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SRL ONLINE ANALYTICAL DEVELOPMENT (U)

by

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Savannah River Site
Aiken, South Carolina 29808

A presentation proposed to be presented at the
IAB Technical Monitor Meeting
Bellevue, Washington
November 7, 1991

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PRESENTATION TO THE CENTER FOR PROCESS ANALYTICAL CHEMISTRY IAB/TECHNICAL MONITOR MEETING, SPONSOR SYMPOSIUM, BELLEVUE WASHINGTON, NOVEMBER 7, 1991 (U)

- C. Wayne Jenkins

The Savannah River Site is operated by the Westinghouse Savannah River Co. for the Department of Energy to produce special nuclear materials for defense. R&D support for site programs is provided by the Savannah River Laboratory, which I represent.

The site is known primarily for its nuclear reactors, but actually three fourths of the efforts at the site are devoted to fuel/target fabrication, fuel/target reprocessing, and waste management. All of these operations rely heavily on chemical processes. The site is therefore a large chemical plant. There are then many potential applications for process analytical chemistry at SRS.

The SRL has an Analytical Development Section of roughly 65 personnel that perform analyses for R&D efforts at the lab, act as backup to the site Analytical Laboratories Department and develop analytical methods and instruments. I manage a subgroup of the Analytical Development Section called the Process Control & Analyzer Development Group. The Prime mission of this group is to development online/at-line analytical systems for site applications.

Today I will discuss three systems that the PC&AD Group is working on to give you an idea of some of our efforts, progress and problems in process analytical chemistry work: absorption spectroscopy, approaches to online hydrogen measurement and high quality gas analysis by Laser Raman spectroscopy.

For nearly 10 years a group led by Pat O'Rourke has been developing an online absorption spectroscopy system. The system is composed of an xenon arc lamp light source, fiber optic cables, a multiplexer, sample interfaces or probes, a spectrophotometer (normally a diode array in the uv/visible) and a computer running chemometric software. The multiplexer allows connection to several different sample locations to the same spectrophotometer as well as to a standard and reference. The system continually checks a reference cell to make corrections for changes in performance of the system as a whole due to variations in the lamp, fibers, coatings on the sample

cells, etc. It also continually checks the standard as a QA check and will give an error message if the standard is out of limits. With the diode array spectrophotometer the system takes a spectrum every 0.1 seconds, averages several and uses the chemometric software with its calibration set of spectra to deconvolute the spectral data into a concentration value for the analyte of interest.

We have found the system to be easy to install, since all that sees the process is a small sample cell, and reliable. The cables are pulled just like electrical cable. The only problem to date has been with the computer.

The sample cell is a critical part of the system. Here are some configurations. They are simple and rugged. Here is a moving mirror probe that we plan to test in a monitoring well at SRS. You can see the screen around the cell to keep sand out. We will be monitoring several wells for a dye injected in another well to determine the hydraulic characteristics of an environmental remediation site.

One of the installed applications is for the measurement of uranyl nitrate. We can measure uranium to 2% accuracy and 0.05% precision, nitrate to 0.1M with 0.05% precision over the range 0.05 to 8M.

Another application is the measurement of acid concentration in actinide streams. This shows the effectiveness of a chemometric model for measuring nitric acid in the near infrared. An NIR spectrometer with a lead sulfide detector was used . Of course what we are measuring in the NIR is the response of the water cage around the H+ ion. In a more complex matrix containing nitric acid, sulfuric acid and aluminum nitrate, we get not as good a prediction, but still not bad. This is sufficient for our purpose, which is for use as an online monitor and interlock system to prevent sending high acid to ion exchange columns. We will actually use this system in streams containing plutonium. Adding Plutonium to the matrix increases the error of acid prediction by 0.1M. This is still acceptable, but we hope to improve by changing to an indium-gallium-arsenide detector and doing more calibration work with plutonium standards.

We also have a system using NIR to measure the quality of D2O moderator. We have demonstrated excellent precision. Here we are actually measuring the amount of H20 impurity in the D20 since D20 is transparent to the NIR but H2O absorbs strongly.

We continue to improve this system. Present work includes an effort to reduce the size of the package, work with AOTF devices and increasing the probes or sample probe capabilities. Here is an in-tank probe that uses a moving mirror to alternate between sample measurement and referencing. The mirror is down for sample measurement; a blast of air or process fluid forces the mirror up for a reference measurement. Here is another mirror probe that moves the mirror to any desired pathlength using a high precision stepper motor.

One area that we are pursuing strongly is the development of in-situ sensors for use with the system. We have been successful in making pH sensors by binding a polymer to the fiber optic lens and trapping an indicator in the polymer. Using bromophenol blue as the indicator trapped in a polybenzimidazole matrix we had a sensor that responded well in the 3-6 pH range, but the indicator leached out at pH 7 and above. We have been working on development of pH and metal ion sensors. We have Prof. N. Datta-Gupta of South Carolina State University under contract to work on synthesis of porphyrins for metal detection. He has collected unique spectra of various metal ions bound to porphyrins in solution. Now we need a way to bind the porphyrins to a fiber optic lens. Due to our past experience with indicators leaching from polymer matrices, we feel that we need a direct binding of the porphyrin directly to the lens. We also are seeking to work with Prof. Bruce King of the University of Georgia on the problem of binding indicators to glass.

Needs in the absorption spectroscopy area: someone to build probes, market entire systems, indicators that will attach to lenses.

One of the problems that we find in many of the site processes is the need to monitor for hydrogen in hostile environments containing water vapor and NOx. This doesn't sound so hard but we have found nothing that will do the job reliably. We are working to install process GC's in some critical applications, but we really don't think that is the way to go long term. We want something reliable and trouble free.

One of the efforts to solve the hydrogen problem is the development of a palladium based sensor. We have been working with Bob Lauf at ORNL on the use of a resistance bridge device that takes advantage of the fact that palladium changes electrical resistance when exposed to hydrogen. One leg of the bridge is exposed while the other three are

masked. 15 volts potential is put across the bridge and the voltage is measured across the midpoint.

This slide shows that when the bridge is exposed to 2% hydrogen in nitrogen, 90% of maximum response is reached in 94 seconds. If you take the derivative of that response you get a sharp signal within a few seconds that comes and recovers in 25 seconds. This would appear to be the basis for a simple sensor. However the signal to noise is not good. You would have a hard time seeing 0.2%. This experiment should go better at elevated temperature, around 130 C. The repeatability should be better since there would be less of an effect from phase change in the palladium due to the absorption of the hydrogen. What we have found is that the condition of the surface of the palladium is much more important. Any reactive gases affect the response.

Therefore NOx is still a problem. This sample exposed to 90% NOx slowed the response to 2% hydrogen in nitrogen. However, the exposure to the hydrogen acts to clean the surface and will return the sensor to its original response characteristics. It still may be possible to use such a sensor in NOx environment by alternating exposure to sample gas and a cleaning gas mixture. However, what is clearly needed is a good filter to let the hydrogen through and not the NOx. We haven't found one yet and when you do, some of the other means of hydrogen measurement may work also. This approach does have the advantage of simplicity and ruggedness.

Another hydrogen technique that we are looking at that has the advantage of not caring what gases are present is online laser Raman. We are working with a system that uses fibers to both transmit the laser light and to return the signal. To make a Raman system cost effective will have to be able to multiplex the instrument through fibers to several sample locations. A single fiber caries the laser light and as many as six fibers bundled around the laser fiber pickup the scattered light and return it to the detector. Actually we use a diode array spectrophotometer as a detector.

In this experiment we just looked in the air for nitrogen, which will act the same as hydrogen to the Raman. Although the signal to noise is not good considering we would be looking for hydrogen below 4% instead of 70%, if we increase the laser power to 5 watts and use 6 pickup fibers, then hopefully we would have a 4% hydrogen signal that would look much like this. We need rugged, more compact and cheaper lasers to make this system viable.

The last effort that I wanted to mention also involves laser Raman. One of our site products is tritium gas, which is produced to meet very stringent and varied isotopic composition requirements. These composition measurements are currently made by high resolution mass spectrometers off-line or in some cases coupled to the process by manifolds, piping and sample valves. In the best cases analyses can be performed in 30 minutes. There are needs that require much faster analysis. Also, in the heavy water design of the proposed New Production Reactor there is a need to perform isotopic analysis of hydrogen, duterium and tritium gas mixtures for process control that lend themselves to online monitoring.

We have been working with online laser Raman for these applications where more accuracy and sensitivity is needed than in the previously discussed hydrogen monitoring case. Bob Sherman at LANL has shown that laser Raman can duplicate the accuracy and precision of mass spectroscopy for hydrogen isotope measurement in an off-line situation.We have been able to get very good preliminary results using a high pressure inline cell and fiber optic cable to deliver the laser light (but not to collect the signal). As you can see, The resolution of the different isotopes and the signal to noise in this experiment are quite good. To optimize this as an online method we need smaller, cheaper laser systems, which are being introduced all the time, because space is usually a concern in the very expensive buildings that are required to house the kind of processes that we deal with. Also we need cheaper detector systems. To get the performance needed we can not use fibers to pickup the signals from several sample points; so a separate detector will be required at each sample location.

To summarize some of our needs:

Spectrophotometry- we need binding chemistry for applying indicators to glass lenses; indicator molecules designed for better selectivity. Let me add my personal opinion that we need a cadre of graduate students working in this area because the development of very simple, rugged, selective sensors is there for the taking if the effort is put forth. We need better light sources with greater brightness in the uv or better filters that will for example blot out mercury lines. Improved infrared hardware: rapid scanning, rugged, lower cost with greater wavelength range. We also need someone to market lens equipped fibers and the various pieces of sample cell hardware and fiber optic multiplexed spectrophotometer systems as a whole.

Hydrogen measurement - effective filters to transmit hydrogen but not NOx.

Raman - Smaller cheaper lasers; fibers with better transmission in the uv and farther out in the infrared.

General - Compact, simple ways to generate a plasma in gases and liquids to allow in situ emission spectroscopy.

I can not acknowledge all of the people that have and are contributing to the programs that I have mentioned, but let me list some of the primary contacts that you might be interested in talking to if you really want to know something about any of these subjects:

Spectrophotometry - P. E. O'Rourke 803-725-2173
Bruce Buchanan (particularly NIR)
803-725-1963
Lewis Balyor (coated lens indicators)
803-725-1872

Hydrogen sensors - Stanley Nave 803-725-1355

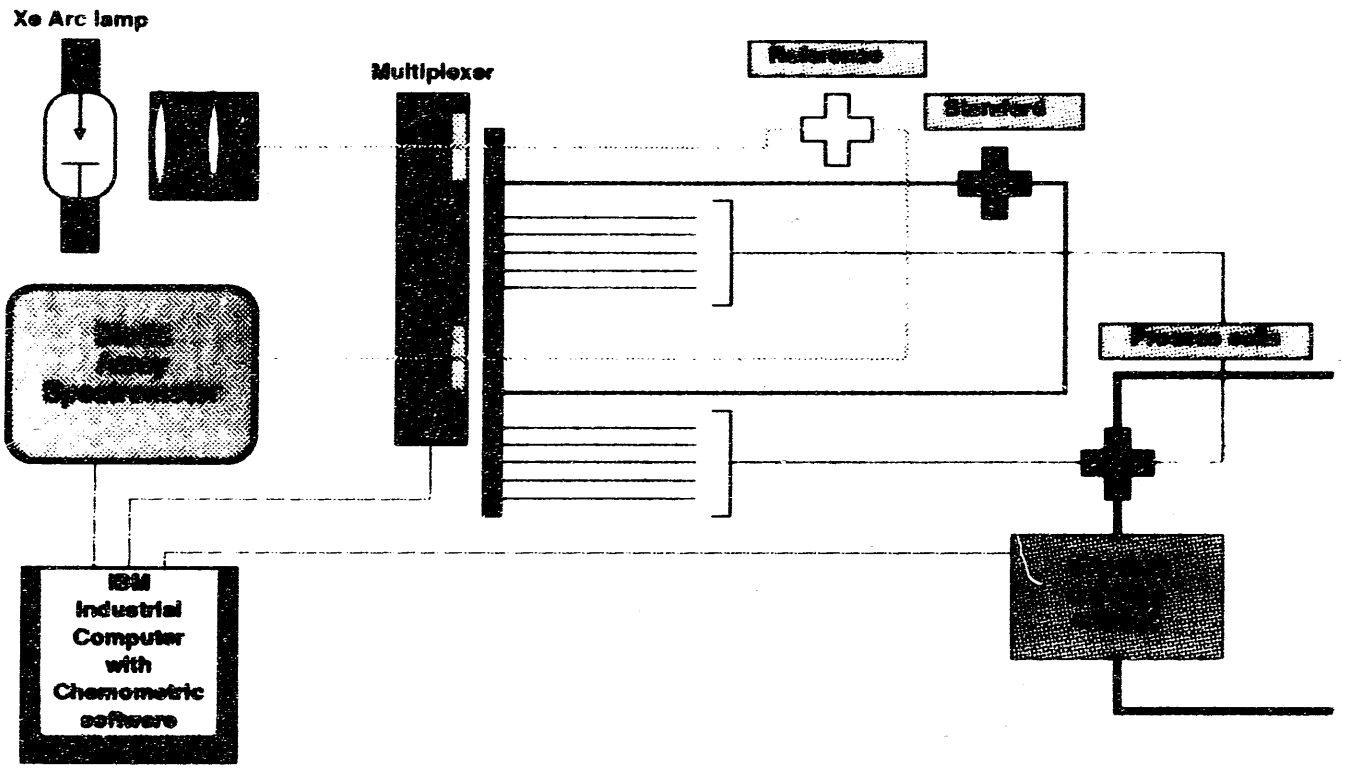
Laser Raman - Bob Malstrom 803-725-3140
O'Rourke
Nave

