

Technical Publication

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Potomac Plant
Potomac, MD
March 15, 1995

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ChemScan® UV-6100 Process Analyzer
Data Summary
On-Line Analysis of Natural Organic Material

at

Washington Suburban Sanitary Commission
Potomac Plant
Potomac, MD

Published by
Biotronics Technologies, Inc.
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(Preliminary Report)

March 15, 1995

Demonstration Site

The Washington Suburban Sanitary Commission (WSSC) Potomac Plant is a 10 MGD water treatment facility serving several suburban areas in Maryland, outside of Washington D.C. Raw surface water is extracted from the Potomac River, mixed with a chemical coagulant (either polyalumina chloride or ferric chloride), settled, filtered, chlorinated and distributed to customers.

Surface water sources may contain high concentrations of natural organic material (NOM) which, if not removed during the treatment process, can result in the formation of carcinogenic by-products during the disinfection step.

ChemScan Technology Summary

Use of the ChemScan UV-6100 Process Analyzer for direct on-line monitoring of natural organic material was demonstrated during late 1994 and early 1995 at WSSC Potomac plant. The UV-6100 is an on-line absorbance spectrometer, designed to detect high resolution light absorbance signatures in the ultraviolet wavelength range. Pattern recognition software is used to extract information about the presence and concentration of specific chemical substances from their absorbance contributions to the overall absorbance signature for a sample.

Demonstration

Natural Organic Material in surface water consist primarily of humic, tannic and fulvic acid compounds, resulting from the decay of plants and other natural processes. These natural organic acids each possess unique absorbance signatures as shown in Figures 1 and 2. In surface water a variety of natural organic material may be present, producing an overall absorbance signature for raw water which is a function of all light absorbing compounds in the water as shown in Figure 3. This light absorbance signature may also be affected by turbidity, dissolved minerals, nutrients and other chemicals in the water.

The typical method for detection of organic matter is through a Total Organic Carbon (TOC) analysis. TOC methods use heat and oxygen, ultraviolet irradiation, chemical oxidants or other methods to convert organic carbon in a volume of sample to CO₂. The CO₂ is measured using an infrared analyzer, chemical titration or (after reduction to methane) flame ionization detector. In any case, total organic carbon analysis requires extensive and precise sample processing and subsequent measurement of a gas by-product from which a TOC value is computed.

The primary objective for the WSSC demonstration was to show that the ChemScan UV-6100 system could provide a direct measurement of NOM using on-line ultraviolet absorbance spectrometry and that these results would correlate with the traditional TOC values resulting from natural organic material in surface water.

A secondary objective was to use the ChemScan UV-6100 system to track the NOM removal through each unit process prior to disinfection. Since the plant had a split flow, with each side of the plant using a different coagulant, the demonstration also provided an opportunity to observe differences in NOM removal rates for each type of coagulant.

RUN DESCRIPTION:

FILE NAME: VL 1

GAIN FACTOR:

NUMBER OF SCANS:

INTEGRATION TIME:

CLOCK RATE:

RUN NUMBER:

TIME BETWEEN RUNS:

A/D VAL

1.5000

1.2000

Figure 1

0.9000

0.6000

0.3000

0.0000

(nm)

ELEM

200.00

240.00

280.00

320.00

360.00

400.00

0

20

40

60

80

100

Tannic Acid, 10.0 ppm equivalent TOC

RUN DESCRIPTION:

FILE NAME: ♣L !

GAIN FACTOR:

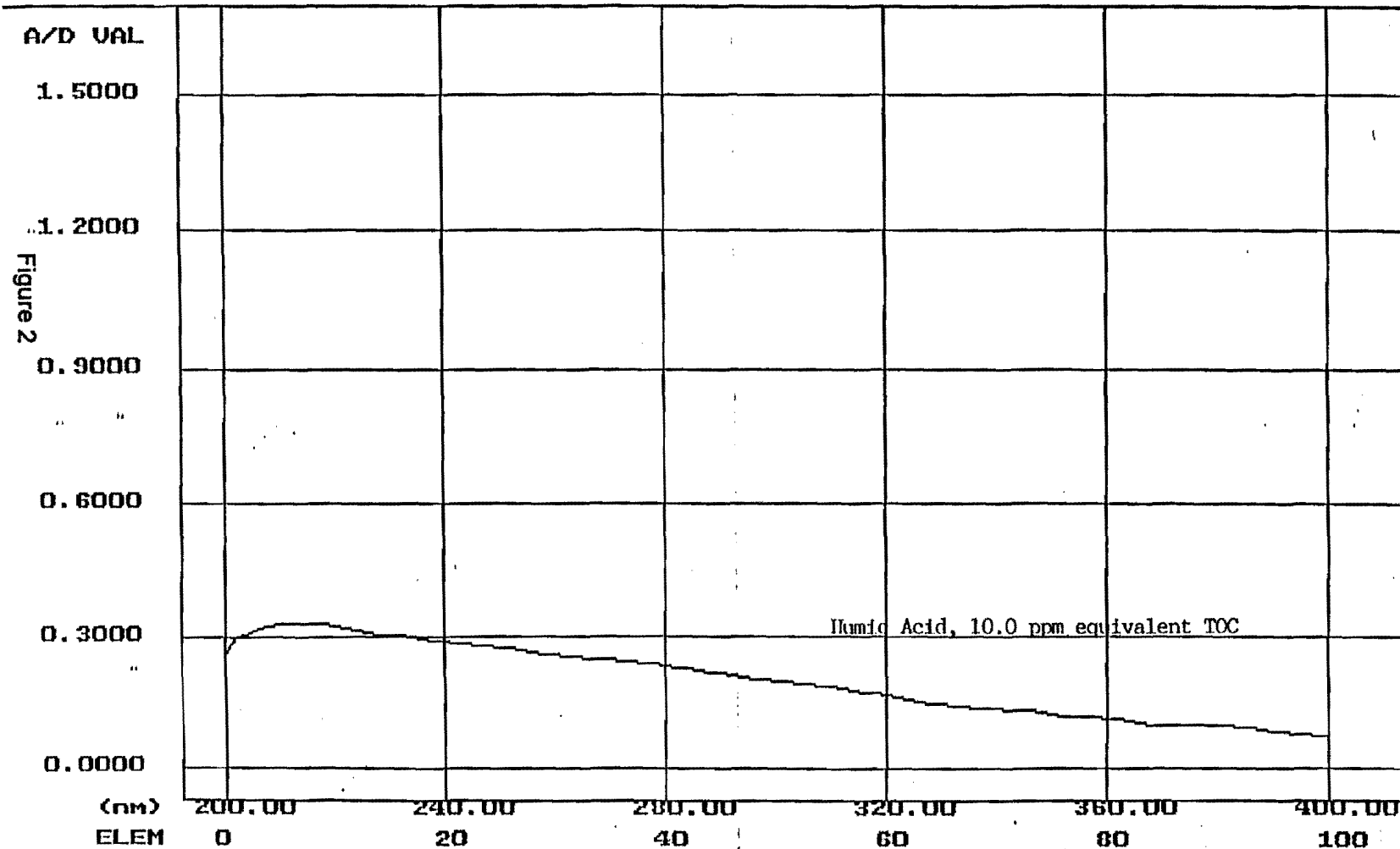
NUMBER OF SCANS:

INTEGRATION TIME:

CLOCK RATE:

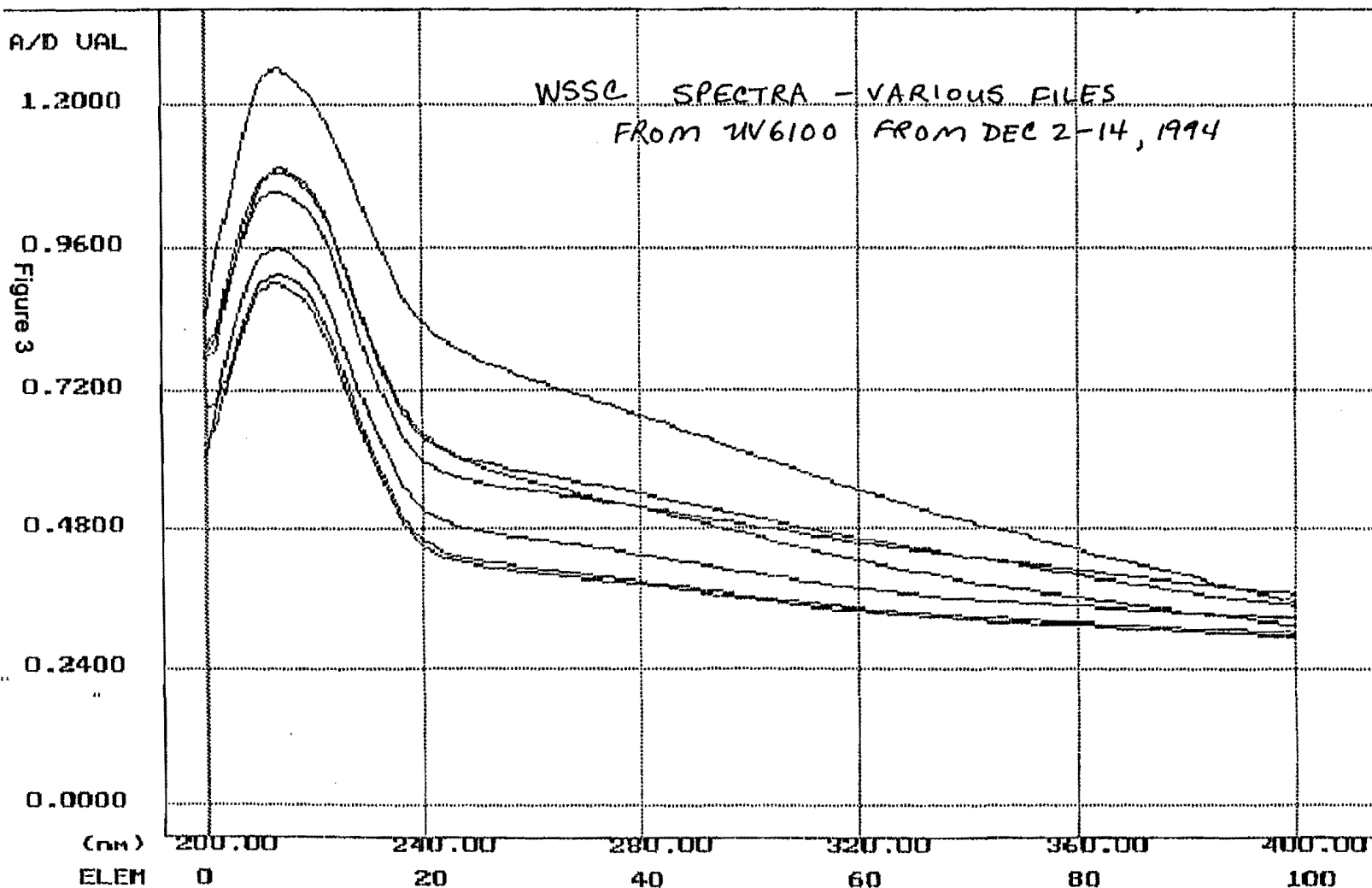
RUN NUMBER:

TIME BETWEEN RUNS:



FILE 1: ws114a01.cst
FILE 2: ws114a02.cst
FILE 3: ws114a03.cst
FILE 4: ws114a04.cst
FILE 5: ws114a05.cst

FILE 6: ws114a12.cst
FILE 7: ws114a20.cst
FILE 8:
FILE 9:
FILE 10:



UV-6100 Initial Calibration

An on-line multiple wavelength absorbance spectrometer, such as the ChemScan UV-6100 requires a "multivariate calibration", which is the result of a correlation analysis from a large number of samples with known concentrations of the chemical of interest (a learning set). Construction of a learning set for calibration to detect NOM presented some unusual challenges. NOM is not one specific chemical substance but a combination of naturally occurring substances which can change in concentration seasonally and day to day as weather conditions change. The background characteristics of raw surface water can also change rapidly with weather, principally affecting the turbidity and the concentration of minerals and/or nutrients in the water.

The ChemScan UV-6100 system is designed to detect 256 wavelengths of information from 200 nm to 450 nm. Visible wavelengths are used as a reference to eliminate the effects of changes in sample turbidity from each measurement made by the analyzer. The principal variables were therefore the chemical substance of interest (NOM) and the sample background (everything else). Multivariate calibrations do not require exact knowledge of all chemical constituents in the sample, as long as the constituents of interest are known and samples with a representative background are included in the learning set.

Standards were prepared using tannic and humic acids in known concentrations. Concentrations were denominated based on the organic carbon content of the standard. The standards were processed through the UV-6100 system and the overall absorbance pattern for the standard was recorded. A file of information from the organic acid standards was used to compile an initial calibration for the UV-6100 system.

UV-6100 Site Specific Calibration

During an initial period of on-line operation, WSSC personnel were instructed to grab samples that had passed through the on-line analyzer and to simultaneously initiate, the analyzer's "record sample" memory to build a file of site specific absorbance signatures that could be matched with TOC results from laboratory analysis of the samples.

The information from the initial round of grab samples was added to the file containing information from the analysis of standards, to produce an updated calibration containing baseline and site specific information. On December 15, 1994 this "new" calibration was installed in the on-line analyzer. The original "old" calibration was also used on a separate output channel for comparison purposes.

Correlation within the learning set for the new calibration was very high as shown on Figure 4.

On-Line NOM Results

The UV-6100 was operated to provide an analysis of NOM every 20 minutes using a sample line connected to the raw intake water for the west side of the plant. Figure 5 shows a graph of "TOC equivalent" values for NOM from the UV-6100 system for a period from January 17, 1995 to February 8, 1995.

Periodic grab samples were extracted and subjected to laboratory TOC analysis throughout the demonstration period. A comparison of on-line vs. laboratory results is shown on Figure 6 for the period from December 2, 1994 through January 12, 1995. The figures from December 2 to

UPDATED WSSC CAL (DEC 15, WSCAL04B.CL2)

