

ChemScan® Process Analyzer

Project Report and Data Summary
Boiler Water Monitoring
Demonstration Report

Wisconsin Electric Power Company
Valley Power Plant
Milwaukee, WI

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Background

The US Army is facing a critical issue in the maintenance of their facilities. The Army does not rely on proprietary treatment programs that consist of formulated multicomponent treatment chemicals and services from a water treatment supplier. Instead, the Army uses less expensive generic treatment chemicals that are separately fed at appropriate points in the boiler system by an on-site operator. This strategy requires highly skilled boiler operators at a time when the most experienced personnel are being lost due to budget reductions and shrinkage in the size of the military.

One strategy to deal with the management of a demanding treatment program is to provide the on-site operator with assistance in the form of an automated system capable of monitoring and controlling the treatment program. This requires a single system capable of detecting all physical and chemical parameters of importance to the feed of treatment chemicals or the control of the treatment program. The strategy also includes the capability of allowing a remote expert to obtain a real time display of boiler chemistry at several sample points and access to a plot of the historical record for each parameter, if desired. This capability permits a small number of experts to assist in the management of the treatment programs at a large number of facilities.

Project Summary

The demonstration of on-line boiler water monitoring at Wisconsin Electric was a part of a larger project funded by the U.S. Army Construction Engineering Research Laboratory. This research demonstrated the feasibility of using a single integrated on-line instrument system for the analysis of multiple chemical substances and other parameters critical to the successful monitoring and operation of U.S. Army cooling water and boiler systems using only on-line UV absorbance spectrometry and conventional sensors.

Two general types of UV absorbance spectrometry were successfully used for chemical analysis in the Army project. The first type, primary absorbance, relies on the detection and analysis of the natural absorbance spectra of chemical substances in a transmissive media or solvent such as water. Even when several chemical substances produce spectra that overlap, a combined absorbance signature for the solution can be detected over a range of wavelengths. Pattern recognition techniques can subsequently be used to detect and quantify a specific chemical based on the contribution made by each chemical's absorbance spectrum to the overall absorbance signature for the solution. Chemical substances successfully detected using primary absorbance include sulfite, tannin, iron, copper, zinc, molybdate, chlorine, tolytriazole, nitrite plus several polymer dispersants and neutralizing amines.

An alternative UV absorbance technique, secondary absorbance, is the basis for many well known analytical procedures. Additives and/or reagents are used in order to create or enhance absorbance spectra for chemical substances of interest. Unlike conventional reagent chemistry, the demonstrations conducted under the project use multiple wavelength analysis techniques to improve accuracy, compensate for interferences and/or perform parallel analysis of multiple chemicals. This reduces the need for physical or chemical alteration of the sample compared to other methods that do not employ multiple wavelength analysis. Parameters demonstrated during the Army project using secondary absorbance include ammonia, hypochlorite, phosphate, silica and sulfate.

Ammonia Analysis Method

Ammonia is used in trace amounts for pH control in high pressure boilers and in industrial boilers using a "coordinated phosphate" treatment program.

The method of analysis for ammonia in boiler feed water is similar to the ChemScan method used in wastewater. Ammonia will combine with free chlorine to form chloramines that will modify the hypochlorite absorbance spectrum in a predictable manner, proportionate to ammonia concentration. pH control is required to stabilize the spectrum and to control the rate of reaction which varies due to the equilibrium relationships of HOCL-OCL⁻ and NH₃-NH₄⁺.

Good results were obtained at concentrations ranging from 0.1 to 0.5 ppm NH₃ using this method, as shown in Figure 1, which compares measured ammonia to actual ammonia in a 15 sample laboratory experiment.

Absorbic Acid Analysis Method

Absorbic acid (Surgard) is used as an oxygen scavenger in boiler feed water. Trace amounts of residual are maintained to assure the absence of dissolved oxygen in the feed water.

Absorbic acid has a strong absorbance signature in the ultraviolet wavelength range. Primary analysis methods were, therefore, used with good results over the range of 0.05 to 0.25 ppm, as shown in Figure 6.

