Because the spectrometric analysis currently performed uses only a single (usually peak) wavelength, a substantial amount of chemical processing must be done prior to analysis so that any possible interference from other chemicals in the sample is suppressed at the wavelength being used for the analysis.

While conventional spectrometric methods commonly detect only a single peak wavelength, it should be recognized that the absorption spectrum for a chemical substance in a liquid solvent exists over a range of wavelengths as illustrated in Figure 1. There is, therefore, a substantial amount of information that is available for analysis but not used for simple forms of spectrometry such as colorimetry. If more of the available information is to be used, a more sophisticated instrument is needed to detect and analyze multiple wavelength information.

A recently developed technique makes use of the fact that nitrates in water exhibit natural absorption spectra in the ultraviolet wave range. (Existing spectrometry techniques use an azo complex to shift this spectra into the visible wave range.) The natural nitrate spectra peaks

in the vacuum ultraviolet range, but does possess a shoulder that extends into a portion of the ultraviolet range where it is capable of being detected under normal conditions.[8] This is illustrated in Figure 2.

A special purpose ultraviolet-visible absorption spectrometer is used for this analysis. This analyzer includes fiber optic probes, silicon photodiode array detectors and embedded processors that apply advanced chemometric algorithms.

The fiber optic probe permits contact with a liquid to be made remote from the analyzer, such as in a flow stream or process tank. This allows an analyzer to be operated in a relatively benign environment remote from actual contact with the liquid media being analyzed. Only the optical probe is in contact with the media.

Array detectors permit simultaneous scans of absorption spectra over a wide range of wavelengths, without the need to mechanically adjust optical components for each wavelength to be detected. Up to 1024 wavelength intervals from 200 to 800 nm can be simultaneously detected. This allows a larger number of features from the absorption spectra to be captured with excellent resolution for nitrate analysis.

Chemometrics makes it possible to accurately estimate the contributions from individual chemical constituents to the absorption spectra for the entire mixture. Chemometric models employ a three step process consisting of the quantification of spectral information for the solution, the preprocessing of this information using one of several available techniques, then the analysis of this processed information using a preselected mathematical model or statistical technique.

A number of experiments have been performed in the laboratory to demonstrate the feasibility of on-line nitrate analysis in complex multicomponent chemical solutions using only the natural absorption spectra from the solution.[9] Results from these experiments are shown in Figures 3 and 4. These figures show comparisons of actual vs. predicted concentrations of nitrate in wastewater for a learning set (used to calibrate the analyzer) and a test set (application of information from the learning set to predict concentrations in randomly selected samples).

REFERENCES

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[3] Benefield, Larry D., and Randall, Clifford W., Biological Process Design for Wastewater Treatment, Prentice-Hall, Edgewood Cliffs, NJ, 1980, pages 77-78

[4] USEPA, Methods for Analysis of Water and Wastes, Publication EPA-600/4-79-020, March 1983, Method 352.1

[5] ibid, Method 353.1

[6] ibid, Method 353.2

[7] Ibid, Method 353.3

[8] Rao, C. N. R., Ultraviolet and Visible Spectroscopy Chemical Applications, 2nd Edition, Plenum Press, New York, 1967, Pages 29-33

[9] Schlager, Kenneth J., Final Report, Fiber Fluorometry (Spectrometry) for On-Line Chemical Analysis of Nutrient Solutions, NASA, Kennedy Space Center, FL, Contract Number NAS10-11656, July 27, 1990