SAVANNAH RIVER LABORATORY
ONLINE ANALYTICAL DEVELOPMENT (U)

C. WAYNE JENKINS

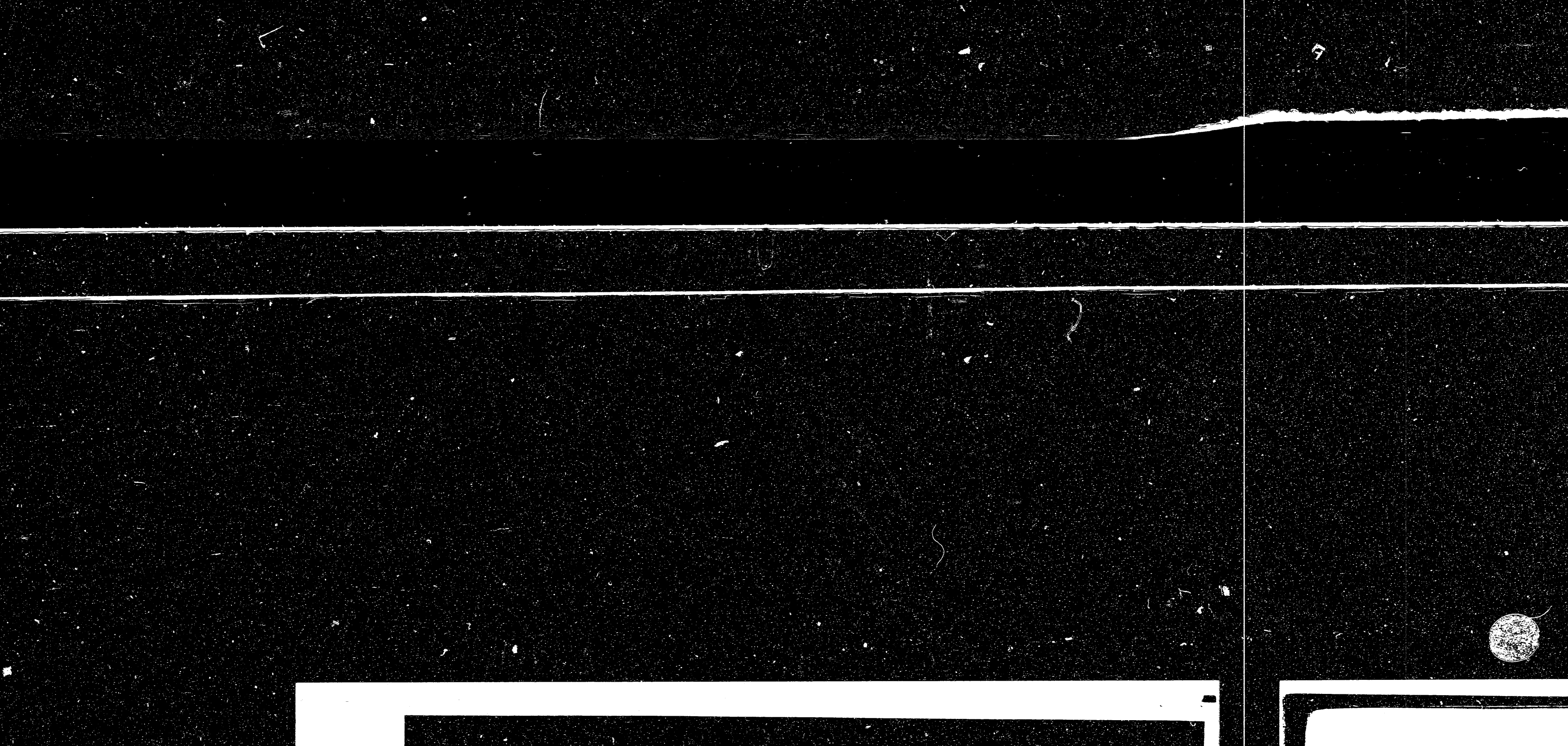
November 7, 1991

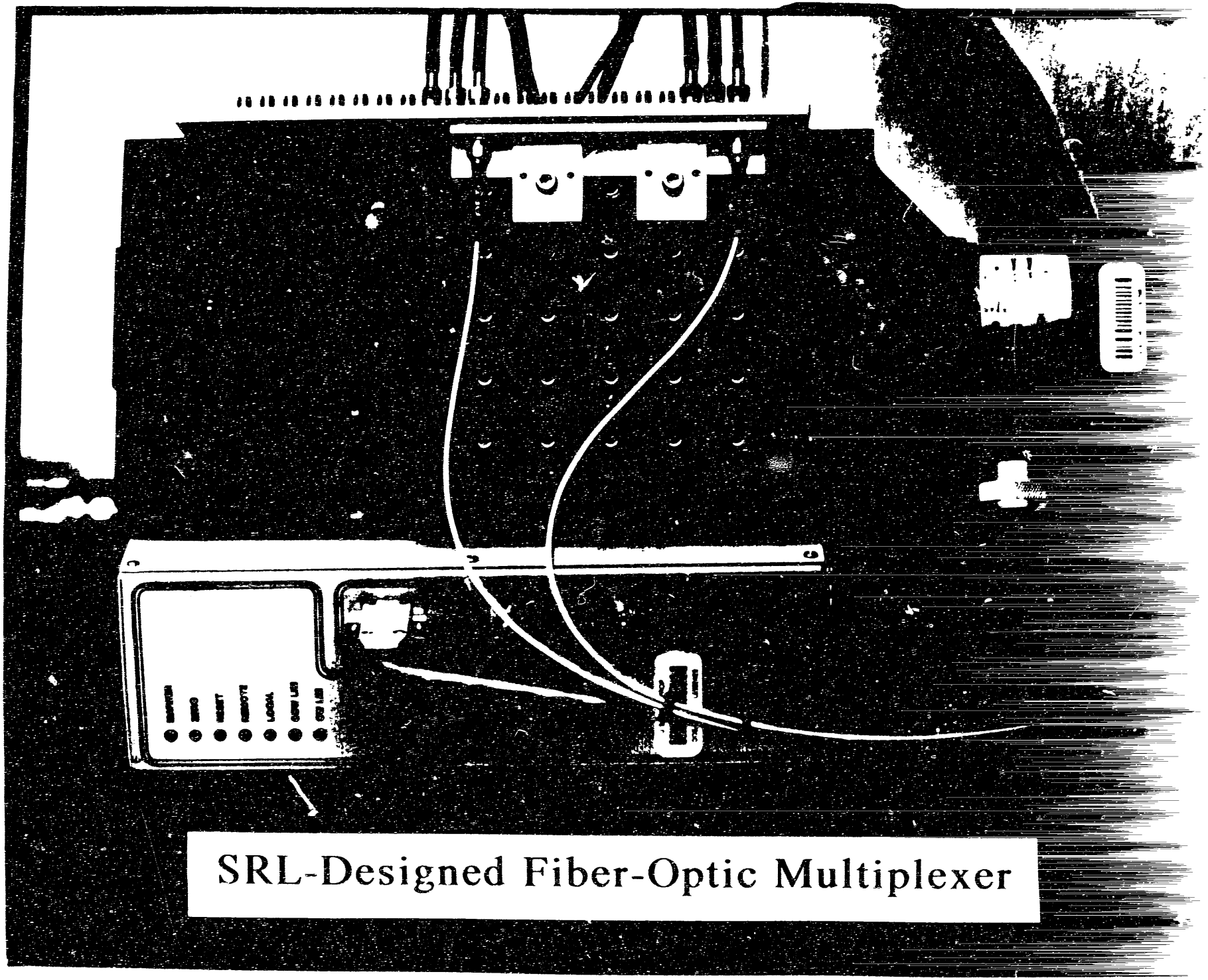
Fiber-optic Spectrophotometer Schematic



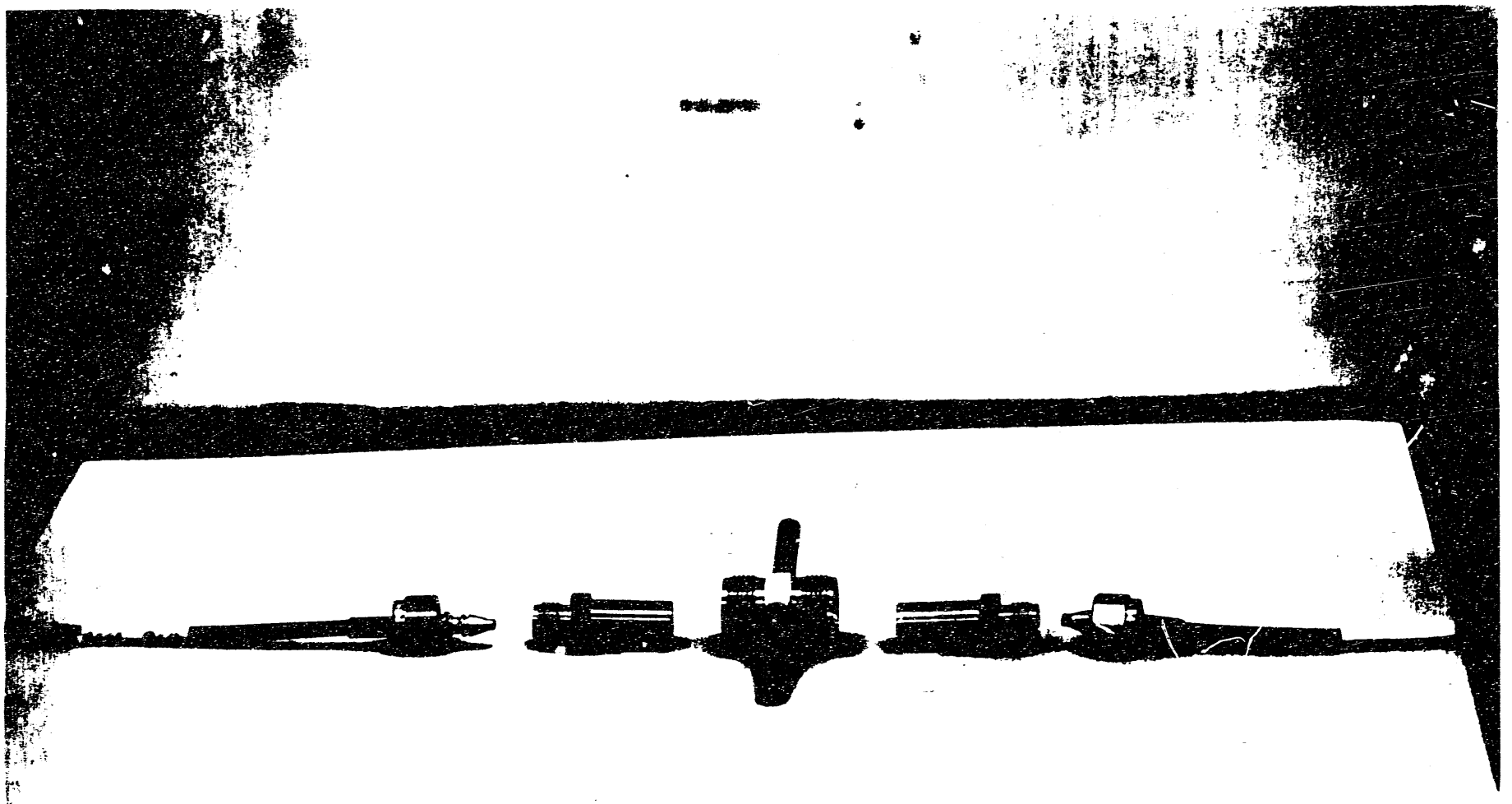
d vrs. Time

80





SRL-Designed Fiber-Optic Multiplexer



316

For nearly 10 years a group
an online absorption spectroscopy system. The system is compose
an xenon arc lamp light source, fiber optic cables, a multiplexer,
sample interfaces or probes, a spectrophotometer (normally a dic
array in the uv/visible) and a computer running chemometric
software. The multiplexer allows connection to several different
sample locations to the same spectrophotometer as well as to a
standard and reference. The system continually checks a reference
cell to make corrections for changes in performance of the system as
a whole due to variations in the lamp, fibers, coatings on the sample