Phosphate Analysis Methods

In recognition of the nearly universal importance of phosphate analysis to the control of water treatment programs, a high priority was placed on the identification of a reliable, on-line analysis method for this parameter. Unfortunately, total reactive (ortho) phosphate exhibits little or no primary absorbance spectra in the ultraviolet wavelength range. Research was therefore concentrated on evaluation of secondary methods for the detection and analysis of orthophosphate. Two potentially feasible methods were identified and tested:

Ferric-Ion Precipitation Method

An initial experiment demonstrated that the absorbance spectra of a ferric reagent is modified upon introduction of a phosphate solution.

A series of initial calibration experiments for the ferric ion precipitation method were performed in tap water to verify the feasibility of the method. Two sets of 16 samples were prepared over a two day period with PO₄³⁻ concentrations ranging from 0 to 75 ppm. Following addition of the FE(III) stock solution and concentrated hydrochloric or sulfuric acid for pH adjustment, the samples were scanned on a laboratory spectrophotometer. Absorbance information over the ultraviolet range was collected and actual vs. measured results using the method were compared as shown in Figure 2. Excellent correlation was verified.

Vanadomolybdophosphoric Acid (VmoPA) Colorimetric Method

Initial experiments were conducted in boiler blowdown water obtained from a local hospital. This water is not representative of boiler water for typical U.S. Army projects due to the use of reverse osmosis

pretreatment and an "all polymer" treatment program. Absorbance scans of the boiler blowdown noted significant absorbance in the 200-235 nm range, possibly due to the influence of polymer dispersant such as polyacrylate and/or the influence of residual sulfite. Background PO_4 concentration in the boiler sample was very low, approximately 0.5 mg/l. This water has a pH of 11.5 and includes sulfite concentrations in the 30-60 ppm range and polymer concentrations in the 12-14 ppm range. In order to simulate a sample that was more representative of Army conditions, 2-12 ppm of Calcium was added to samples prepared from the boiler water. Ten samples were prepared containing PO_4^{3-} concentrations over a range of 15-105 ppm and with variable Ca concentrations. A standard concentration of VMO PA reagent was added and the samples were measured for absorbance at multiple wavelengths. Each sample was scanned three times, producing a set of 30 files. Analysis of the absorbance data for this learning set produced an average error of 1.2 ppm with an R^2 of 0.9956 as shown on Figure 3.

Boiler Water Demonstration Summary

Two on-line demonstrations of multiple parameter analysis in boiler water were performed during this project. Both demonstrations were conducted at the Valley Power Plant facility operated by Wisconsin Electric Power Company in Milwaukee, Wisconsin. This plant not only generates electric power but also distributes steam through a piping network for process heating, comfort heating, cooking and other uses in downtown Milwaukee. Because a portion of the steam is used for food processing, the water treatment program chemicals must be USDA approved. This facility has four primary boilers, operating on a coordinated phosphate control program. Ammonia is used for pH control and ascorbic acid (Suregard) is used as an oxygen scavenger.

An on-line analysis of phosphate, dissolved oxygen, pH and conductivity was performed on boiler blow down samples over a three day period starting September 27, 1994 and ending on September 29, 1994. A ChemScan UV-6100 on-line Processing Analyzer and Sample Conditioning Unit was used for phosphate analysis with the Vanadomolybdophosphoric acid method. Dedicated in-line sensors were used for dissolved oxygen, pH and conductivity. An analysis was performed every 15 minutes, with all data sent over a modem connected phone line to a PC located at a remote location, where the data was logged and displayed using LabVIEW software. Figure 4 represents the PC display format that is updated after each new reading. Current values for each parameter are displayed, as are high and low set point alarms for phosphate concentration. A comparison between the UV-6100 phosphate analysis and an on-line Hach phosphate analyzer dedicated to the same sample line is shown in Figure 5.

An on-line demonstration of ammonia and ascorbic acid (Suregard) analysis was performed over a five day period from October 26 to October 31, 1994. This demonstration was witnessed by U.S. Army personnel on October 26, 1994. The purpose of the demonstration was to show the capability for simultaneous on-line analysis of multiple parameters using ultraviolet absorbance spectrometry. Ascorbic acid was analyzed using primary absorbance in a UV-6100 process analyzer equipped with a 100 mm path length flow cell. Ammonia was also analyzed using secondary absorbance on the same process analyzer system plus an external Sample Conditioning Unit similar to the unit used for phosphate analysis in the prior on-line demonstration. An analysis of both parameters was conducted every 15 minutes and sent over a modem connected phone line to a PC located at a remote location for logging and display using LabVIEW. Figure 6 shows a display of values for both parameters over the five day period, compared to periodic laboratory values for these parameters.