R2=0.997, AVG RES=0.099, T=183.0

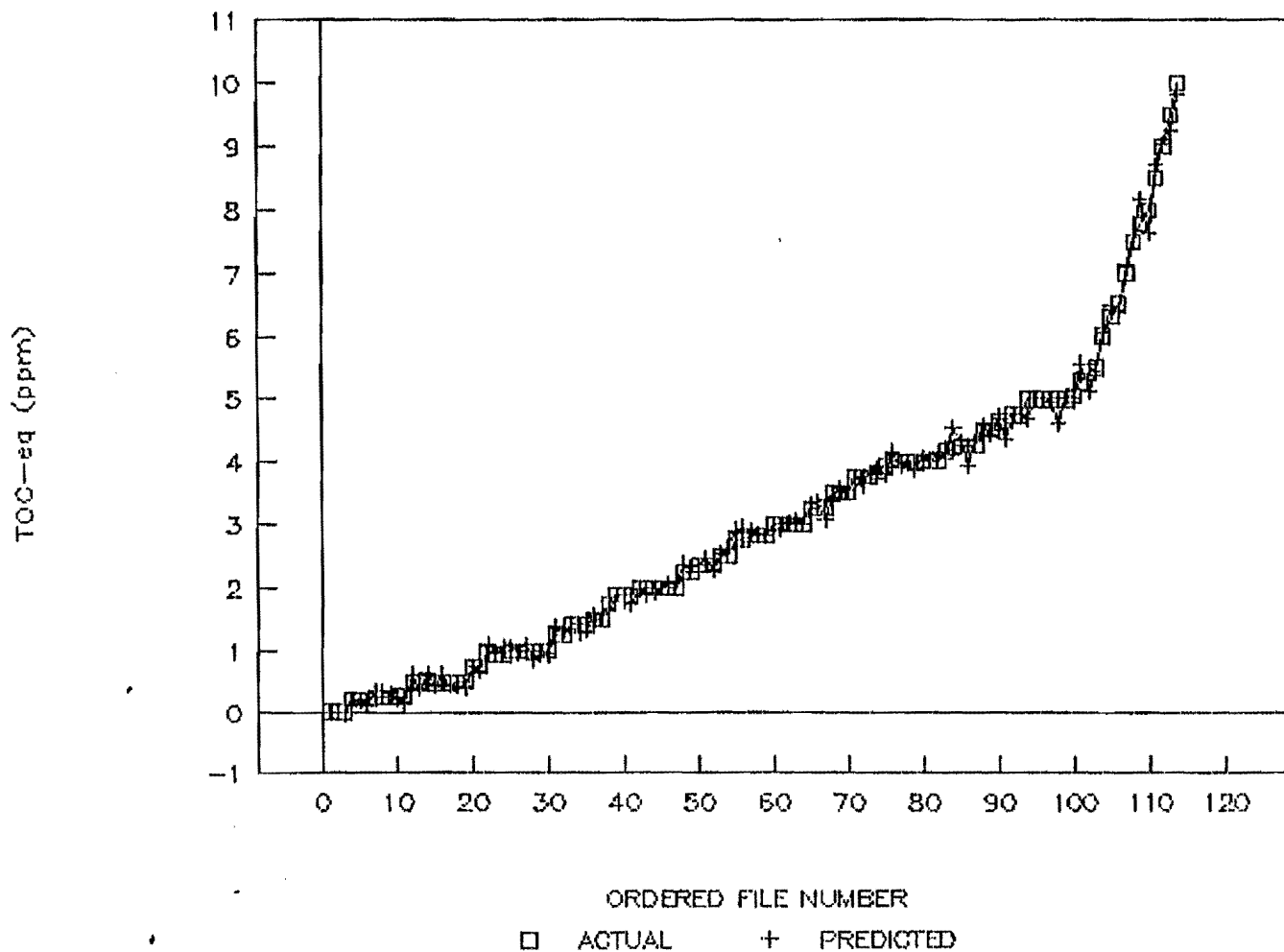


Figure 4

WSSC DEMO — TOC(eq) via UV6100

WSCAL04B (DEC15 UPDATE)