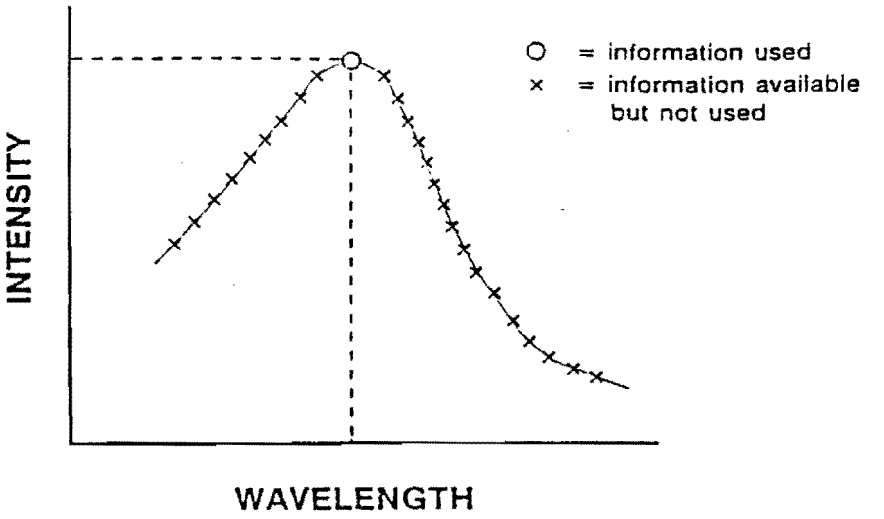
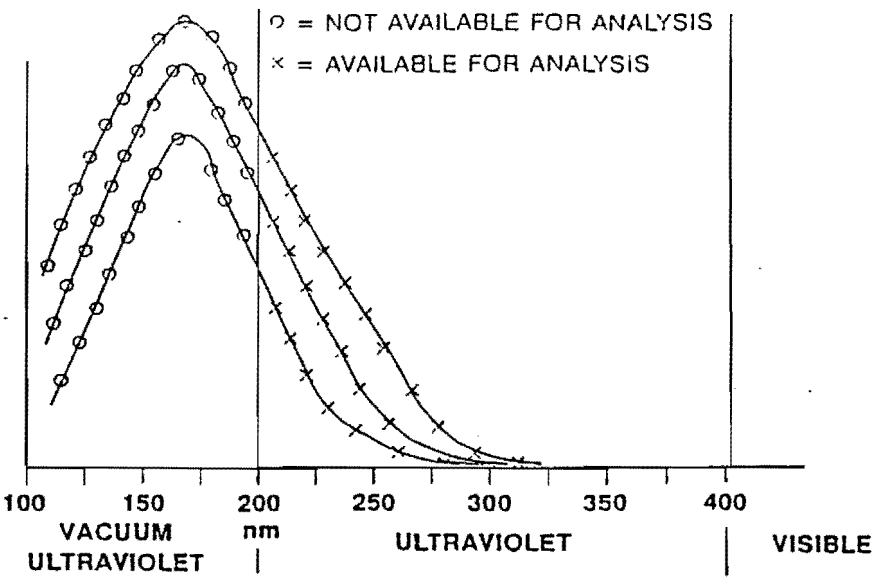


Figure 1. Peak Analysis



THE PEAK AND A SUBSTANTIAL PORTION OF THE SPECTRUM IS IN THE VACUUM ULTRAVIOLET AND NOT ABLE TO BE DETECTED USING CONVENTIONAL INSTRUMENTS. THE PORTION OF THE SPECTRUM ABOVE 200nm IS AVAILABLE FOR DETECTION AND ANALYSIS.