NH3 VIA NaOCl ON L9; 100mm PATH

LS=TS; R2=0.999, T=124.6, AVG RES=0.003

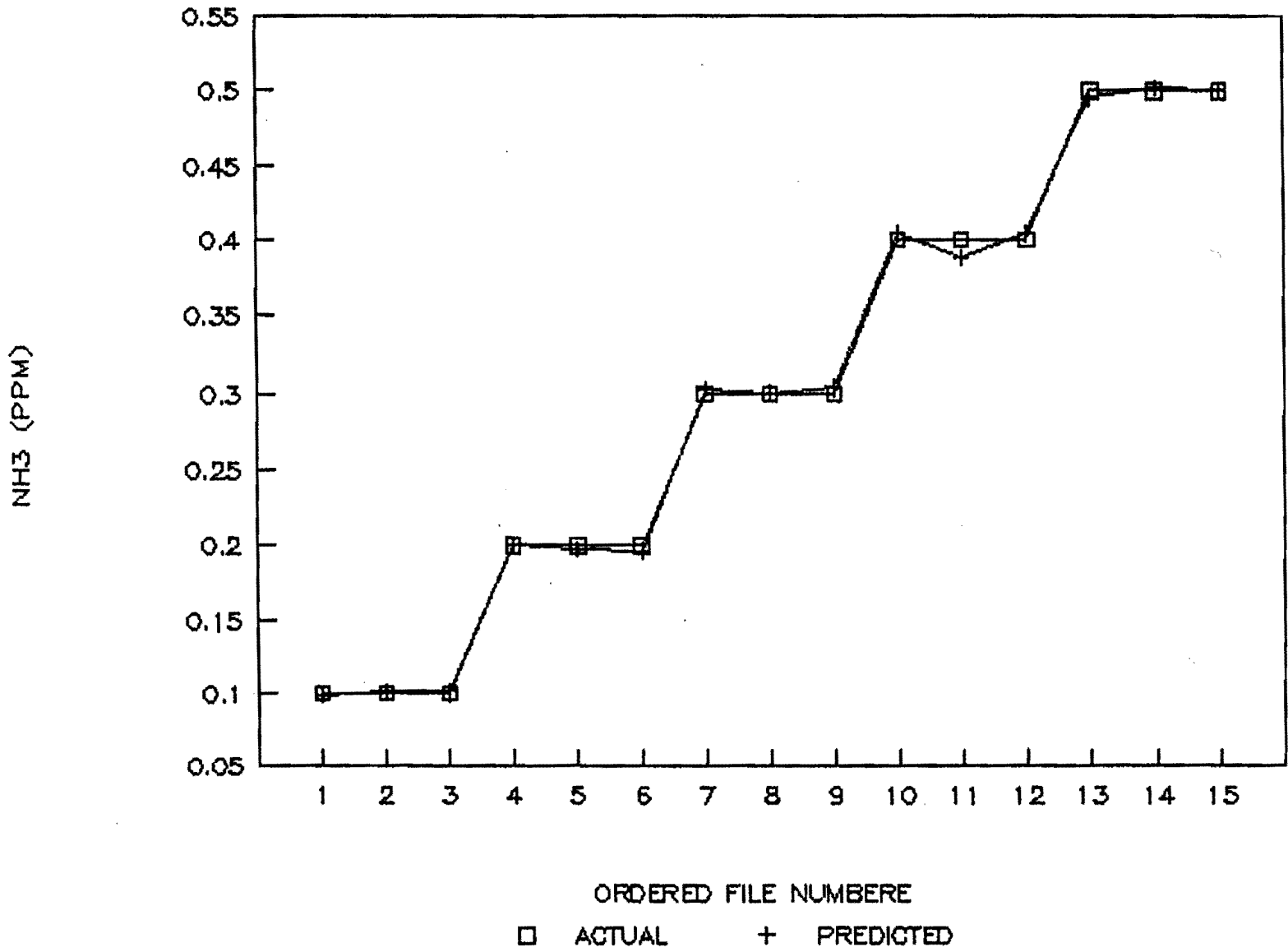