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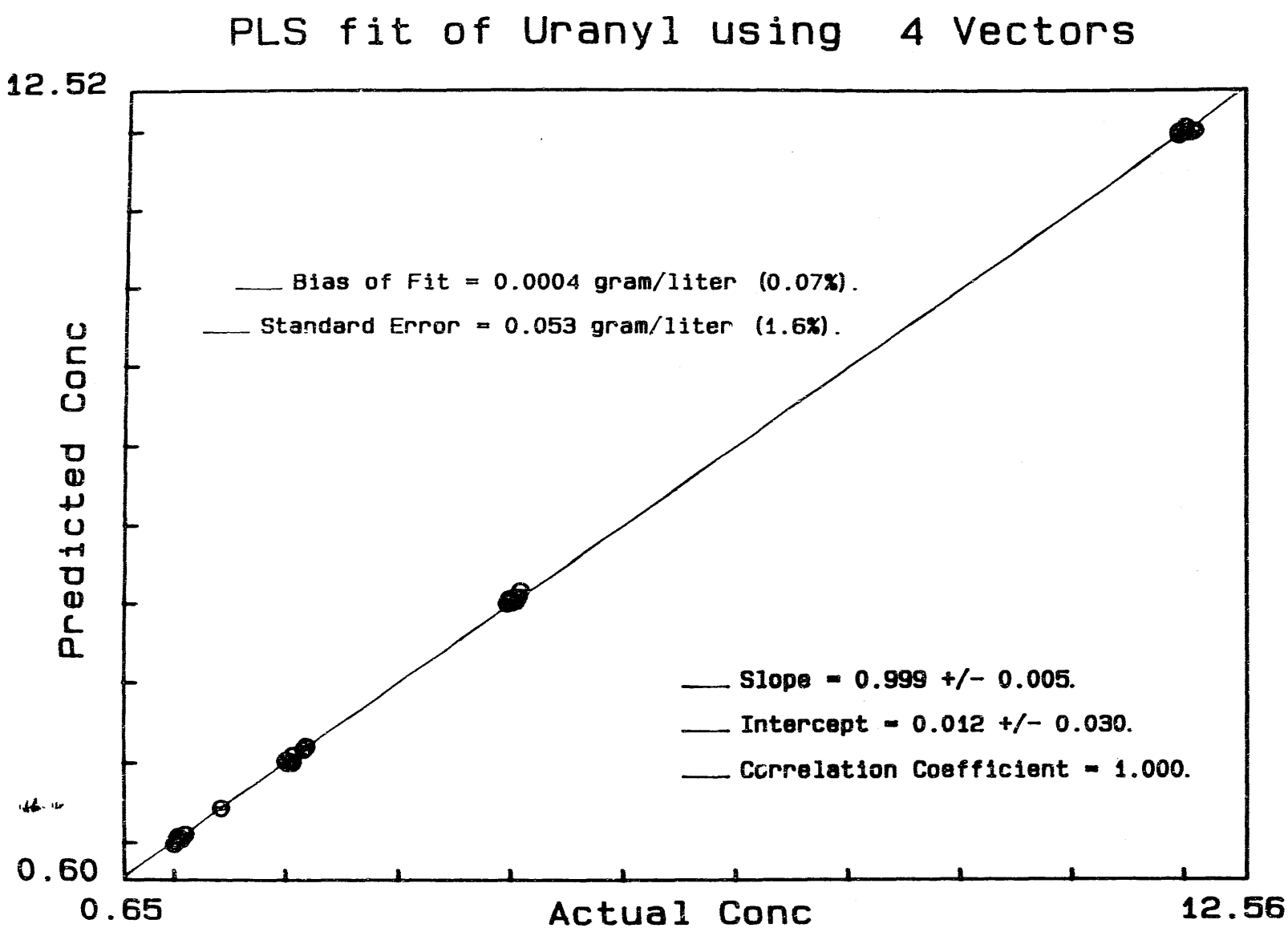
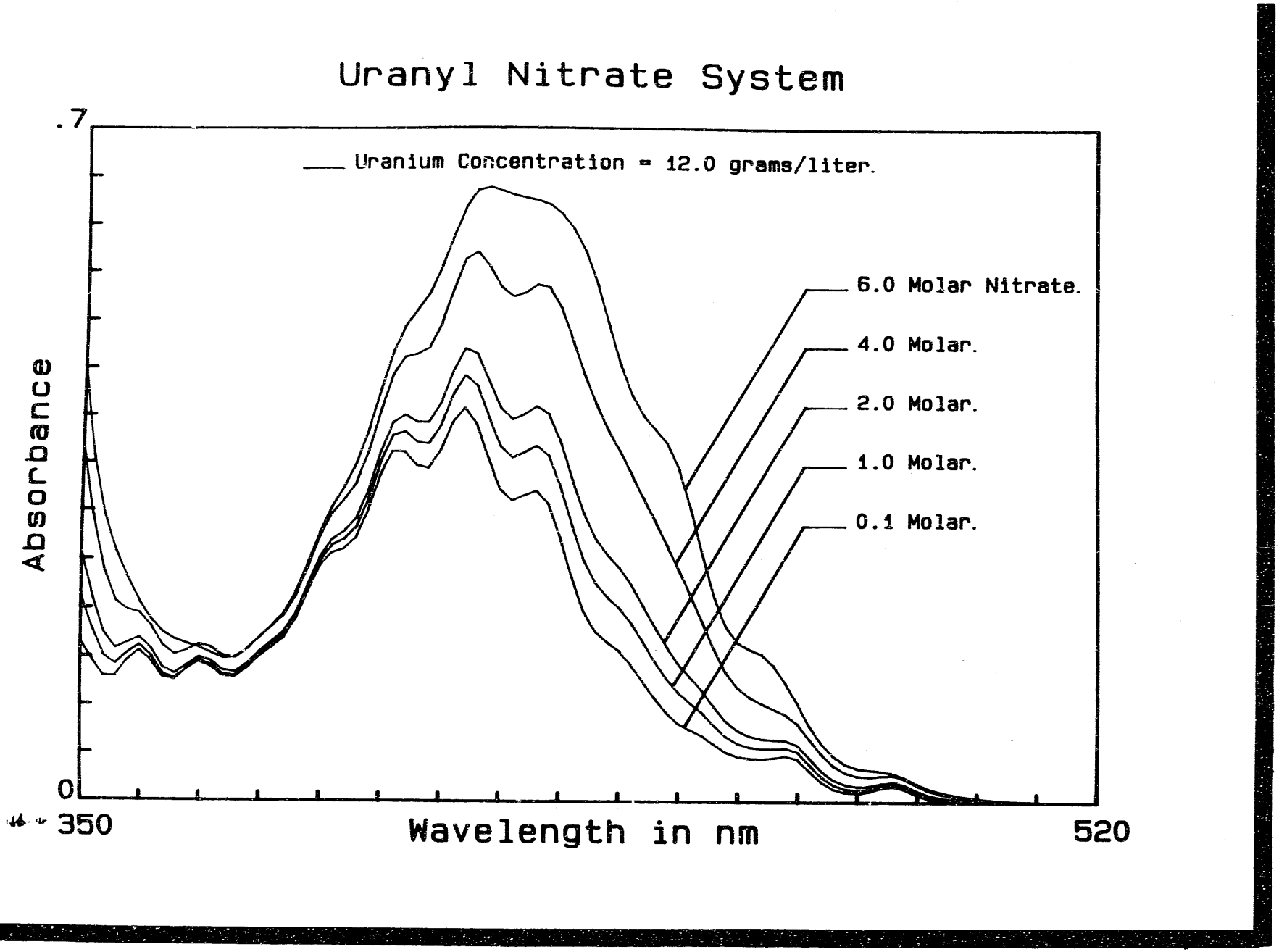
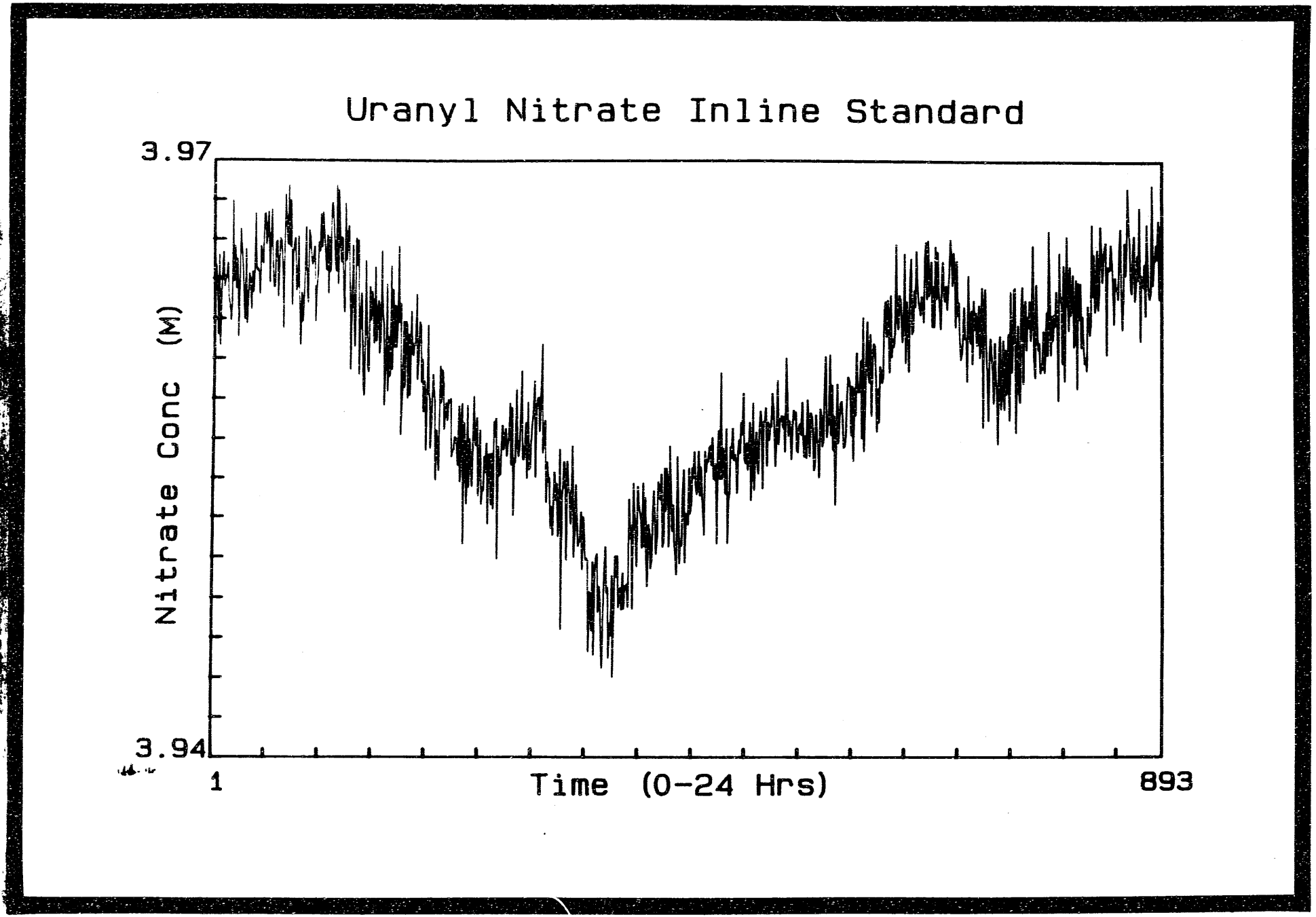