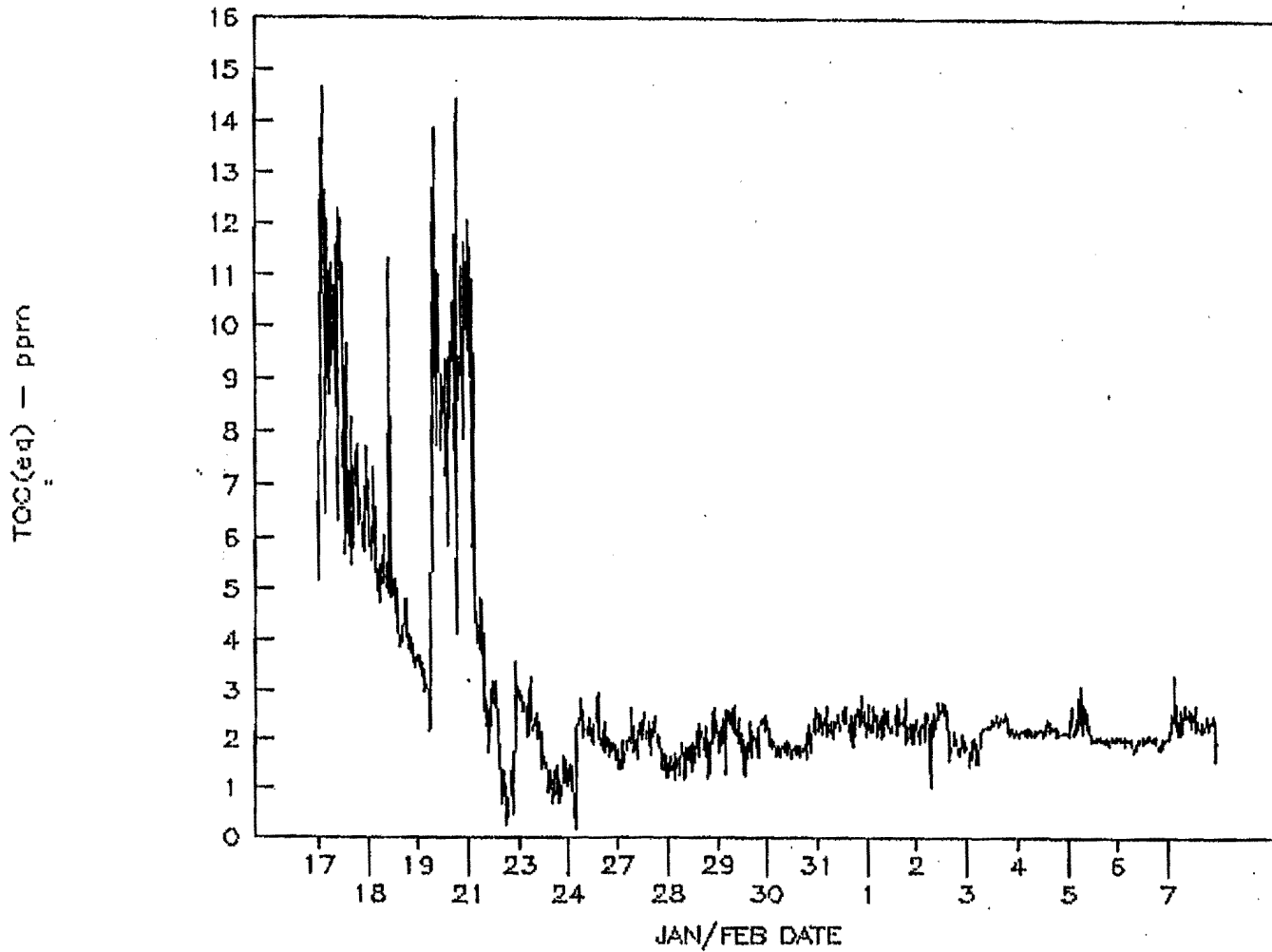


Figure 5

UV6100 – WSSC NOM DEMONSTRATION

DEC 94 – JAN 95

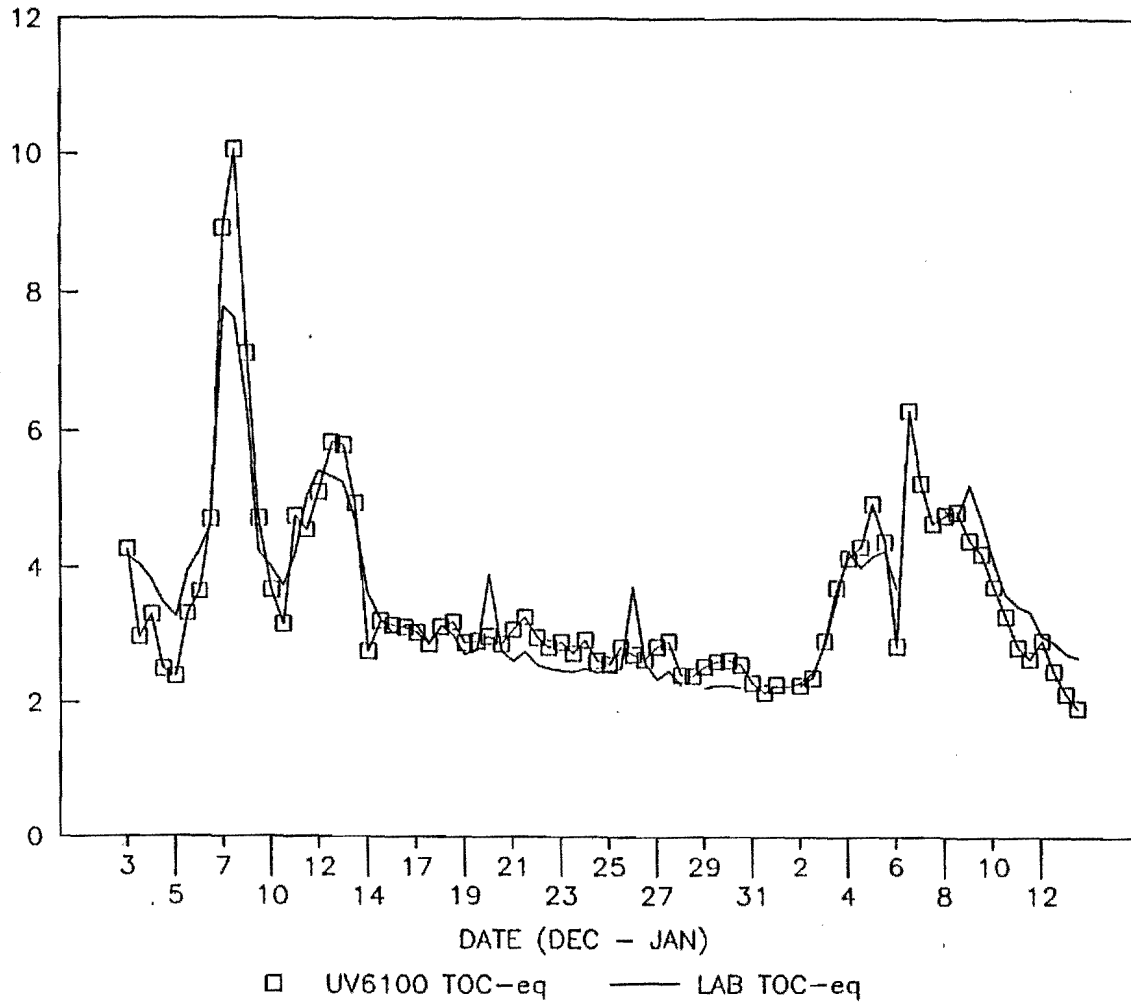


Figure 6
TOC-eq (ppm)

December 15 are based on a comparison with the "old" calibration (standards only) while the period after December 15 is based on comparison with the "new" calibration (standards plus site samples). Comparisons show excellent correlation (R^2 above 0.90) and very good "tracking" (ability to follow the ups and downs of TOC equivalent concentration) for this period.