Figure 1

IRON PREDICTION OF PO4

$R^2=0.994$, Avg Res=1.58

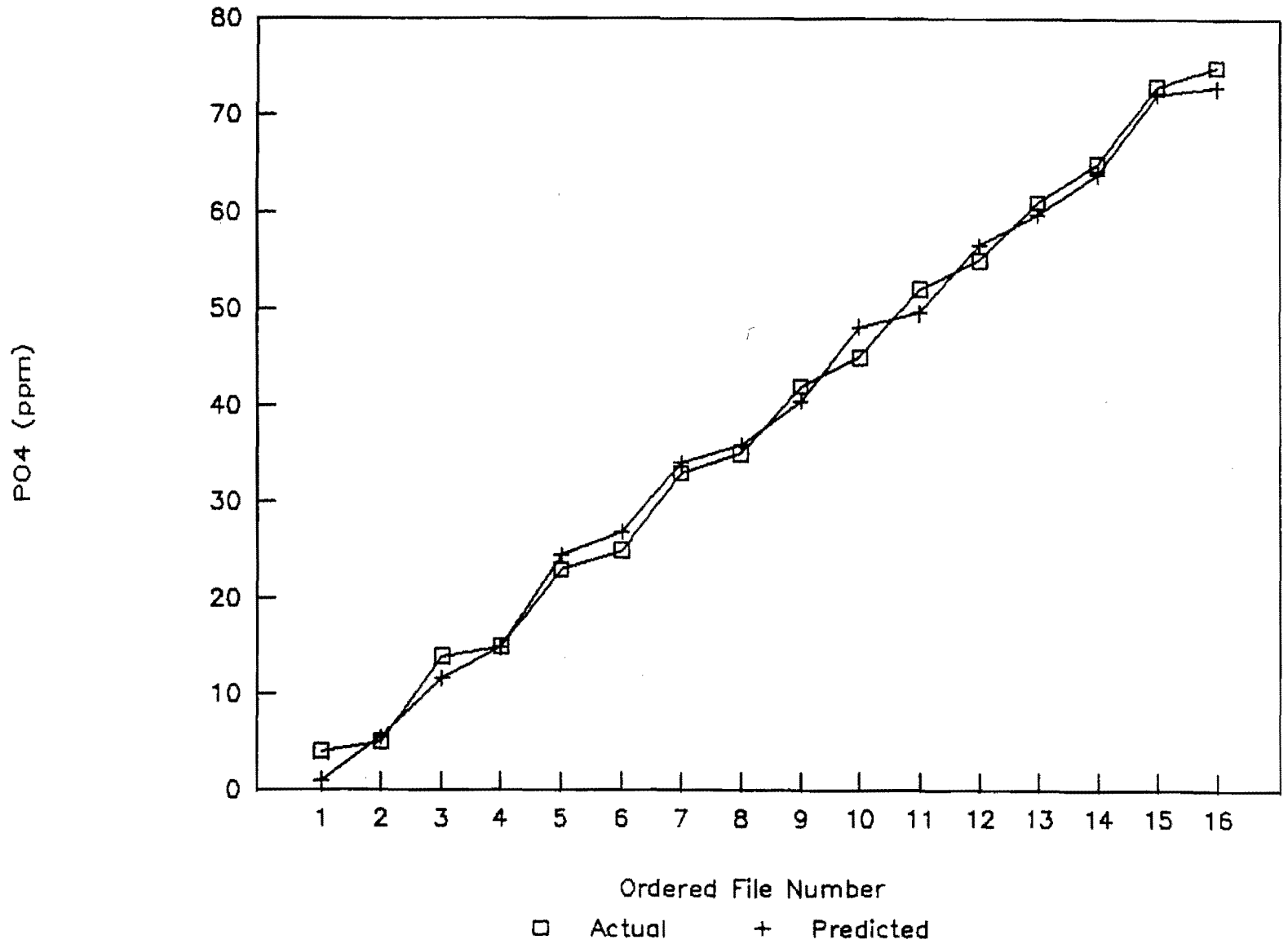