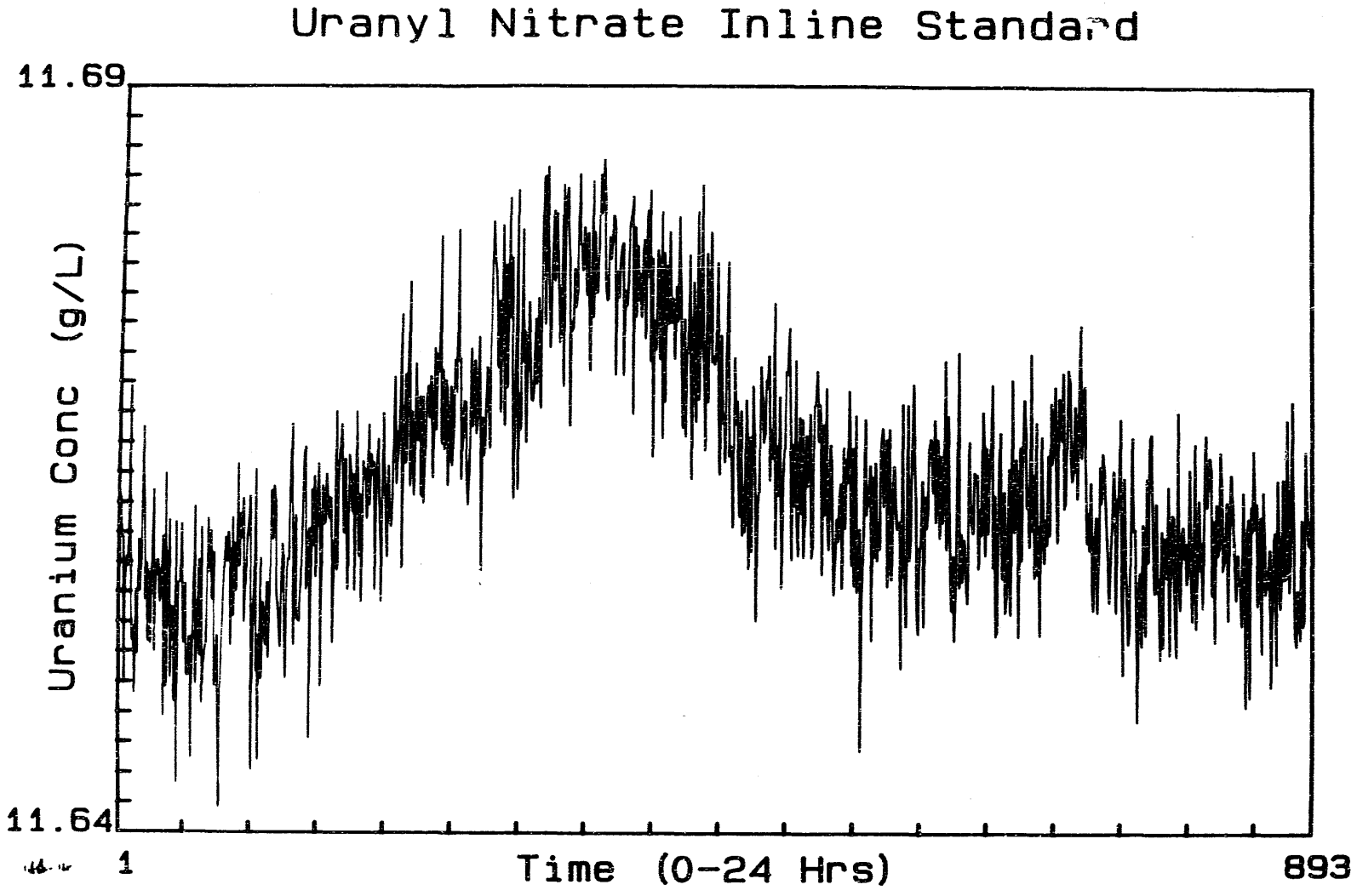
Calibration Curve for Uranyl PLS Model



Effect of Nitric Acid on the UV/Vis Absorption of Uranyl Nitrate



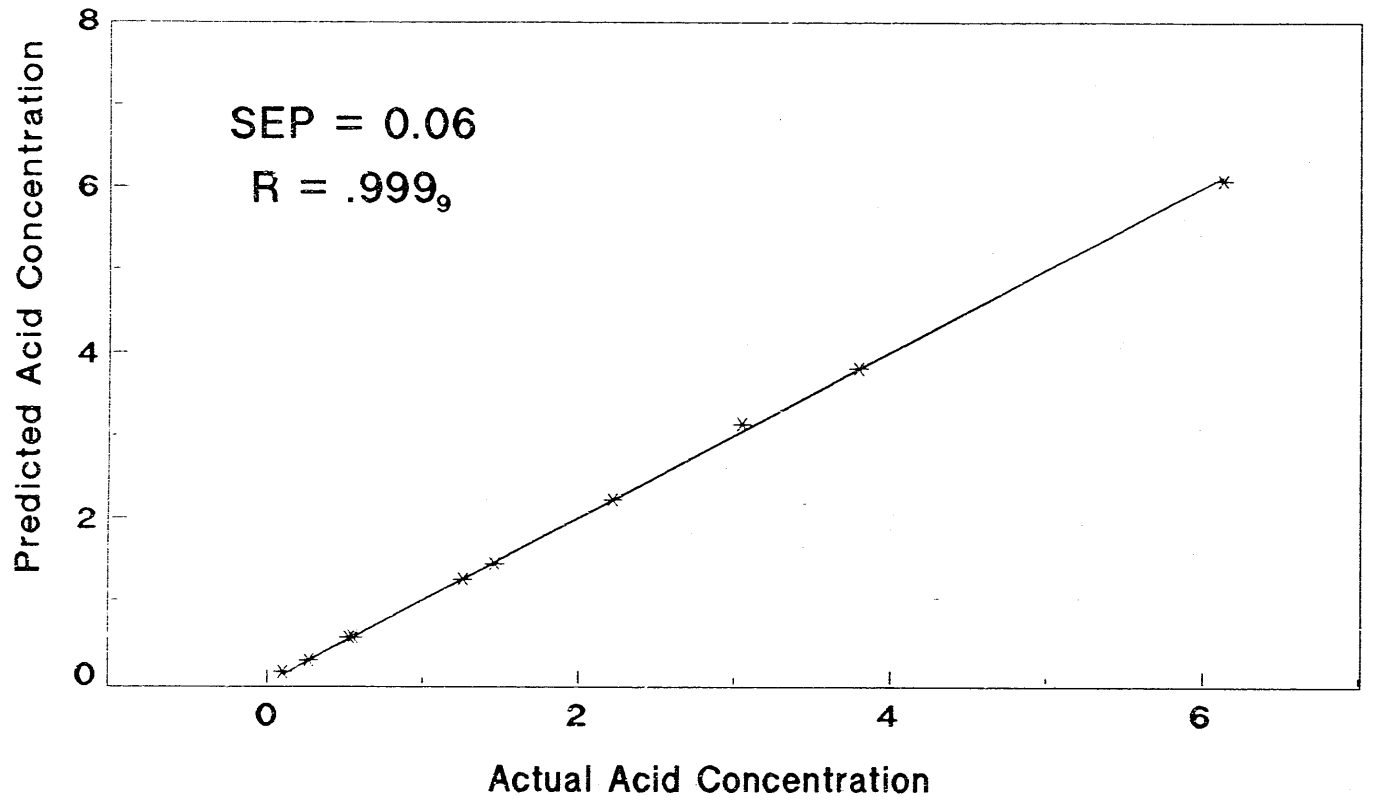
Nitrate Concentration of Inline Uranyl Nitrate Standard



Uranyl Concentration of Inline Uranyl Nitrate Standard

Prediction PCR Model

Only Nitric Acids



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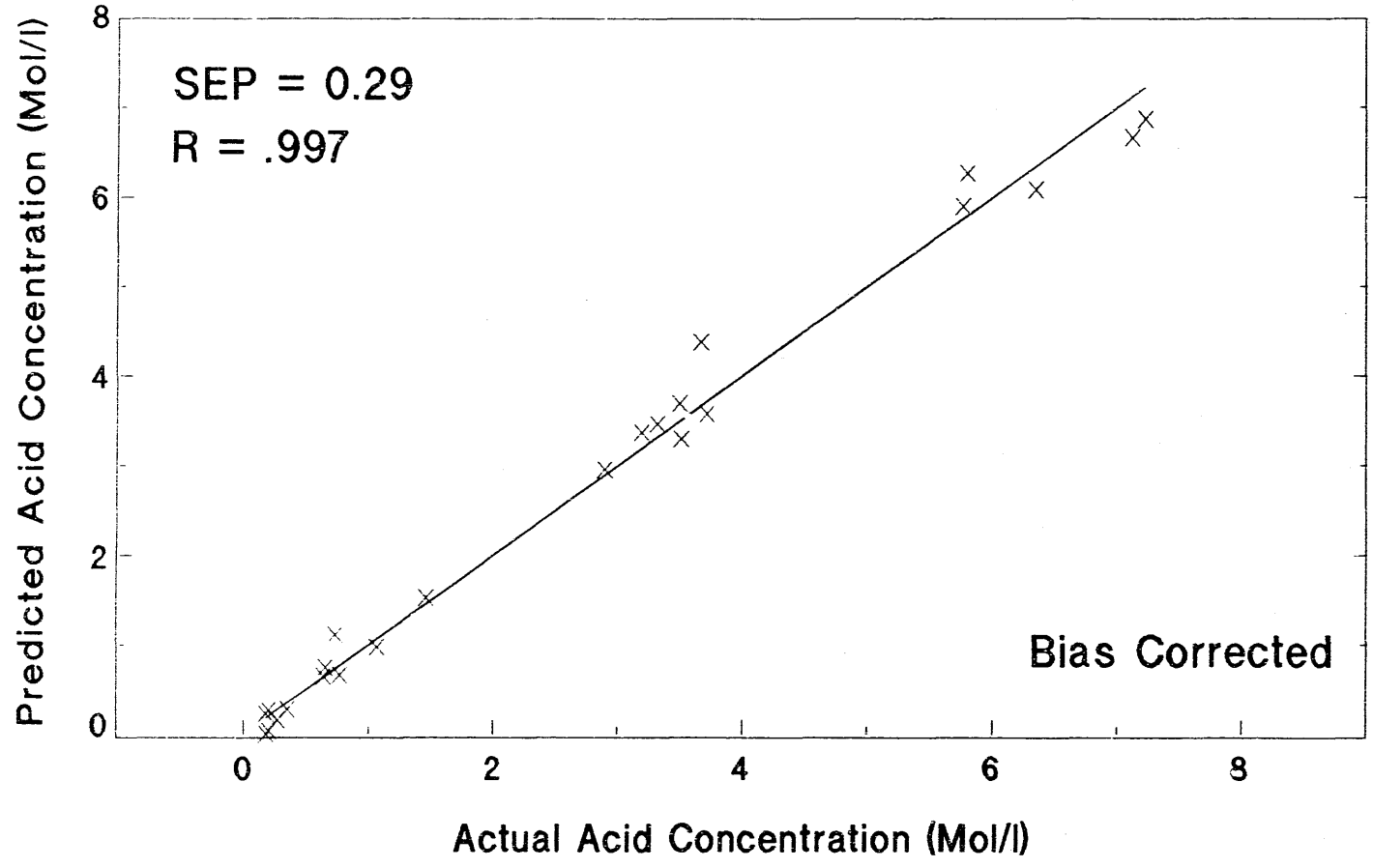
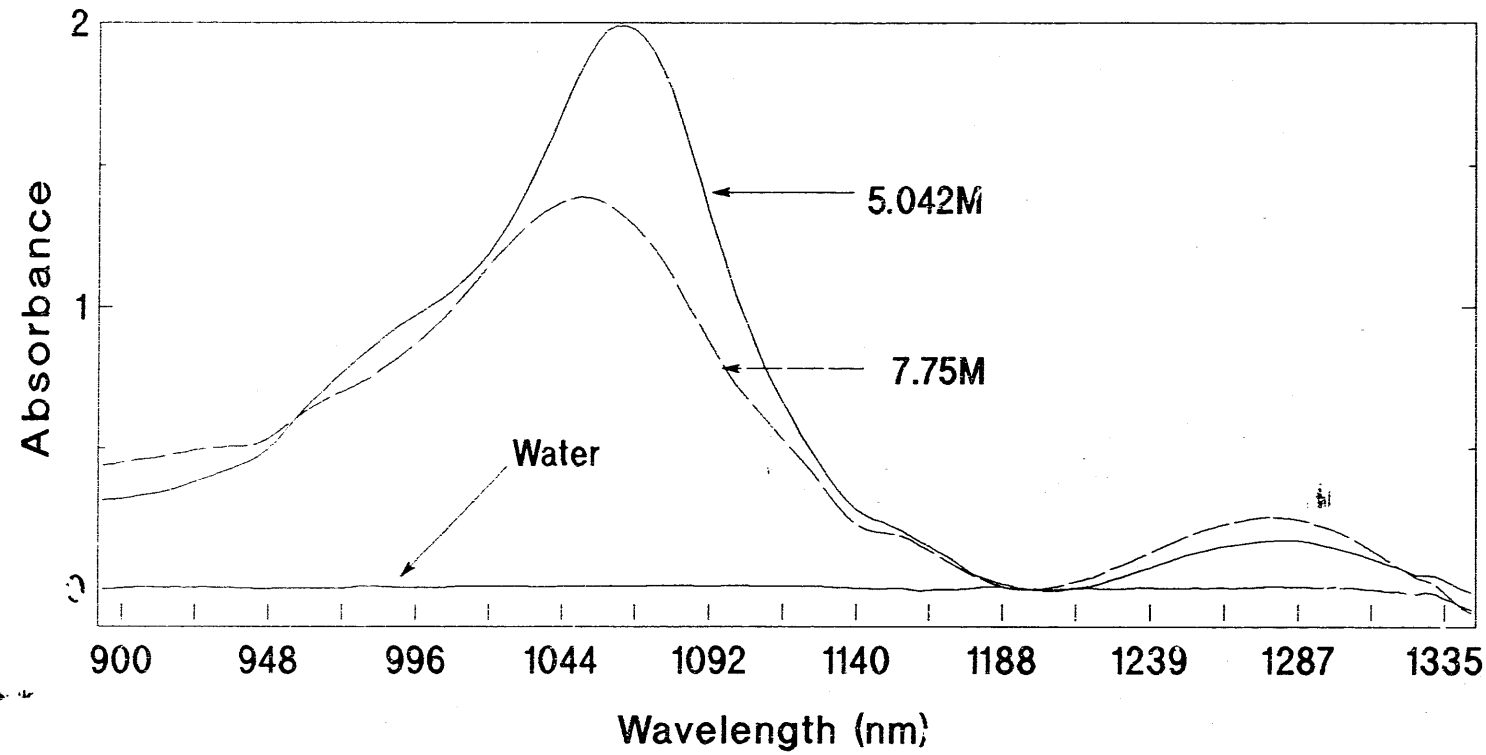
Verification Predictions