Figure 2. Nitrate Spectra

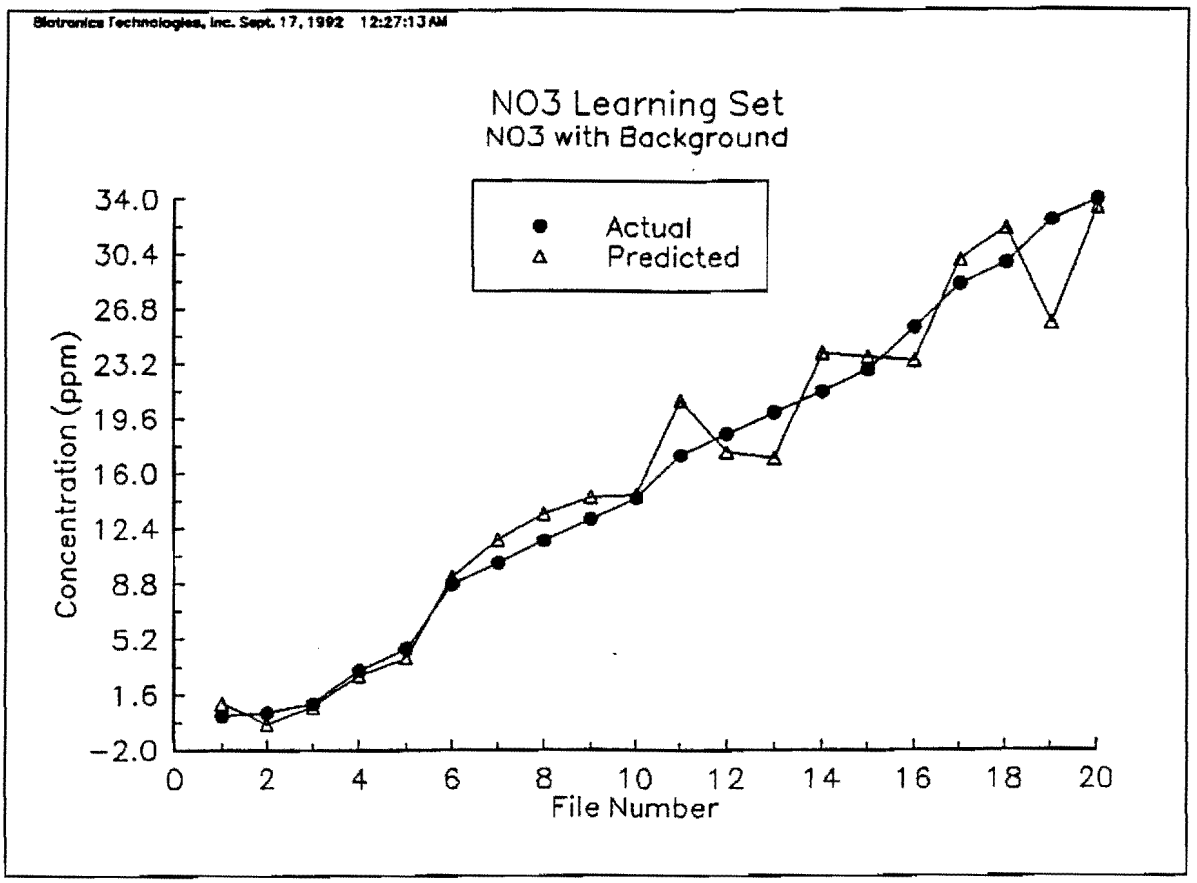


Figure 3.

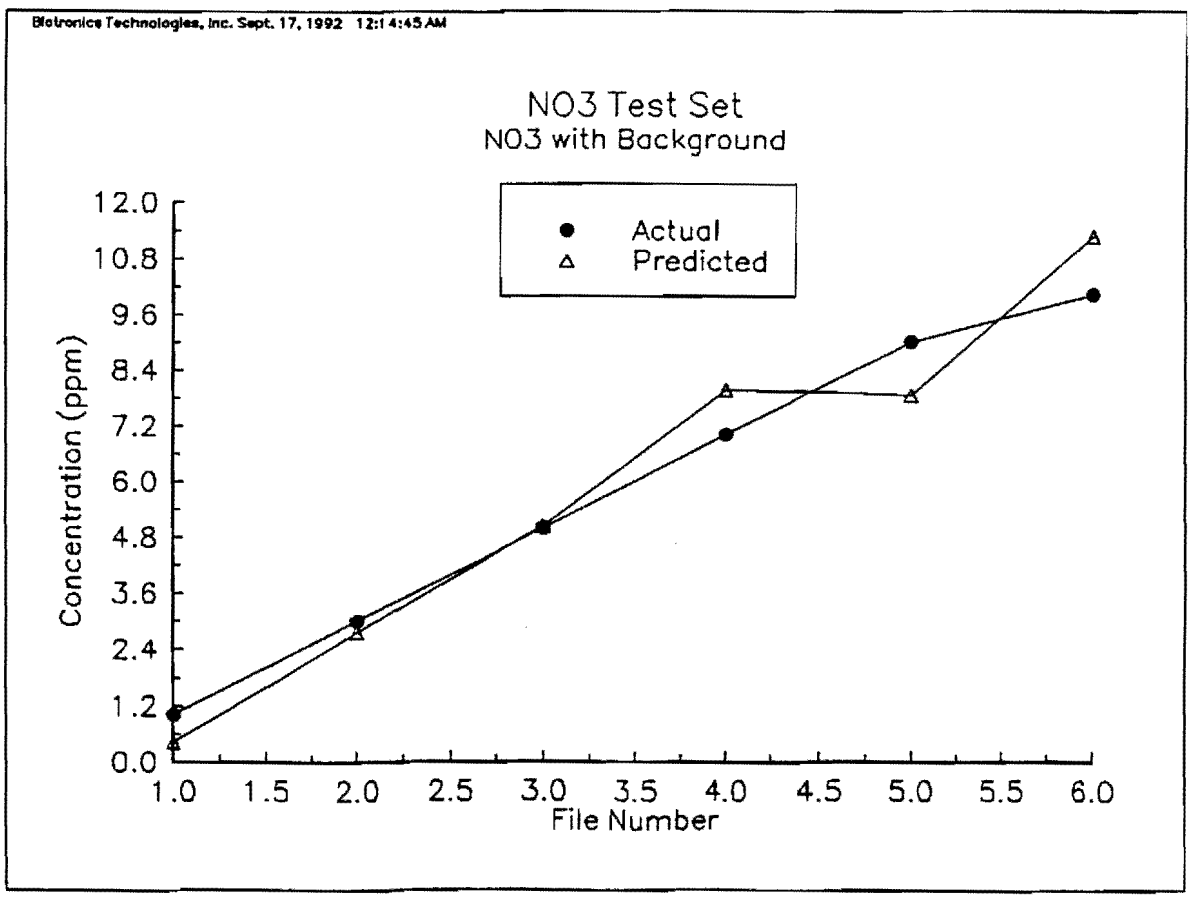


Figure 4.