Figure 2

V-Mo METHOD FOR PO4: BOILER LS

R2=0.9956, T=79.2, AVG RES=1.2

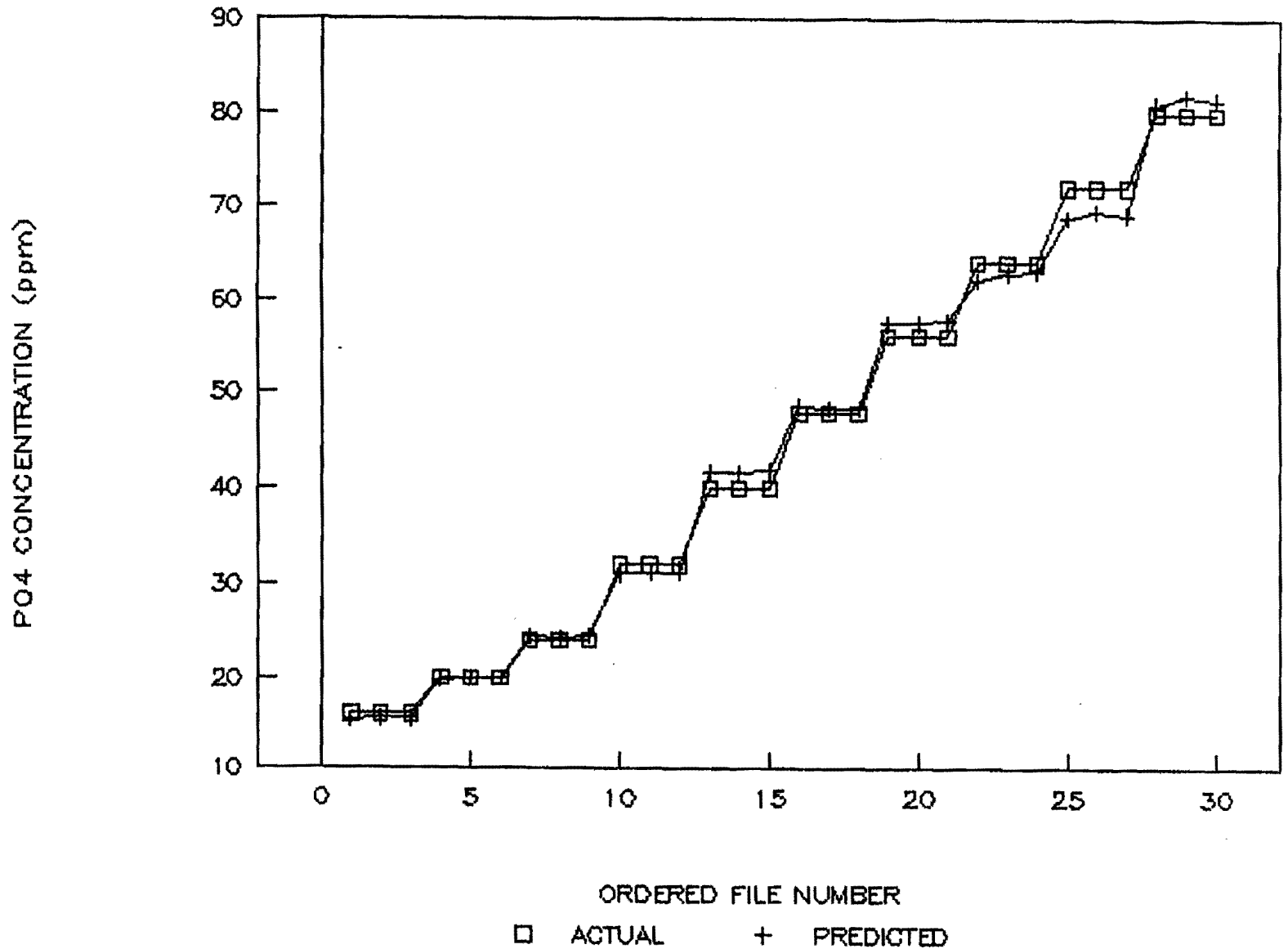