On-Line Issues

The demonstration was adversely affected by several events. Heavy rains during the early January period produced very high concentrations of particulate matter in the raw water. Concentrations were much in excess of the normal 150 ppm limit for ChemScan to operate without prior sample filtration. The high particulate concentration plugged the flow through cell, requiring disassembly and physical cleaning of the cell.

As water temperature dropped during January and February, the cold water samples flowing through the much warmer analyzer (located at the sample taps in the WSSC laboratory) produced condensation on the windows connecting the detection optics to the flow cell. This problem was corrected through the use of a desiccant adjacent to the optical windows.

During February, WSSC began to add $KMnO_4$ at the raw water intake points. Since this chemical has very strong light absorbance characteristics in the ultraviolet and visible wavelength range, a revised calibration should have been made to account for this new background chemical. In addition $KMnO_4$ will stain quartz glassware after a sufficient period of direct contact. The addition of $KMnO_4$ at WSSC caused the windows on the flow cell to develop a film that required frequent chemical and physical cleaning. Had the use of $KMnO_4$ been anticipated, the instrument could have included an automatic manifold to automate the zeroing and cleaning task and to minimize fouling by flushing the flow cell with finished water prior to the idle period between readings.

Other Results Achieved

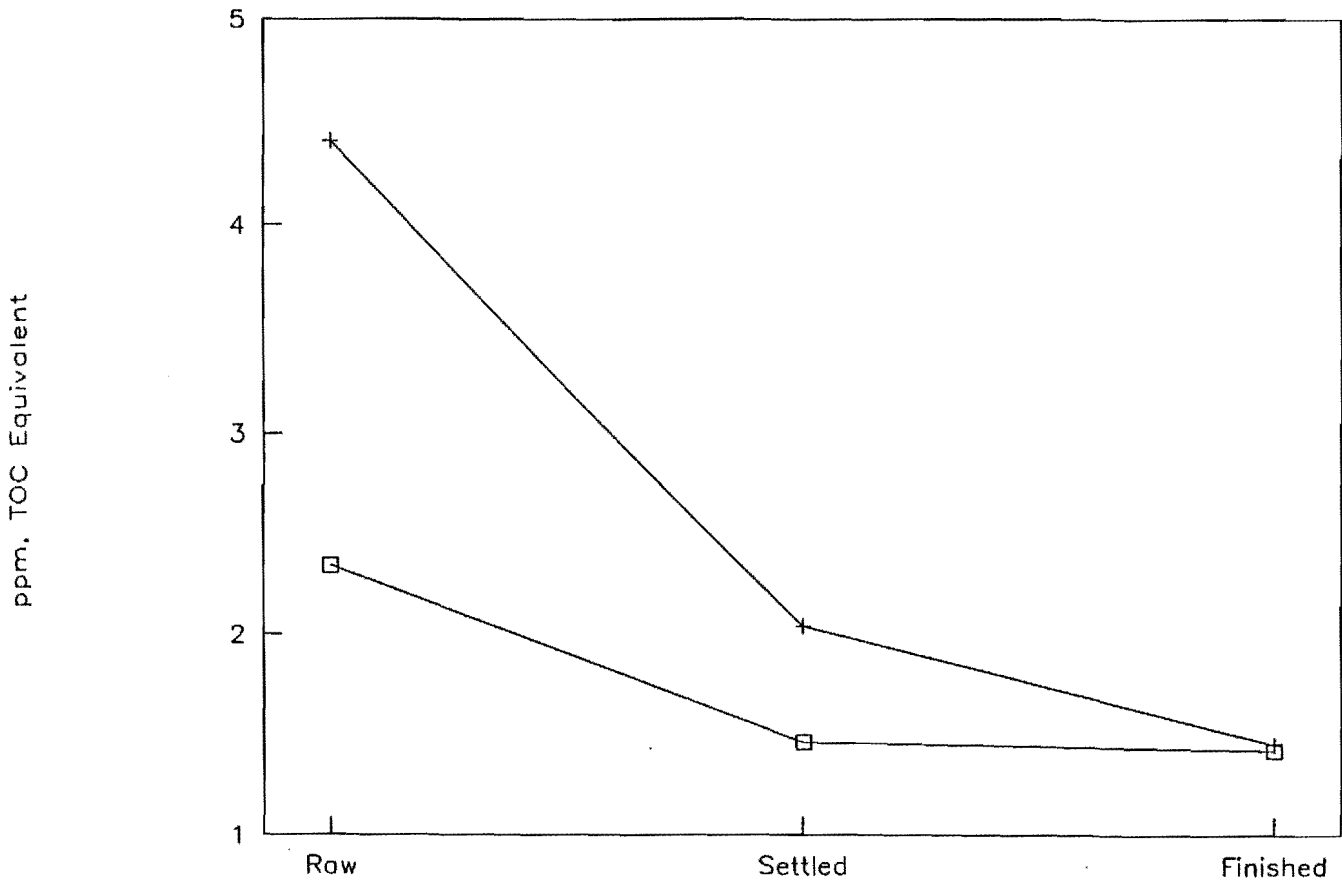
A determination was made concerning possible correlation of the on-line TOC equivalent values for NOM with turbidity variations in the samples. The NTU values for each grab sample was recorded using independent measurements from an on-line turbidity analyzer. These values were correlated with values from the on-line NOM analysis. This analysis verified that the on-line NOM analysis was independent of the turbidity variations in the sample. While the degree of agreement (R^2) between on-line NOM and laboratory TOC was very high (in excess of 0.90), the agreement between on-line NOM and NTU turbidity was much lower (under 0.70).

