DOE/ER/13347--5

Progress Report for Second Year of Contract Number DE-FG02-85ER13347

to

The U.S. Department of Energy

Attention: Dr. Clement R. Yonker
Process and Techniques Branch
Division of Chemical Sciences
Office of Basic Energy Science
ER-142, MSG-236
U.S. Department of Energy
Washington, D.C. 20585

Hadamard Transform Spectrometry: A New Analytical Technique

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Date of Submission November 15, 1992

A Progress Report
March 15, 1992 to November 15, 1992

This progress report contains the following sections:

1. Hadamard Transform Photoacoustic Spectrometry and Depth Profiling. Mr. Steven L. Wright, Graduate Student in the Chemistry Department. Professor Joseph V. Paukstelis, Chemistry Department.

2. Hadamard Transform Imaging with a 2D Hadamard Encoding Mask. Ms. Karen J. Latas, Mr. Edward A. Orr, Mr. Steven L. Wright, Graduate Students in the Chemistry Department. Mr. A. Norman Mortensen, Graduate Student in Electrical and Computer Engineering. Professor Joseph V. Paukstelis, Chemistry Department. Professor Stephen A. Dyer, Electrical and Computer Engineering.

3. Hadamard Transform Raman Spectrometry. Mr. Edward A. Orr, Mr. John M. Poholarz, Mr. Steven L. Wright, graduate Students in the Chemistry Department. Mr. J. Lance Porter, Mr. Mark Spinar, Graduate Students in Electrical and Computer Engineering, Professor Joseph V. Paukstelis, Chemistry Department. Professor Stephen A. Dyer, Electrical and Computer Engineering.

4. Work on the Growth of VO_2(s) Crystals for Hadamard Masking Material. Mr. Edward A. Orr, Graduate Student in the Chemistry Department.

5. Publication arising from this project.

6. Talks presented on this work.

1. Hadamard Transform Photoacoustic Spectrometry and Depth Profiling. Mr. Steven L. Wright, Graduate Student in the Chemistry Department. Professor Joseph V. Paukstelis, Chemistry Department.

The assembly of a Hadamard transform photoacoustic (HT-PAS) spectrometer using a Jarrell-Ash double monochromator and a MTEC photoacoustic cell was described in last year's progress report and preliminary results with a 50 nanometer spectral window were presented. We have now chosen to develop a simple high throughput low resolution visible HT-PAS spectrometer to demonstrate the feasibility of depth profiling with a HT-PAS spectrometer using either variation of the modulation frequency or phase sensitive detection at the appropriate modulation frequency. A schematic diagram of the HT-PAS spectrometer appears in Figure 1. The components are all commercially available and the special features are our second generation Hadamard encoding mask based on a polymer dispersed liquid crystal (PDLC) material and the use of a linear variable filter mounted on the Hadamard encoding mask to serve as the spectral separator. By means of constructive and destructive interference, only one spectral resolution element (of 127) is allowed to pass for a given position along the length of the linear variable filter. To illustrate the depth profiling ability of the HT-PAS spectrometer a layered sample was prepared consisting of a thermally thin (20 μm) surface layer of neodymium oxide dispersed in a polystyrene matrix on a thermally thick (2.5 mm) interior layer of holmium oxide dispersed in a polystyrene matrix.

The spectra of pure neodymium oxide and pure holmium oxide obtained with our HT-PAS spectrometer appear in Figure 2 for comparative purposes. Figure 3 shows