Figure 3

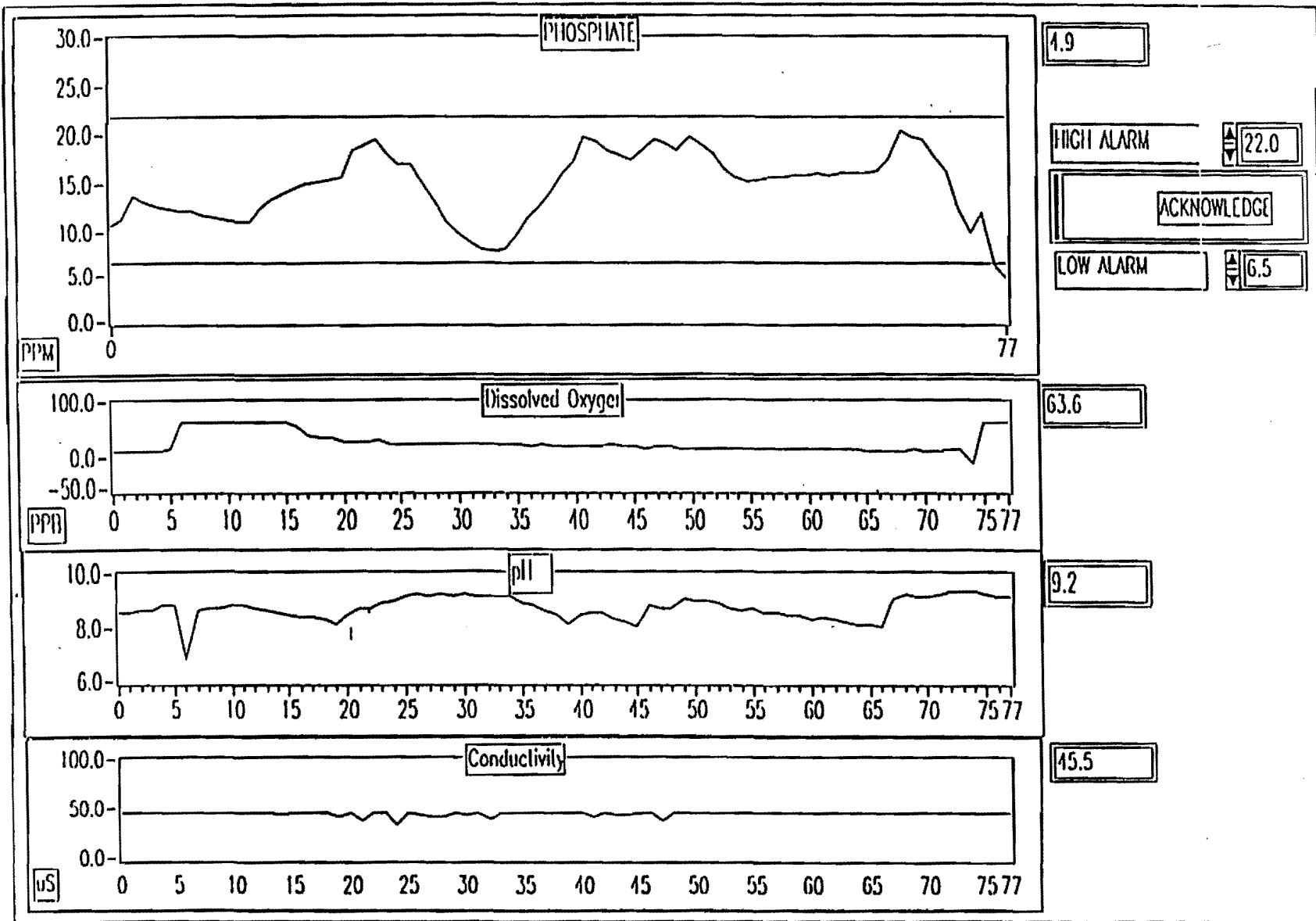


Figure 4

UV6100/SCU ONLINE AT WISCONSIN ELECTRIC