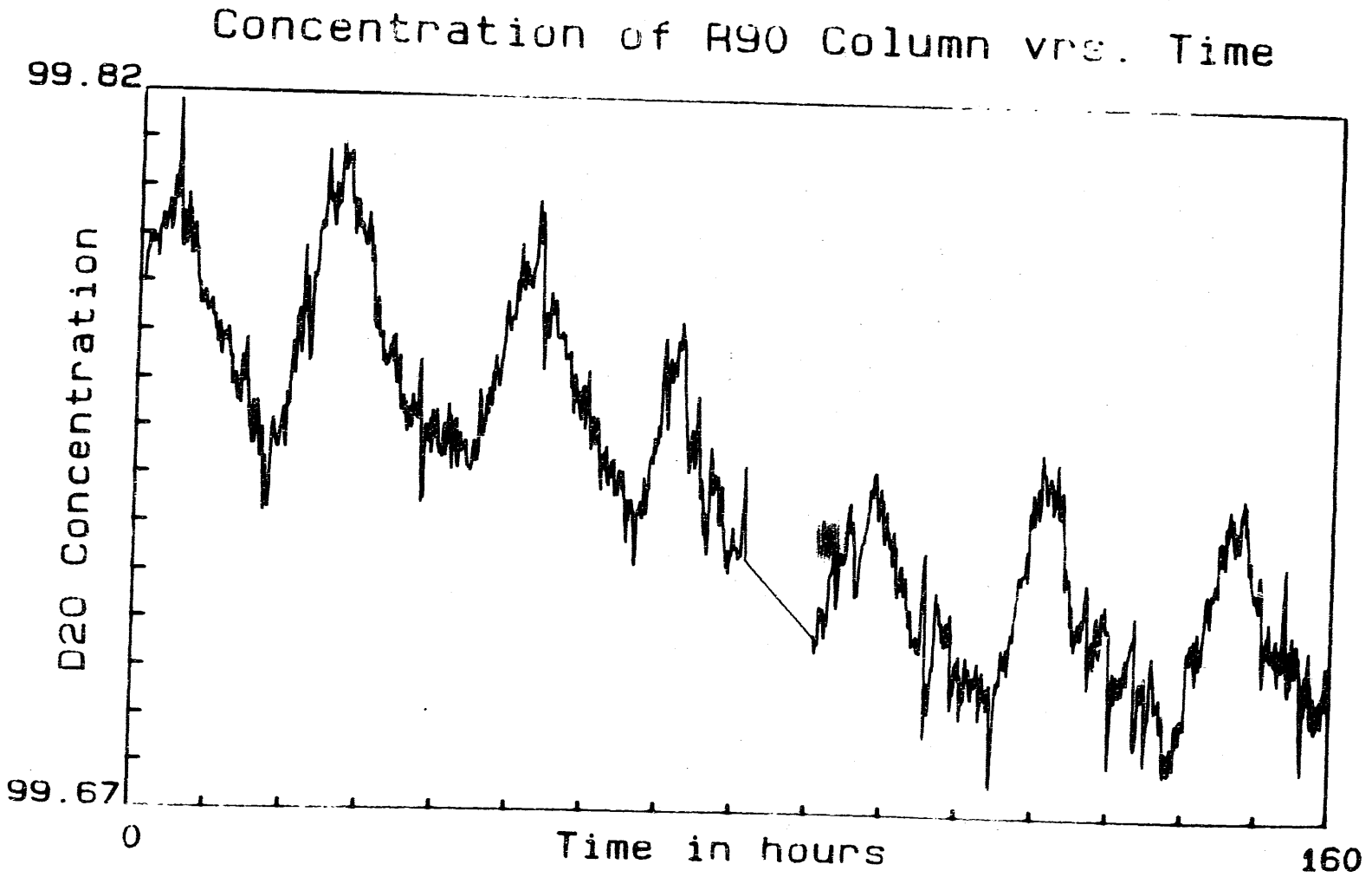
Using Nitric Acid/Al(NO3)3/U(NO)3

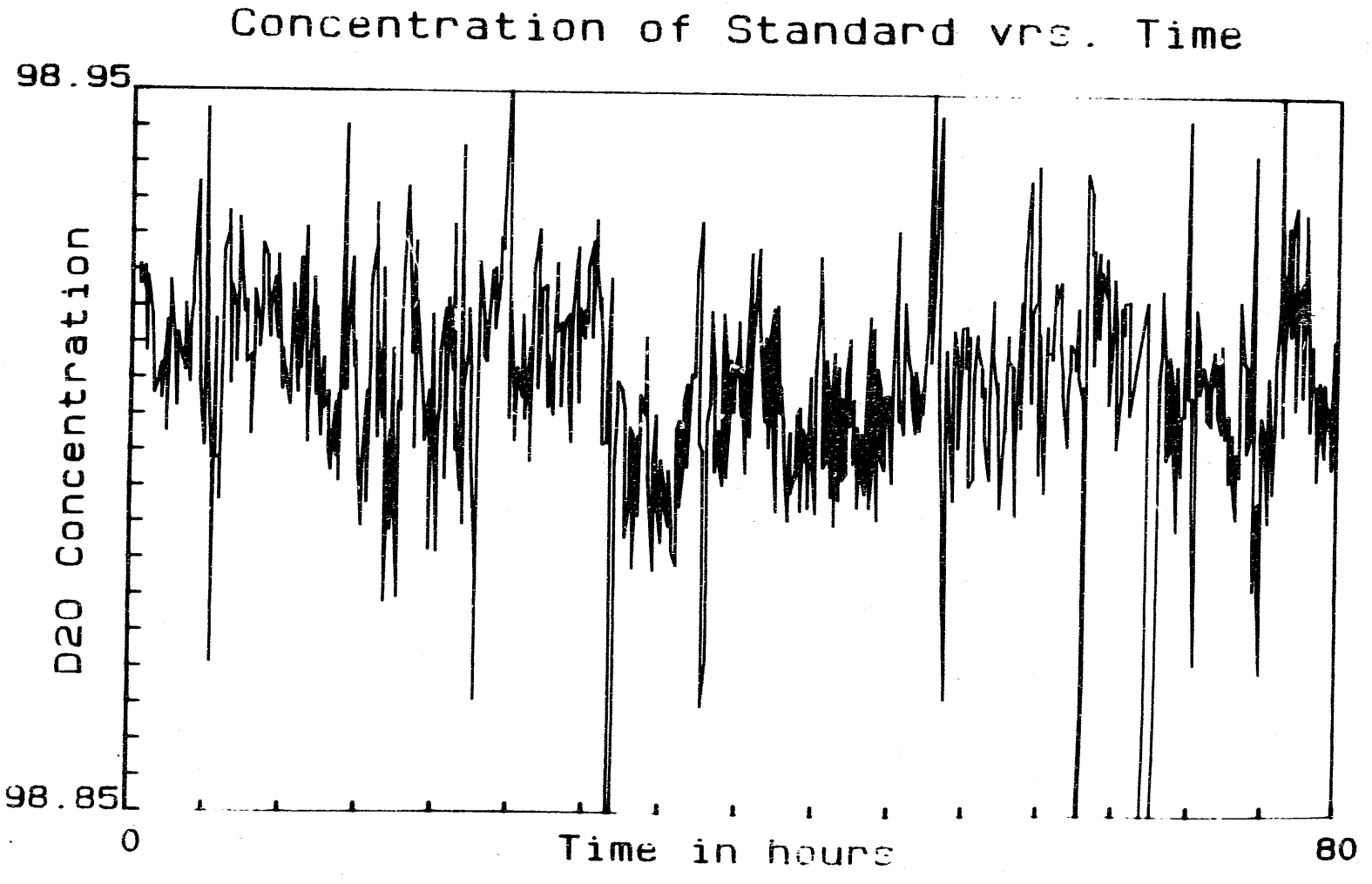


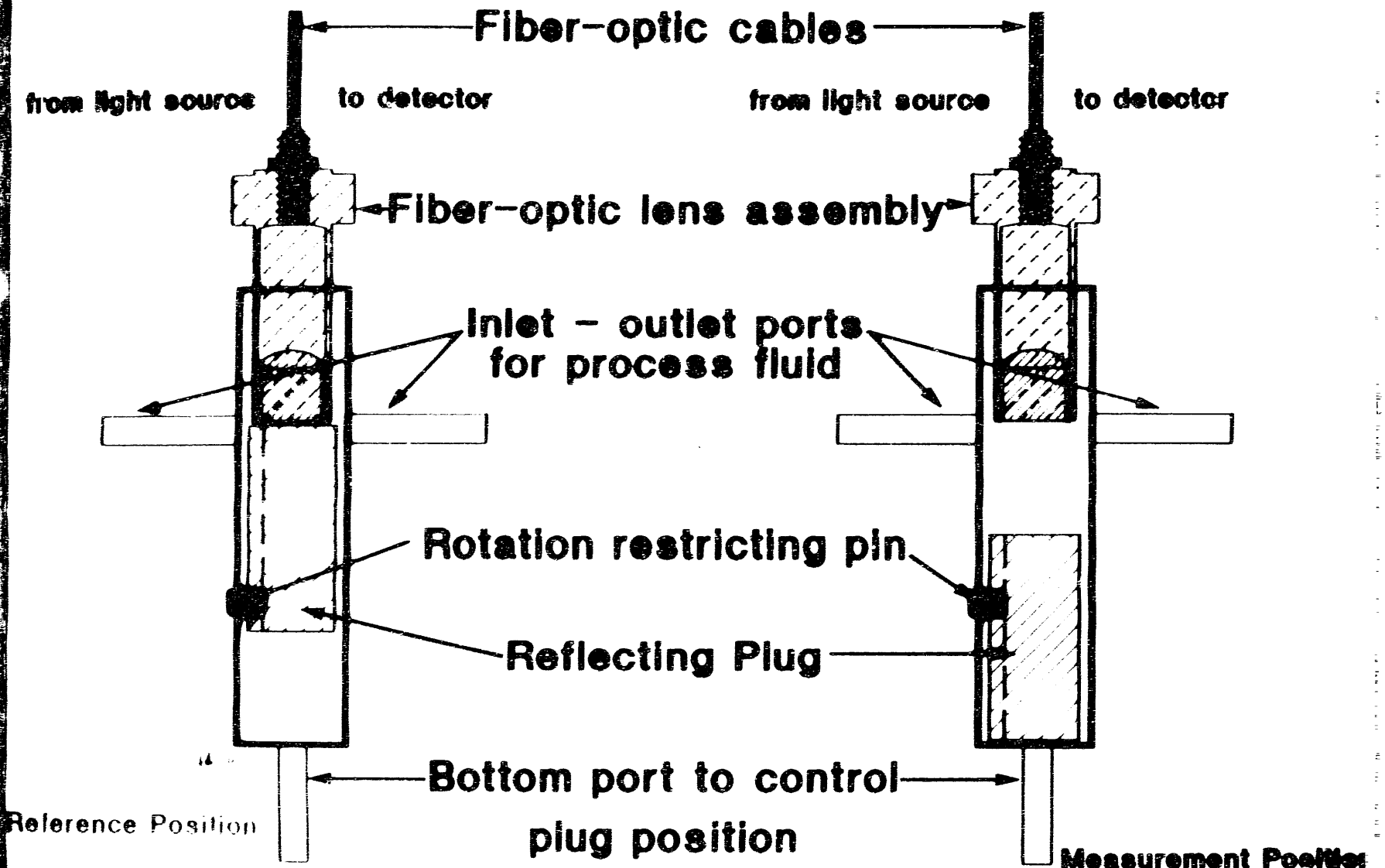
Analytical Development Section
Savannah River Laboratory

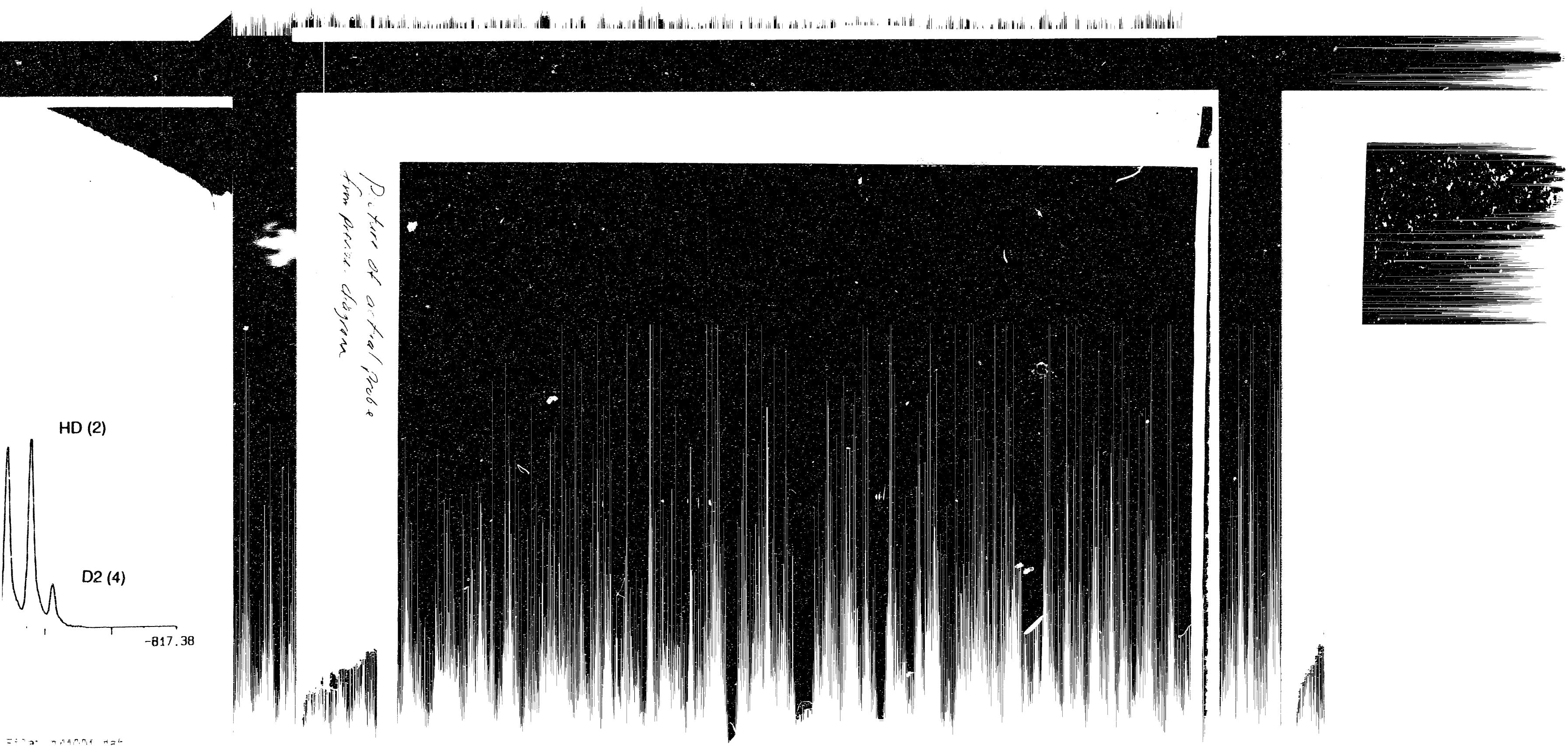
Acid Spectra with Pu Present




Concentration of R90 Column vrs. Time
99.82
99.67
D20 Concentration
0
Time in hours
160


Concentration of Standard vrs. Time
98.95
98.85
D2O Concentration
0
Time in hours
80


Fiber-optic cables
from light source
to detector
from light source
to detector
Fiber-optic lens assembly
Inlet – outlet ports
for process fluid
Rotation restricting pin
Reflecting Plug
Bottom port to control
plug position
Reference Position
Measurement Position
– flow through bottom port
– forces reflecting plug close to lens
(may flow process fluid, air or other fluid)
– no flow through bottom port –
– Plug settles to bottom of cell –



Picture of optical Pred
from paper diagram

Picture of probe in
beaker of solution

n

ission

Westinghouse Savannah River Company

Fiber Optic Based Sensors for pH and Metal Ions

SRL : Lewis Baylor and Pat O'Rourke

South Carolina State U.: Prof. N. Datta-Gupta

Design and synthesis of porphyrins for metal sensors.

U. Georgia: Prof. Bruce King and Susan Stephens

Organic chemistry know-how and binding uranyl indicators.

Previous work:

Physical entrapment of a pH indicator in a polymer matrix on a fiber-optic lens assembly.

Successfully measured pH in range 3-6.

Indicator leached out of matrix at pH > 7.

Direct binding of an indicator to a substrate.

Accomplished by other workers for reflectance measurements.

We would like to do transmission measurements, as we did for the pH indicator/polymer matrix sensors above.

Savannah River Laboratory

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Current Work: Direct Binding

Method 1:

a)Silane couple glass. b)Bond cyanuric chloride to amine function of silanized glass. c)Couple indicator through amine or alcohol functionality to triazine ring.

Problem: Have bound cyanuric chloride to either the silanized glass or to the indicator in solution, but not both at once.

Method 2:

a)Silane couple glass. b)Link amine group of silanized glass to p-nitrobenzoyl chloride. c)Reduce nitro group. d)Diazotize and e)add to solution of indicator.

Azo linkages bond non-specifically to phenyl rings.

Potential problem: May deactivate some of the indicator molecules, thus reducing the sensor's signal.