SCHEMATIC DIAGRAM
of
HT-PAS SPECTROMETER

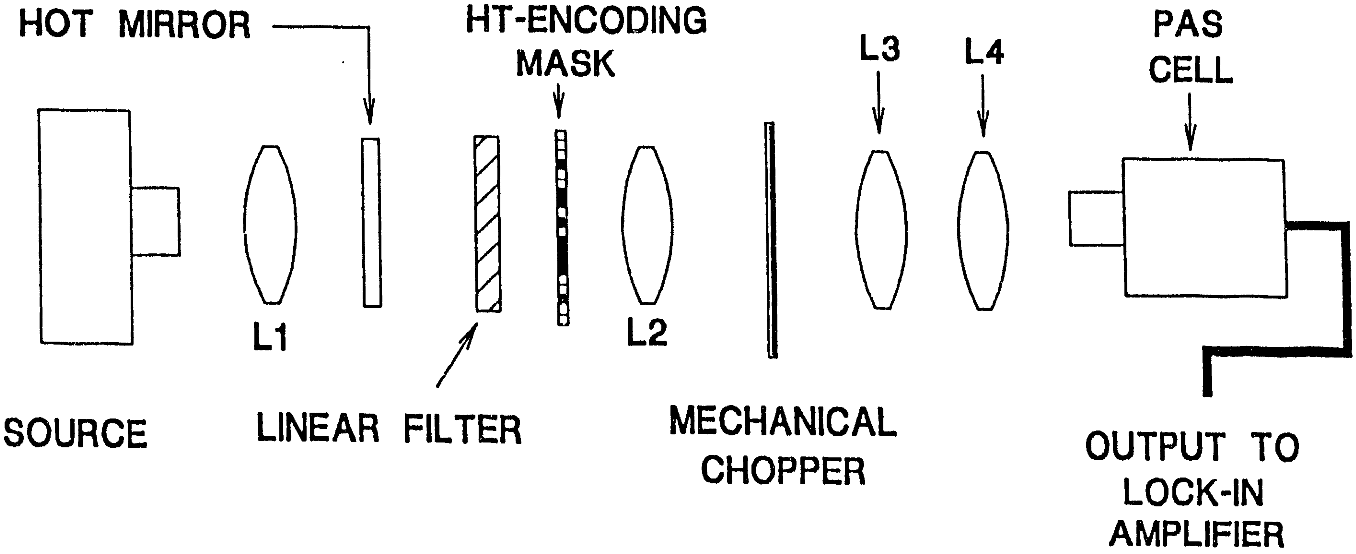


Figure 1. Schematic diagram of the HT-PAS spectrometer.

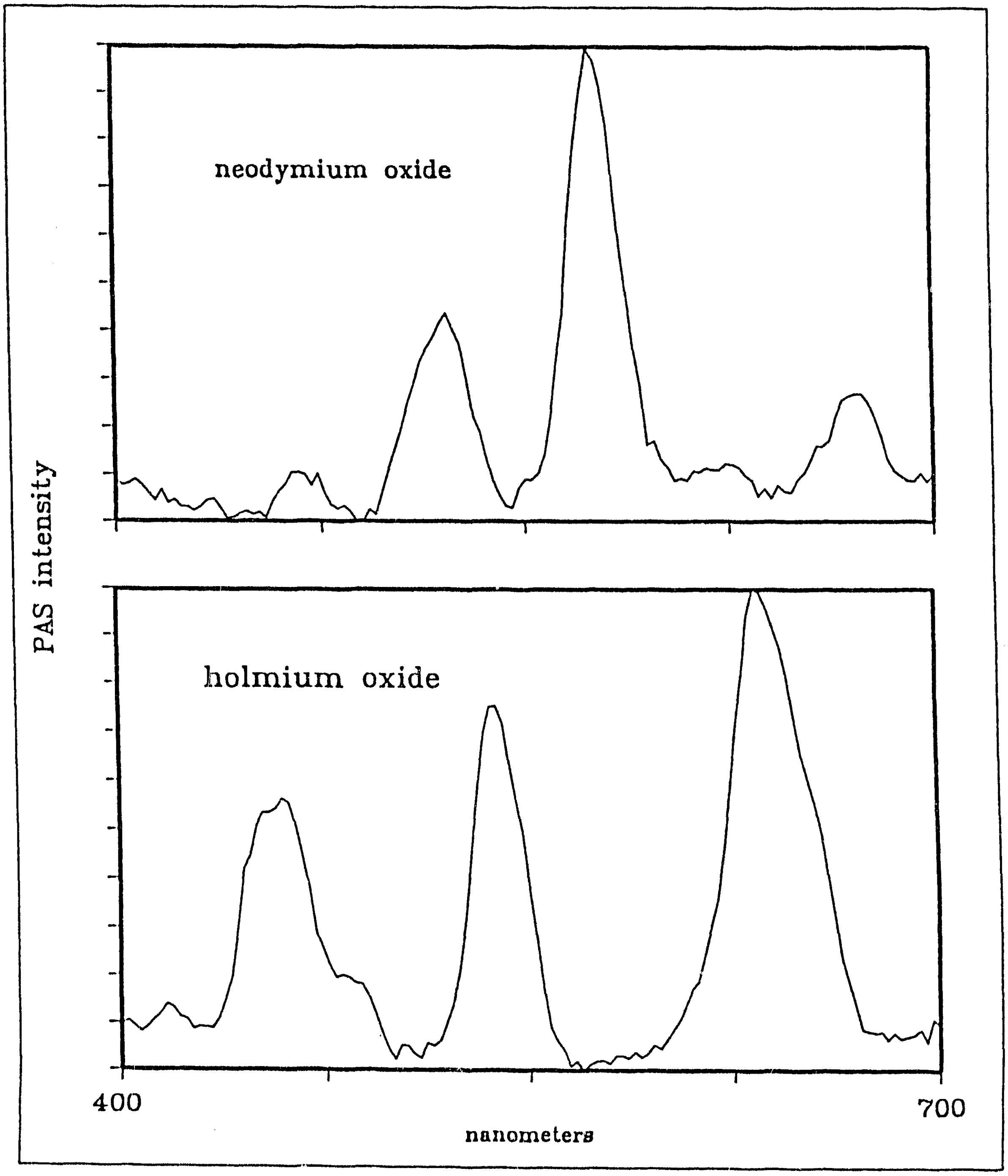


Figure 2. Visible Hadamard transform photoacoustic spectra of neodymium oxide and holmium oxide