SEPT 27-28, 1994

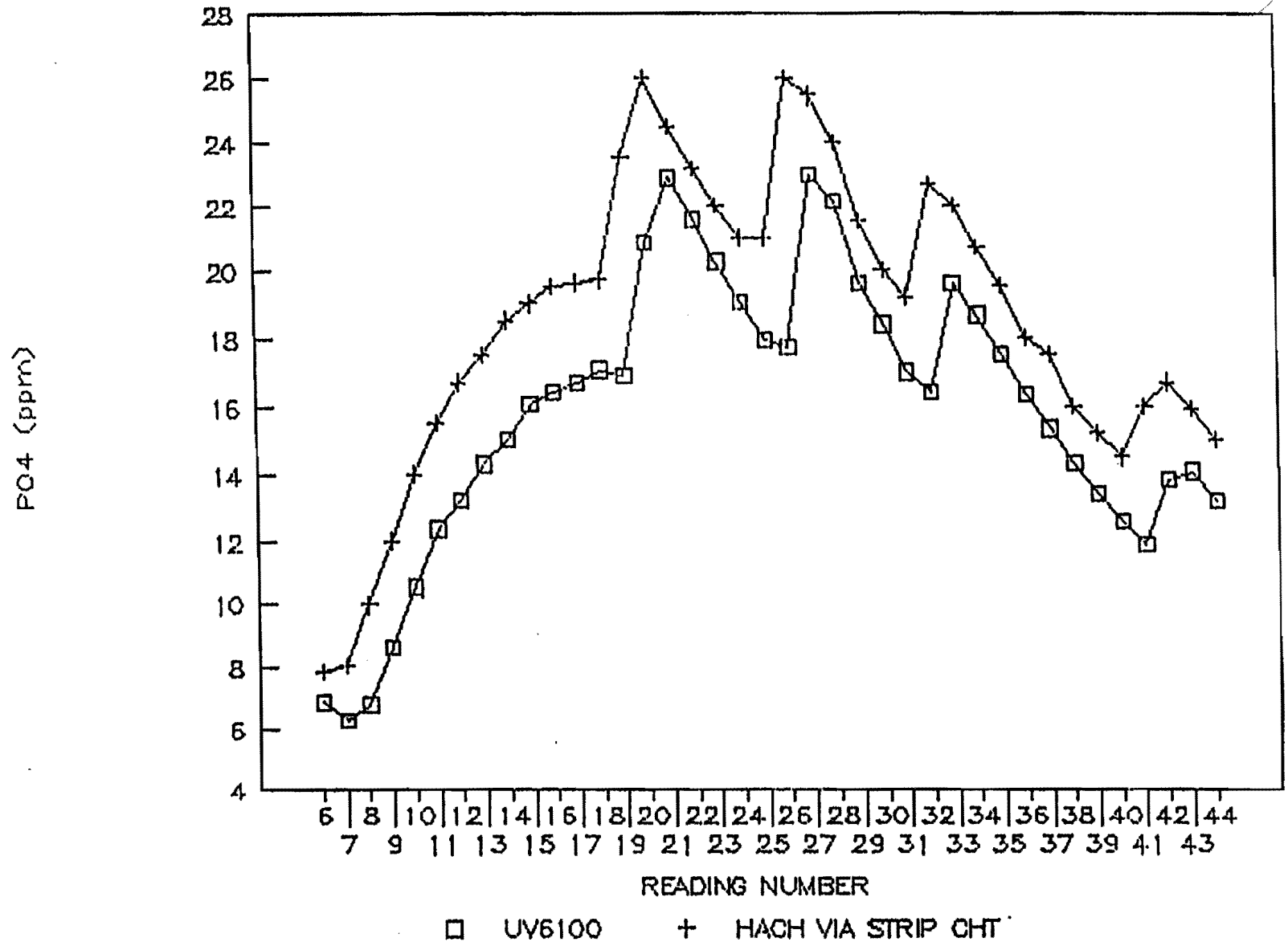
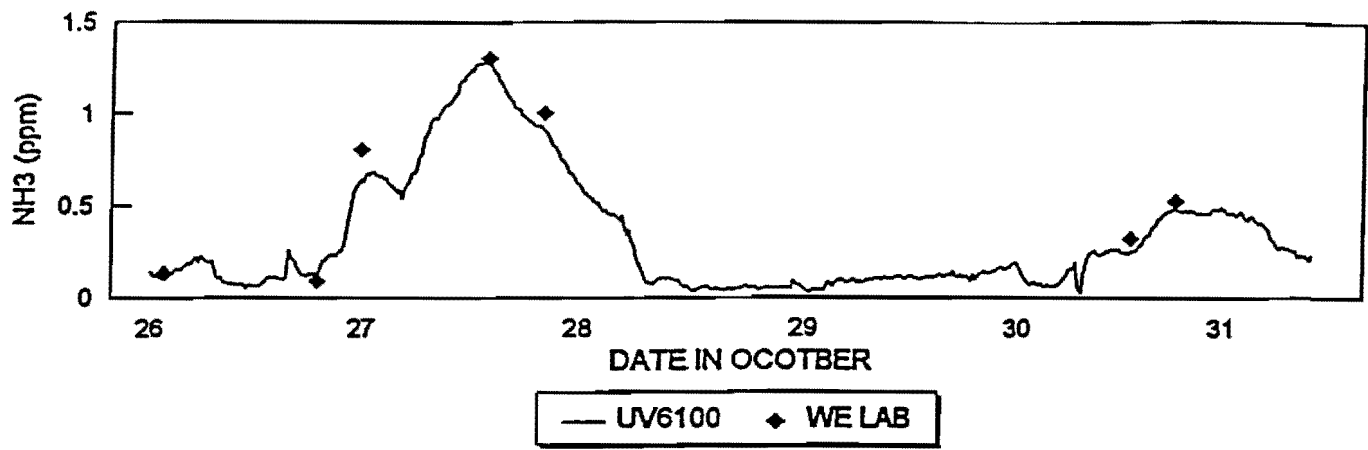