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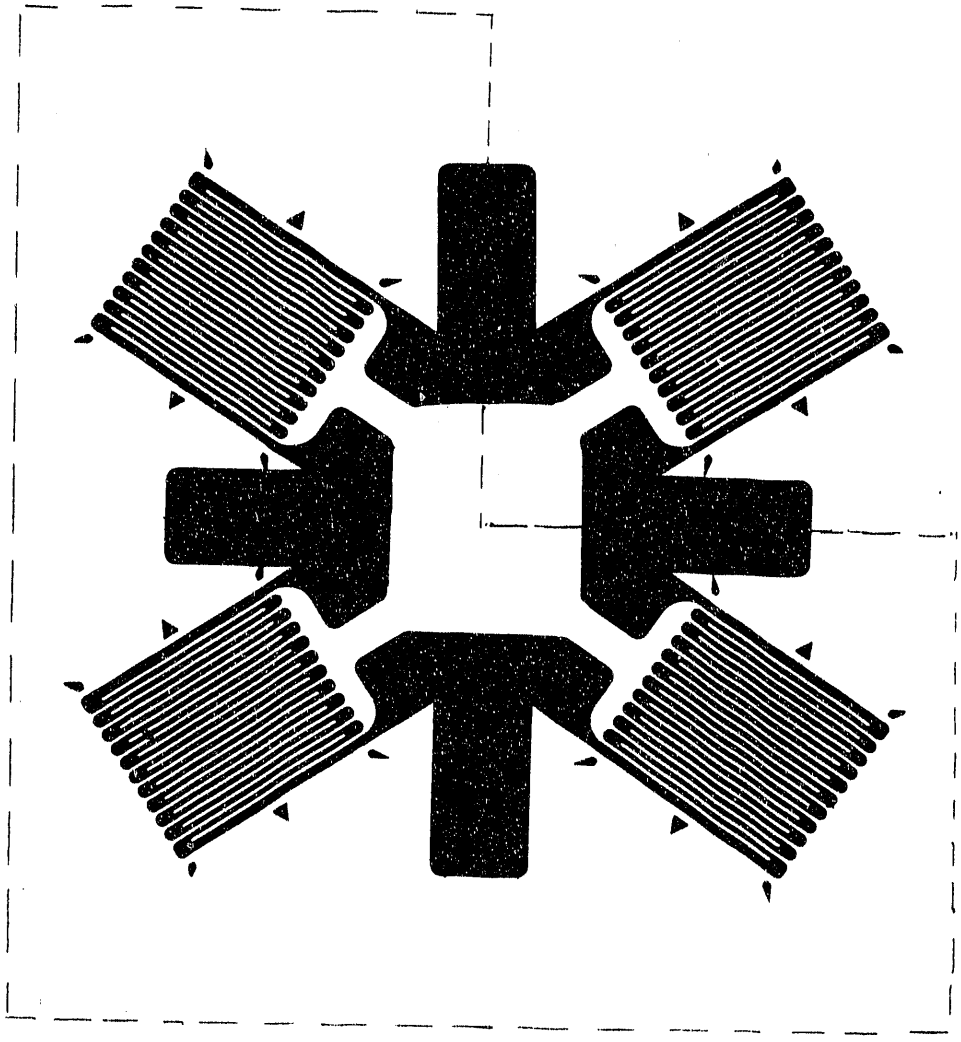
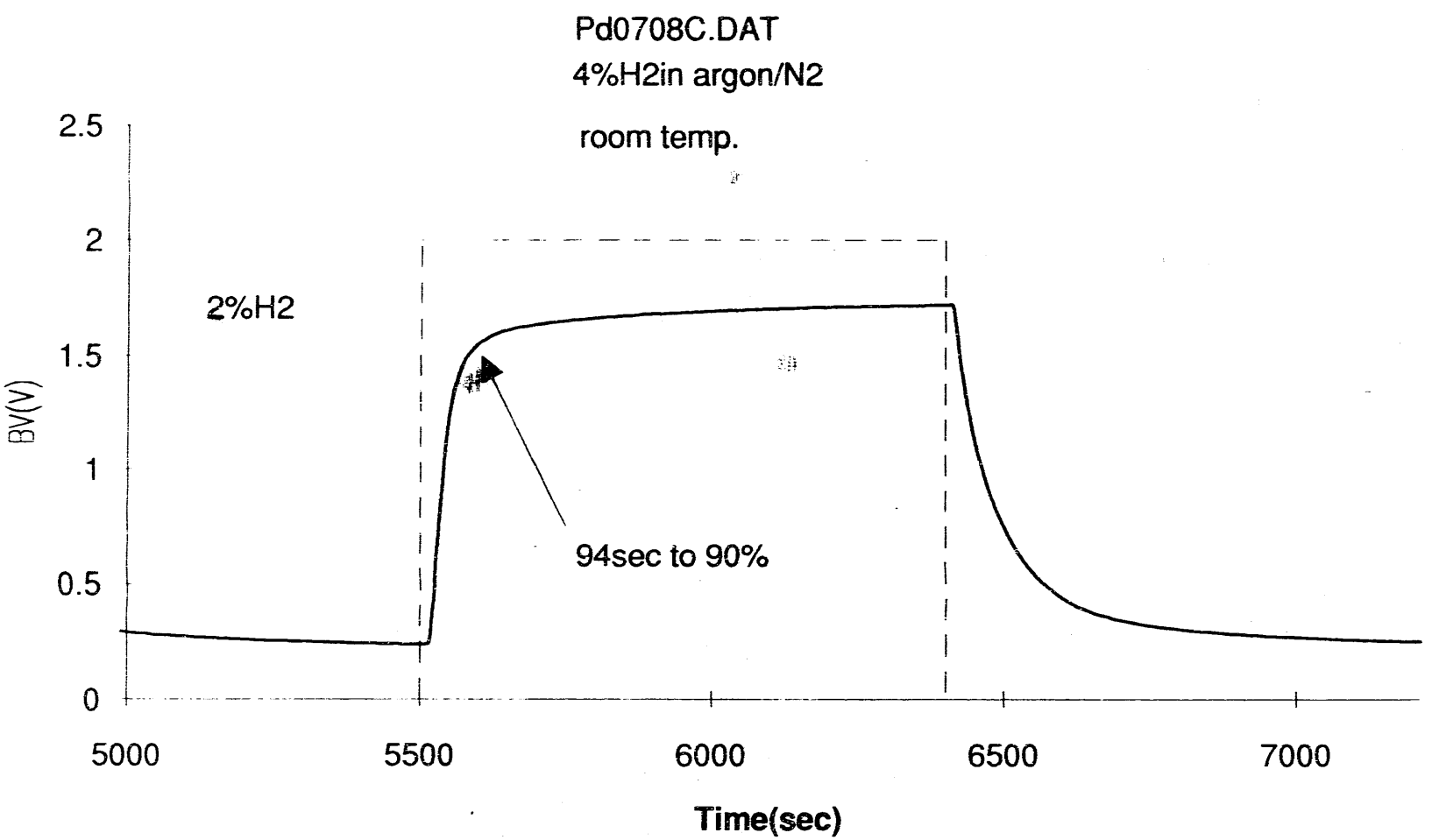
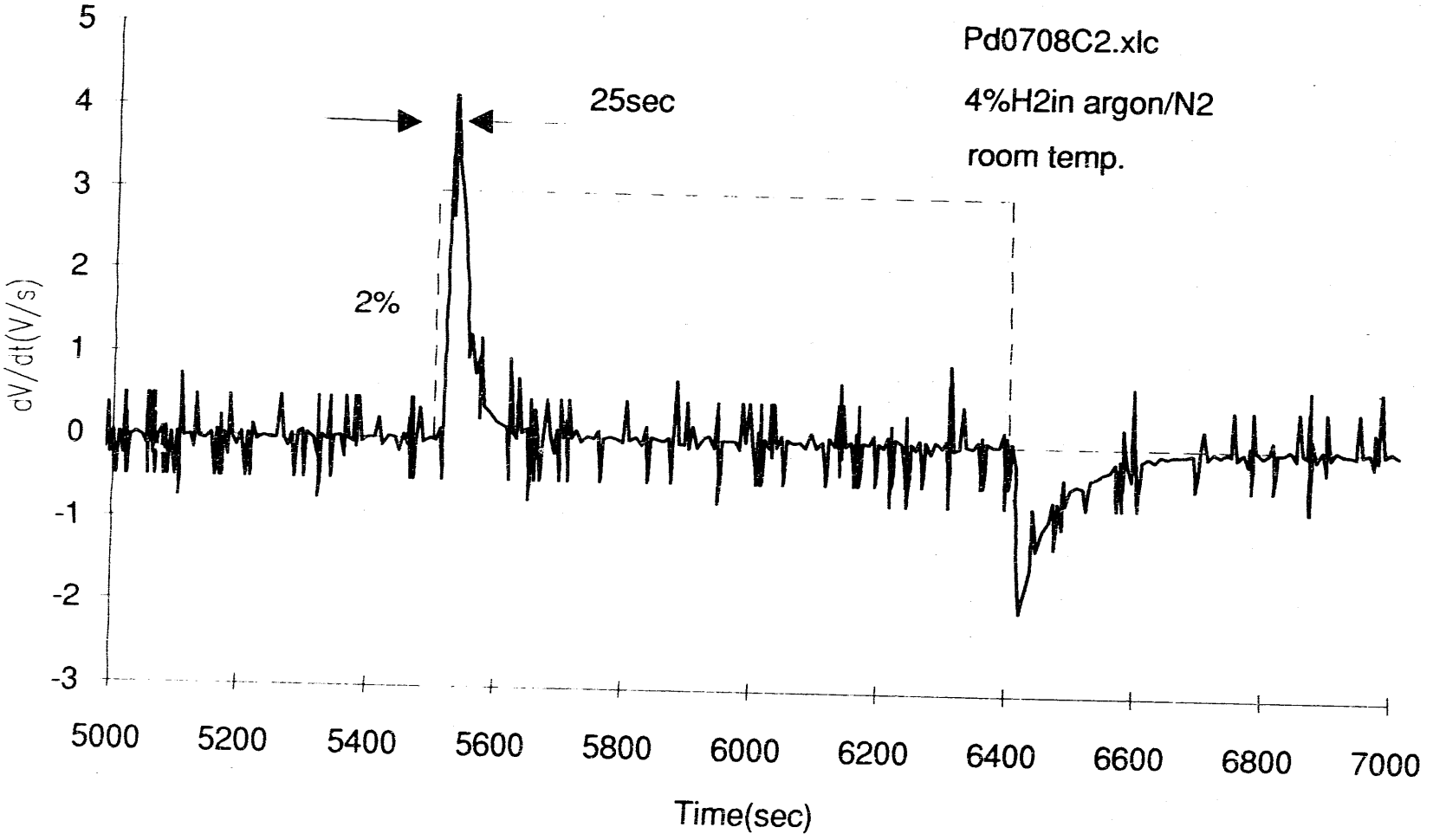


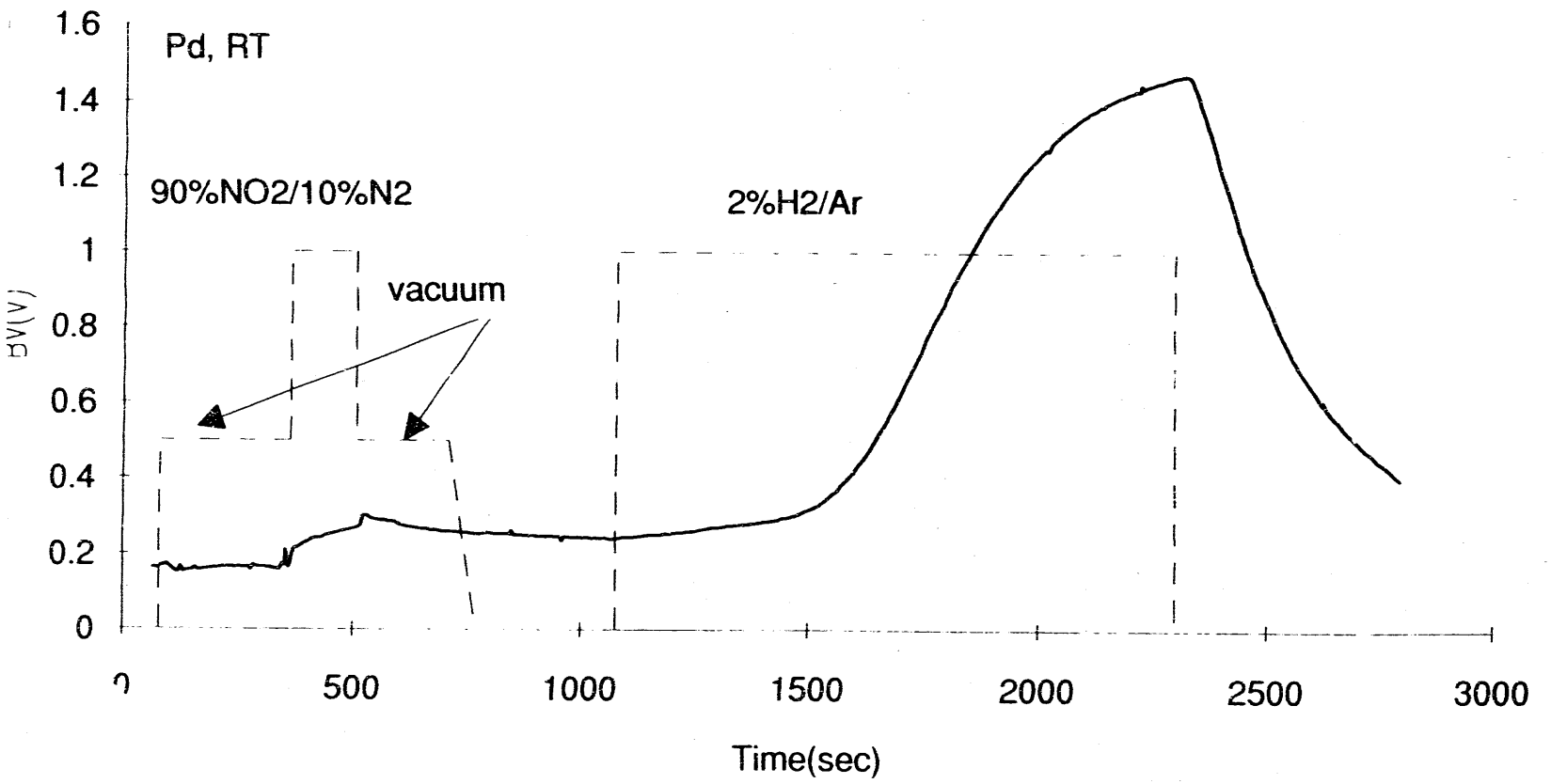

Pd0708C.DAT
4%H2in argon/N2
room temp.
2.5
2
1.5
1
0.5
0
BV(V)
2%H2
94sec to 90%
5000
5500
6000
6500
7000
Time(sec)