The UV-6100 instrument was located at the sample taps in the WSSC laboratory. These taps provided ready access to raw, settled and finished (filtered) samples from both the east side and west side of the Potomac plant. It was therefore very easy to take the UV-6100 system off-line, and use the system for analysis of grab samples from each stage of the treatment process for each side of the plant. Experiments were periodically performed to process and record the TOC equivalent concentrations for a series of samples to show the NOM removal through the process. In a permanent installation, a manifold could be used to automatically switch between these sample points.

Examples of the results from these experiments can be seen in Figures 7 and 8. Figure 7 shows a lower raw water NOM concentration on the east side of the plant, with some reduction through PAC coagulation. The west side has much higher NOM concentration and a substantial reduction through ferric coagulation. Some additional NOM removal is accomplished through filtration on the

WSSC Potomac Plant

Unit Process NOM Removal



ChemScan Analysis, 9:25 AM, 1-13-95

□ East, PAC + West, Ferric

Figure 7

west side, but not much additional removal was accomplished in the east. Finished water concentrations were similar.

Figure 8 shows a different pattern during February, with similar starting concentrations, substantial reduction in the east using PAC but very little in the west using ferric. A substantial NOM reduction in the west was experienced through filtration, with finished waters ending up with similar NOM concentration.

These experiments also verified the independence of the NOM analysis from turbidity, with very poor (under 0.50) correlation between NTU values and the on-line NOM values.

Because the full absorbance spectra from 200 nm to 450 nm was recorded for many of the samples extracted at WSSC, an attempt was made to construct a turbidity specific calibration for the UV-6100 using a different set of wavelengths than were used for on-line NOM analysis.

Results from this analysis can be seen in Figure 9, with good agreement (R^2 of 0.89) between the on-line (predicted) turbidity values and the turbidity values for samples recorded from an independent on-line turbidity analyzer.