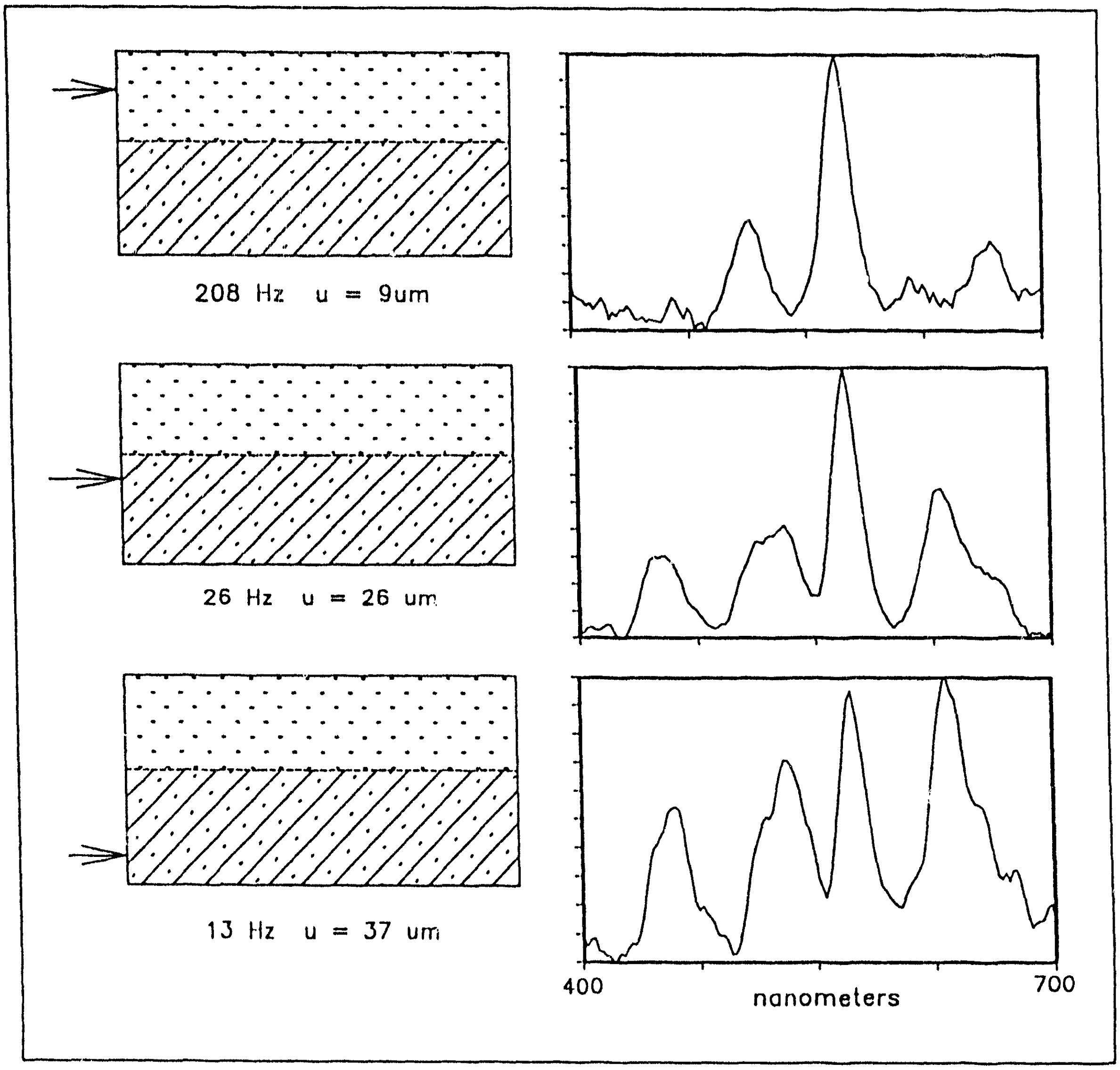


Figure 3. An illustration of depth profiling by variation of the modulation frequency using the layered sample: (a) modulation frequency, f, 208 Hz; thermal diffusion length, μ, 9 μm; (b) f, 26 Hz, μ, 26 μm; (c) f, 13 Hz; μ, 37 μm.

three different spectra of the layered sample acquired with three different modulation frequencies corresponding to three different extents of depth penetration (thermal diffusion length, μ). The top spectrum in Figure 3 contains only the spectral features of neodymium oxide from the surface layer. The middle spectrum in Figure 3 shows the spectral features of holmium oxide from the interior layer beginning to appear in addition to the spectral features of neodymium oxide from the surface layer. The bottom spectrum in Figure 3 contains the spectral features of both layers with comparable intensity consistent with a penetration into the interior layer comparable to the thickness of the surface layer.