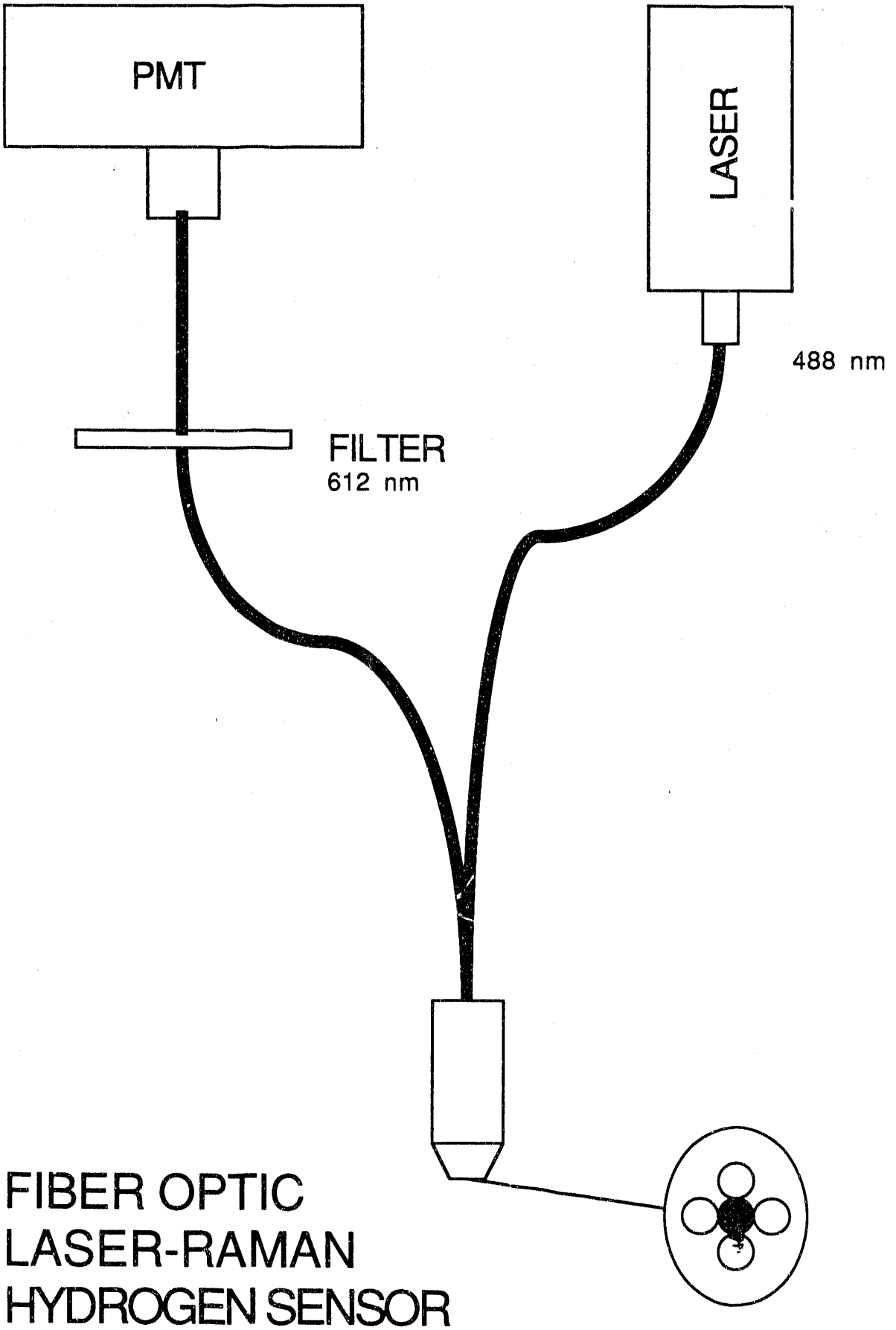
PD0708C2.XLC



PD0709A.XLC

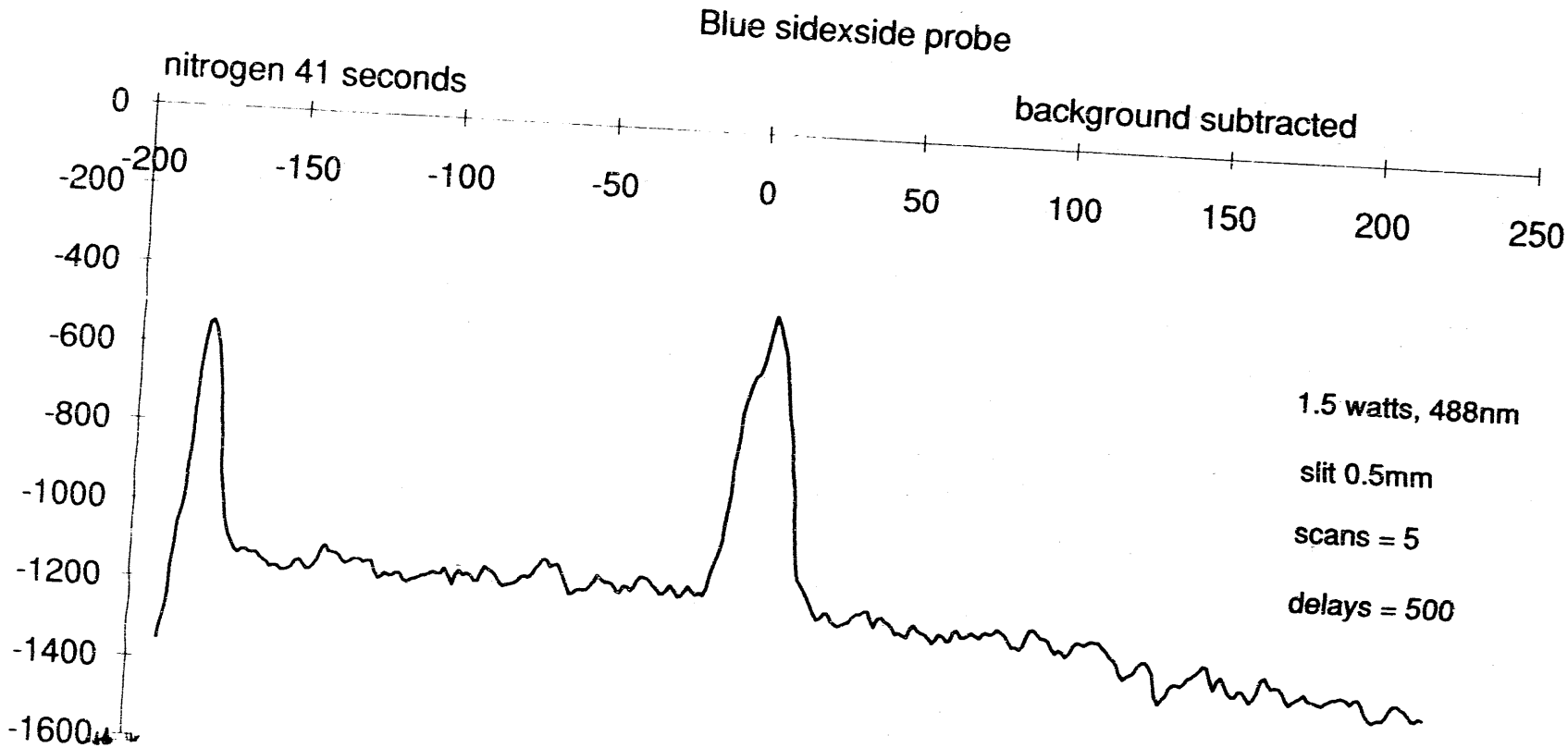
Pd0709A.DAT





FIBER OPTIC LASER-RAMAN HYDROGEN SENSOR

N0729F-M.XLC

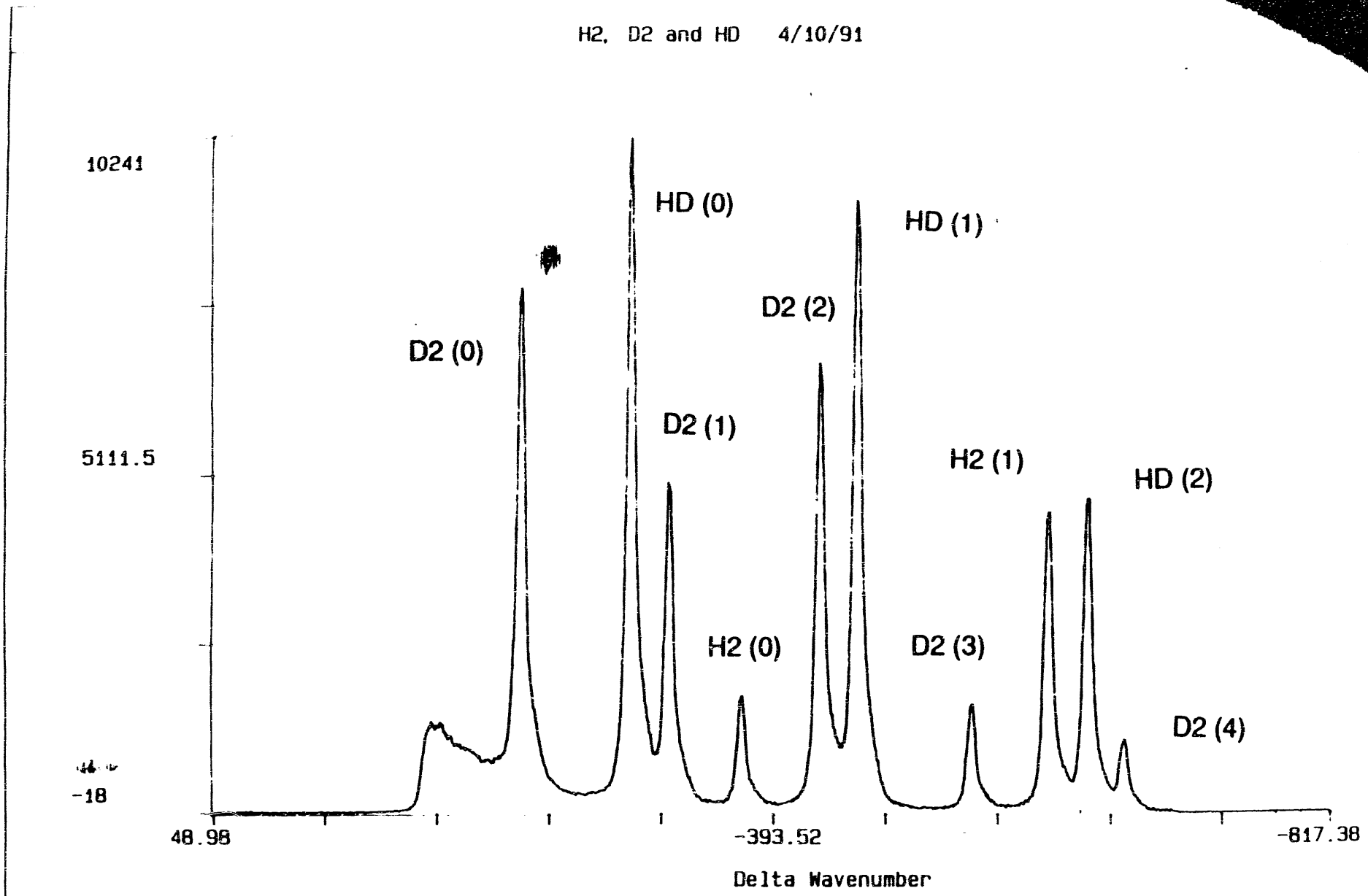

Blue sidexside probe
nitrogen 41 seconds
background subtracted
0
-200
-400
-600
-800
-1000
-1200
-1400
-1600
-200
-150
-100
-50
0
50
100
150
200
250
1.5 watts, 488nm
slit 0.5mm
scans = 5
delays = 500
Delta wn(cm-1)

98.85
D20 Concentration
98.95
0

Laser Raman

- Fast
- In-situ
- Non-Destructive
- Direct Molecular Measurement

Figure 4



488.0nm; 1.0 watt; 2370 torr

Exposure Time: 2 Scans: 10 Ign. Scans: 0 Spectra: 1 DA Mode: 1 File: n41001.dat

Figure 6

NEEDS

- o Spectrophotometry
  - Chemistry for Binding Indicators to Lenses
  - Chemistry for Selective Indicator Molecule Design
  - Academic Support of Sensors
  - Brighter Light Sources and/or Filters
  - Improved Infrared Hardware
  - Vendors of Components and Systems
- o Hydrogen Measurement
  - Selective Hydrogen Filters
- o Raman
  - Smaller, cheaper lasers
  - Fibers Better in UV and Farther in Infrared
- o Compact, Simple Plasma Generators for In Situ Emission Spectroscopy

SRL CONTACTS

- o Spectrophotometry
  - Pat O'Rourke, 803-725-2173
  - Bruce Buchanan (particularly NIR), 803-725-1963
  - Lewis Baylor (coated lens indicators), 803-725-1872

- o Hydrogen Sensors
  - Stanley Nave, 803-725-1355

- o Laser Raman
  - Bob Malstrom, 803-725-3140
  - O'Rourke
  - Nave

END

DATE FILMED

7/28/92