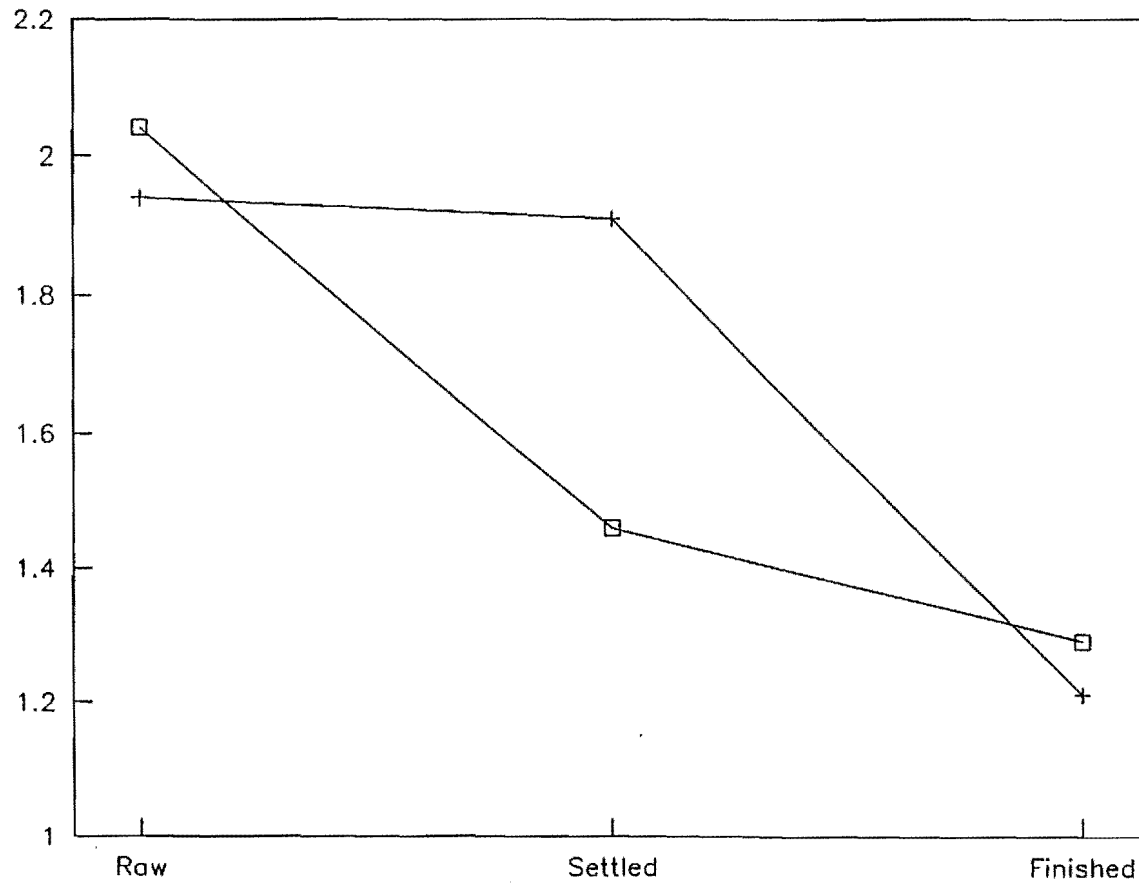
Conclusion

The UV-6100 Process Analyzer was demonstrated to be capable of performing a direct on-line analysis of Natural Organic Material in raw and process water samples under normal conditions, with results showing a strong correlation with laboratory TOC analysis and independence from turbidity variations. Some interference problems from high solids and new treatment chemicals were noted and could be overcome through the use of appropriate calibration and a sample control manifold, including more frequent automatic zeroing and cleaning.

The analyzer was also shown to be capable of performing on-line turbidity analysis, with results similar to those from other on-line turbidity analyzers.

WSSC Potomac Plant

Unit Process NOM Removal



ChemScan Analysis, 5:02, 2-21-95

□ - East, PAC + West, Ferric

Figure 8

WSSC TURBIDITY VIA UV6100

TURB07.CL2, DATA FROM DEC 2 - 14

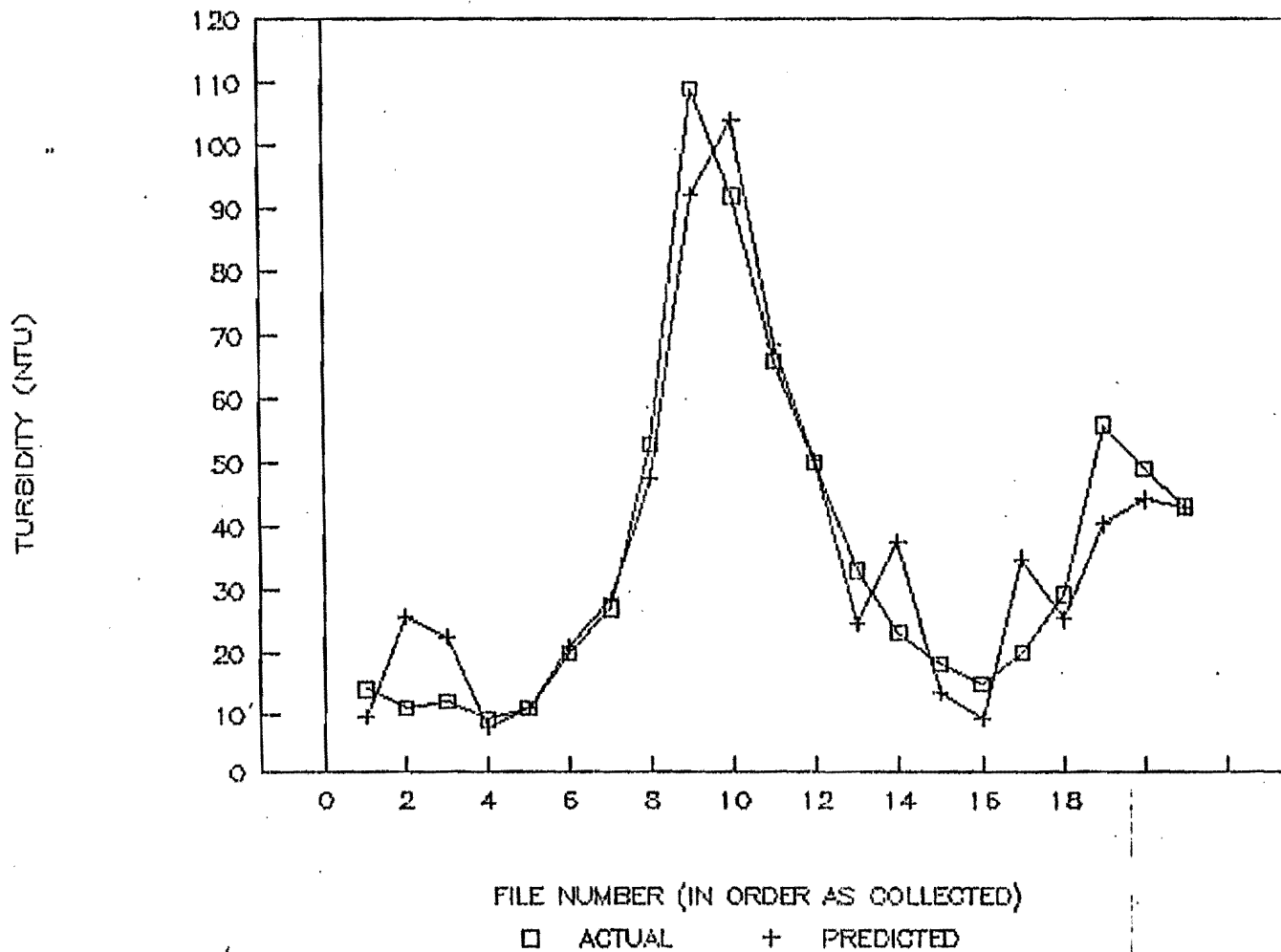


Figure 9