The advantages of phase sensitive detection when depth profiling layered samples is illustrated in Figure 4 where the sine waves to the left of the spectra represent average signals from the two layer and illustrate the phase differences in signals for different depths of penetration. The observed photoacoustic signal is a combination of all signals generated within one thermal diffusion length (μ). When phase information is not required an amplitude spectrum is obtained by adjusting the reference phase angle of the lock-in amplifier so as to maximize the amplitude of the photoacoustic signal. This amplitude maximum generally occurs at a point where signals from all depths within one thermal diffusion length make some contribution to the total photoacoustic signal. To selectively view a given layer within one thermal diffusion length the appropriate reference phase angle must be selected so as to maximize the signal of the layer we wish to observe and to minimize or reject unwanted signals. The top spectrum in Figure 4 (which is also the bottom spectrum in Figure 3) and the three spectra in Figure 3 were all obtained by

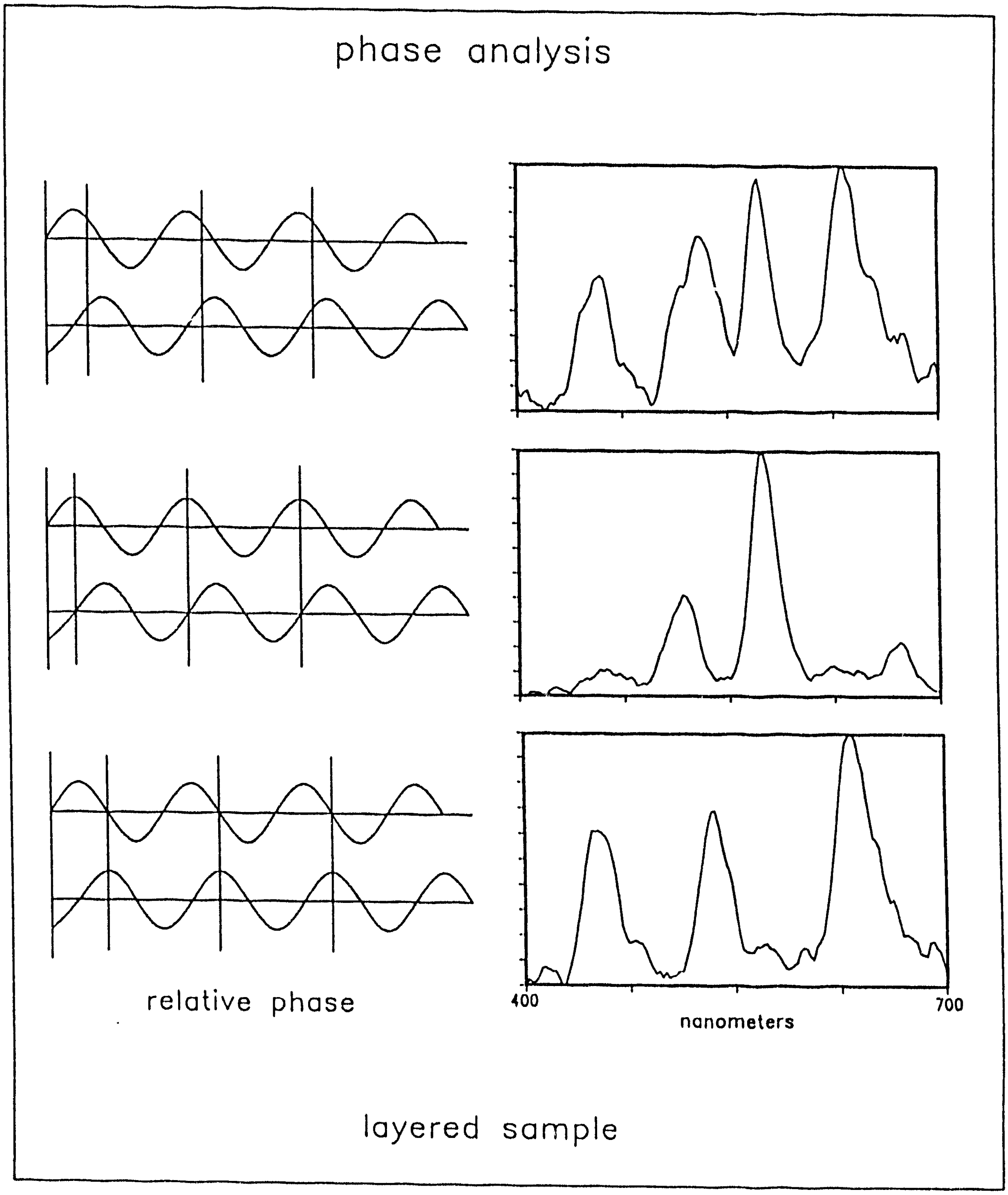


Figure 4. An illustration of selective depth profiling using phase sensitive detection at a modulation frequency, f, of 13 Hz and corresponding thermal diffusion length of 37 μm: (a) both layers contribute to the total photoacoustic signal; (b) maximization of the contribution from the surface layer; (c) maximization of the contribution from the interior layer.

adjusting the reference phase angle of the lock-in amplifier so as to maximize the amplitude of the photoacoustic signal. The vertical lines on the sine waves to the left of the spectra in Figure 4 illustrate the selection of the reference phase angle of the lock-in amplifier to maximize the amplitude of the photoacoustic signal (top spectrum) or to maximize the signal from the surface layer (middle spectrum) or to maximize the signal from the interior layer (bottom spectrum). Actually the only way to completely reject a signal is if it is exactly in quadrature with the signal of interest. Since layers will have finite thickness so there is a phase gradient throughout their depth, there are some components we want to reject which are not in quadrature with the selected reference phase angle. Thus, a perfect separation of signals from a layer from all other signals may not result but good separations are possible. In our sample comparisons of the pure neodymium oxide spectrum in Figure 2 with the surface layer spectrum of neodymium oxide in the middle spectrum in Figure 4 and of the pure holmium oxide spectrum in Figure 2 with the interior layer spectrum of holmium oxide in the bottom spectrum in Figure 4 show that this technique has given very encouraging results.