Figure 5

UV6100/SCU DEMO AT WISCONSIN ELECTRIC
AMMONIA IN BOILER FEEDWATER



UV6100 DEMO AT WISCONSIN ELECTRIC
SUREGARD IN BOILER FEEDWATER

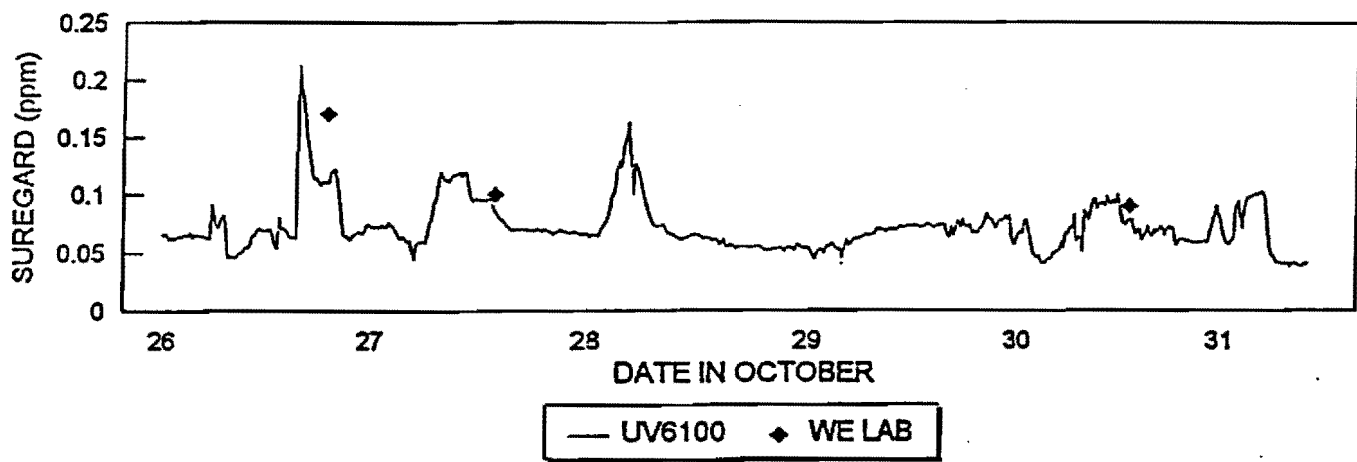


Figure 6