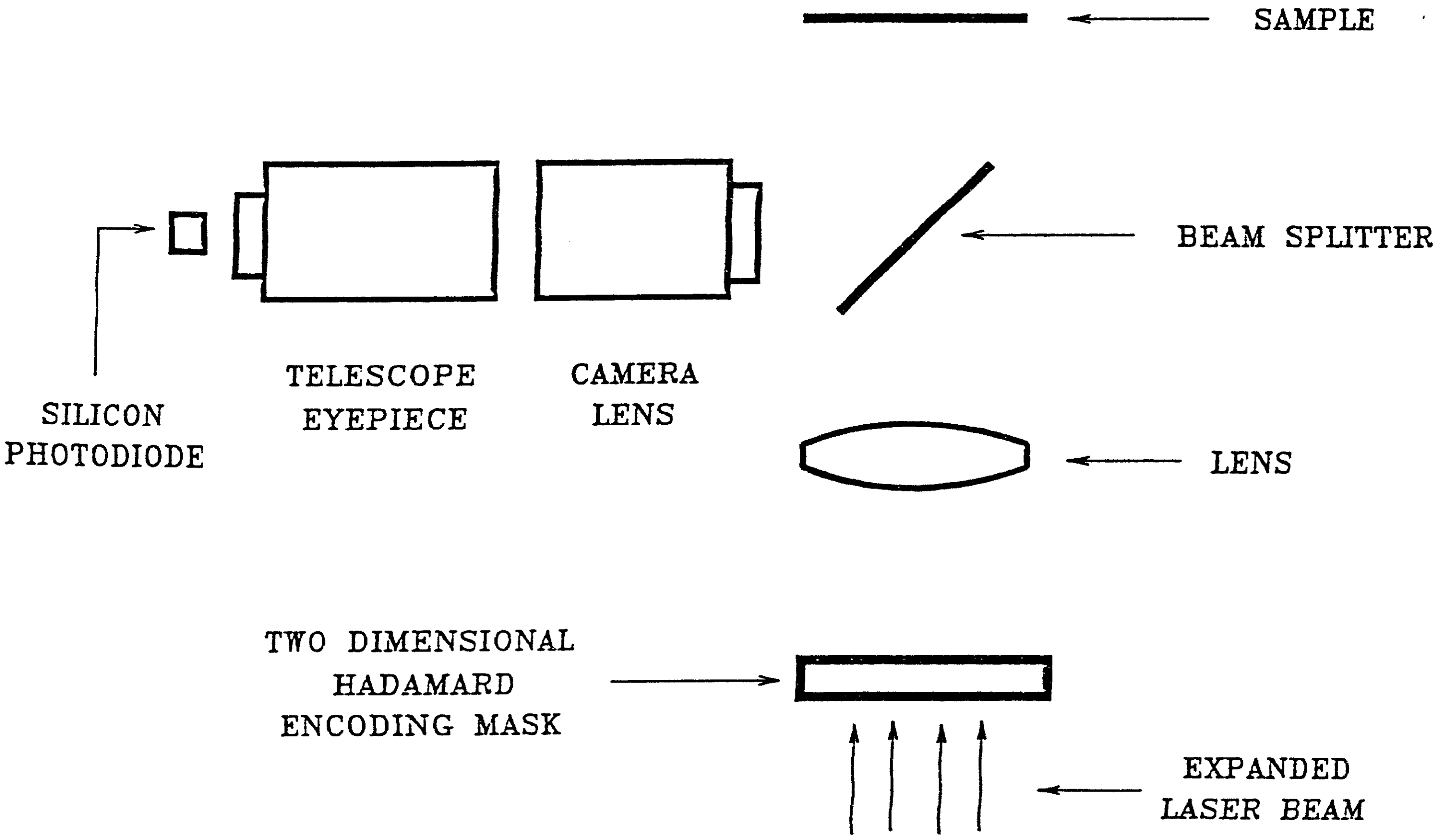
The feasibility of Hadamard transform photoacoustic spectrometry has been demonstrated. The expected signal-to-noise improvement using Hadamard transform optics over conventional dispersive optics was illustrated in last year's progress report (Figures 1 and 2 in that report) and was also obtained using the HT-PAS spectrometer in Figure 1. Because all spectral elements are modulated at the same frequency (in contrast to Fourier transform (FT) spectrometers which do not use the step scan design), selective depth profiling using either variation of the modulation frequency or phase sensitive detection at the appropriate modulation frequency is possible.

2. Hadamard Transform Imaging with a 2D Hadamard Encoding Mask. Ms. Karen J. Latas, Mr. Edward A. Orr, Mr. Steven L. Wright, Graduate Students in the Chemistry Department. Mr. A. Norman Mortensen, Graduate Student in Electrical and Computer Engineering. Professor Joseph V. Paukstelis, Chemistry Department. Professor Stephen A. Dyer, Electrical and Computer Engineering.

Our plans to utilize a two-dimensional (2D) Hadamard encoding mask for imaging studies were presented in last year's progress report. The 2D Hadamard encoding mask contains 100 pixels as a 10 x 10 array in a square of area 1 cm^2 and operates in a similar manner to our first generation Hadamard encoding mask for spectral resolution by surrounding a cholesteric liquid crystal with a set of two polarizers. The development of the controlling software to operate the 2D Hadamard encoding mask has been completed. Our plans to investigate the mapping of aluminum impurities in gallium-arsenide wafers by monitoring the laser induced fluorescence (LIF) upon irradiation with the 488.0 nm line of an Ar^+ laser (see last year's progress report) have been superseded by plans to develop 2D Raman imaging of compounds on thin-layer chromatography (TLC) plates using surface enhanced Raman scattering (SERS) generated with colloidal silver. We have now progressed to the point of observing the SERS Raman image of a spot on a TLC plate consisting of 3 nanograms of pararosaniline hydrochloride.

The imaging studies began with simple test images in a preliminary configuration shown in Figure 5 where an expanded laser beam (25x) at 488.0 nm from an Ar^+ laser was encoded with the 2D Hadamard encoding mask prior to incidence on a beam splitter. The fraction of the expanded and encoded laser beam transmitted by the beam splitter was incident on a fluorescent image and the fraction of the resulting laser induced fluorescence (LIF) reflected by the bean splitter was incident on a silicon photodiode. The total LIF signal with no spectral discrimination was used to define the image. The first image to be used was the letter F drawn on a black surface with fluorescent paint and that output appears in Figure 6. The next image was five spots of rhodamine 6G on a TLC plate and that output appears in Figure 7.

With the experience gained with the large LIF signals from the simple images generated with the configuration in Figure 5, we designed and constructed the configuration shown in Figure 8 for obtaining a SERS Raman image on a TLC plate using an expanded laser beam (25x) at 514.5 nm from an Ar^+ laser. Here it is the scattered radiation from the sample that is encoded rather than the source radiation prior to incidence on the sample. Figure 9 contains the SERS Raman spectrum of pararosaniline hydrochloride as a spot on a TLC plate obtained by removing the 2D Hadamard encoding mask from the configuration shown in Figure 8 and operating the Raman spectrometer (Spex 14018 double monochromator) as a scanning dispersive instrument with a photomultiplier detector (RCA C31034). From Figure 9 the Raman frequency shift to use for SERS Raman imaging was chosen as 911 cm^{-1}. Our first SERS Raman image appears in Figure 10 and was obtained with the configuration shown in Figure 8 with the



SCHEMATIC DIAGRAM OF 2D OPTICS

Figure 5. Schematic diagram of the 2D optics in a preliminary configuration.

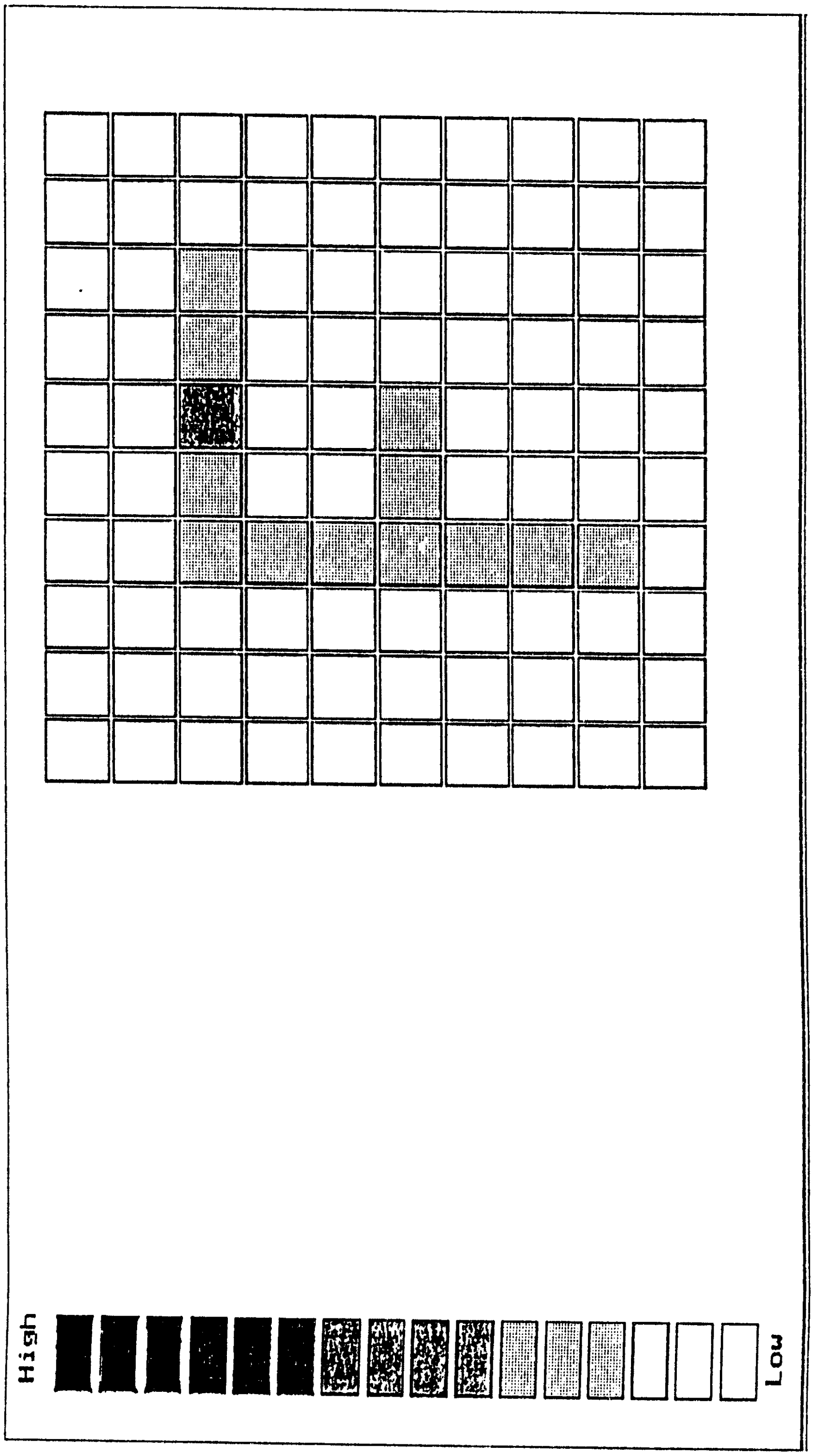
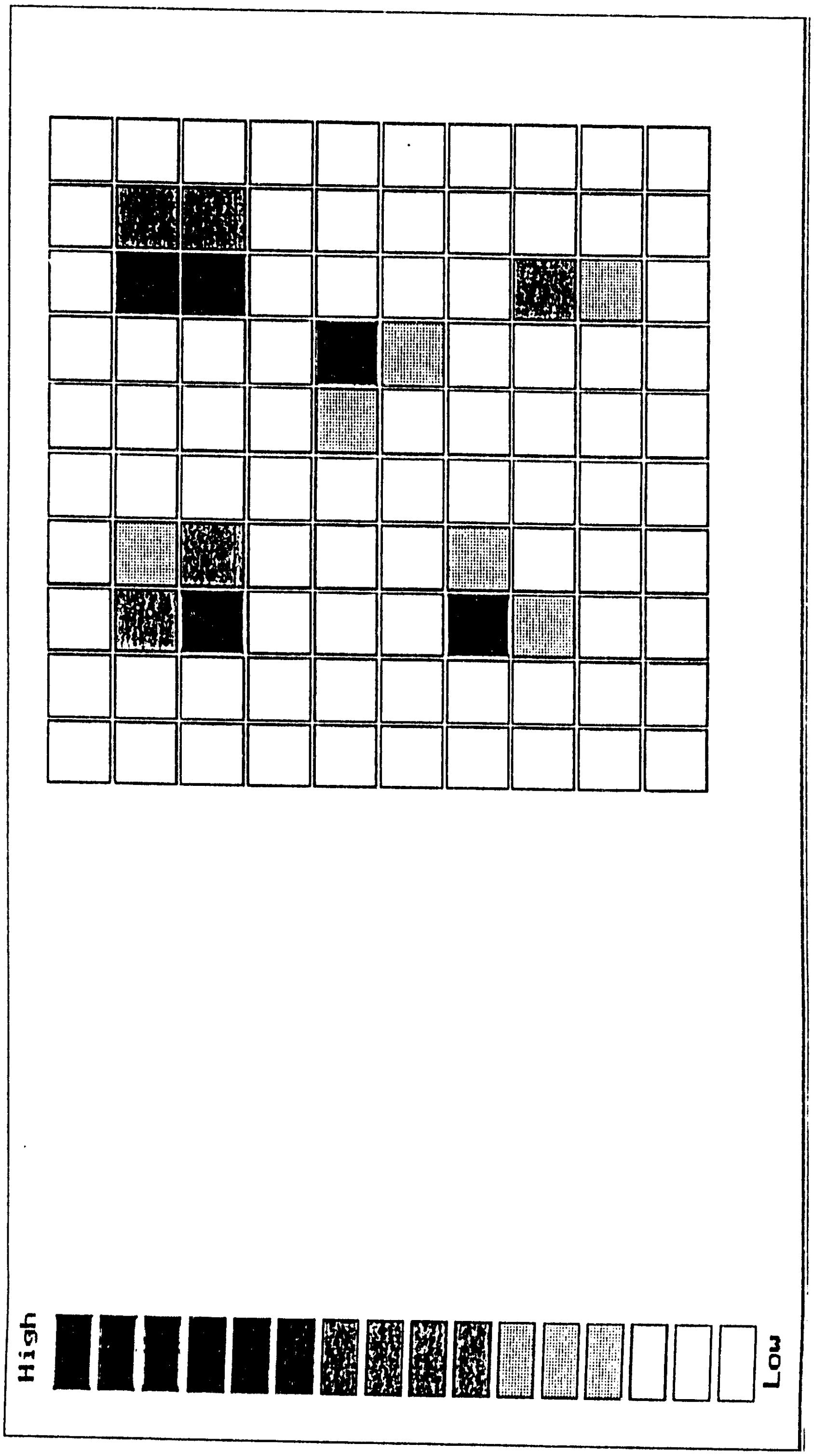


Figure 6. The image of the letter F drawn on a block surface with fluorescent paint.



FIVE SPOTS OF RHODAMINE 6G

ON A TLC PLATE

Figure 7. The image of full spots of rhodamine 6G on a TLC plate.

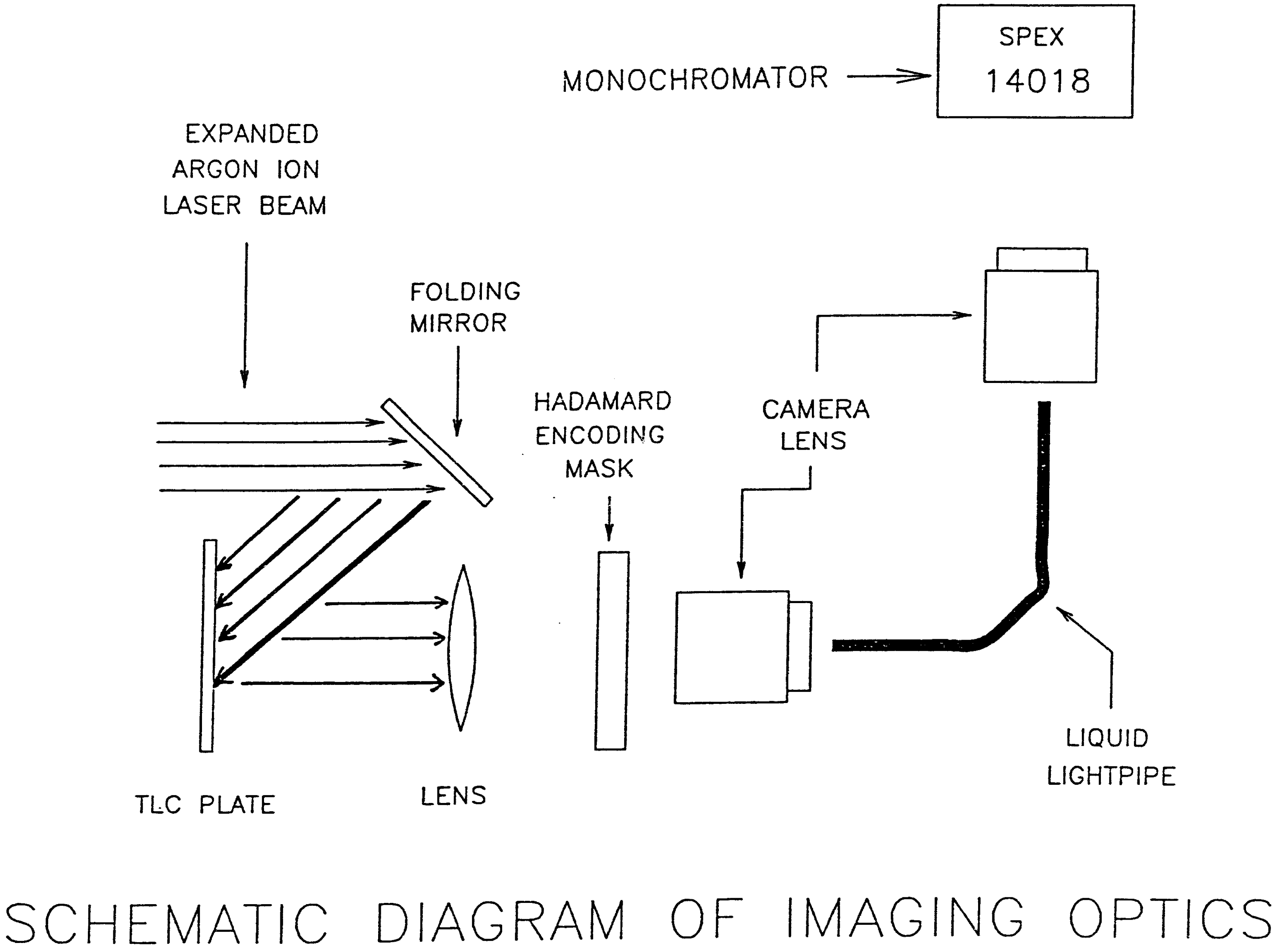


Figure 8. Schematic diagram of the imaging optics for obtaining a SERS Raman image on a TLC plate.

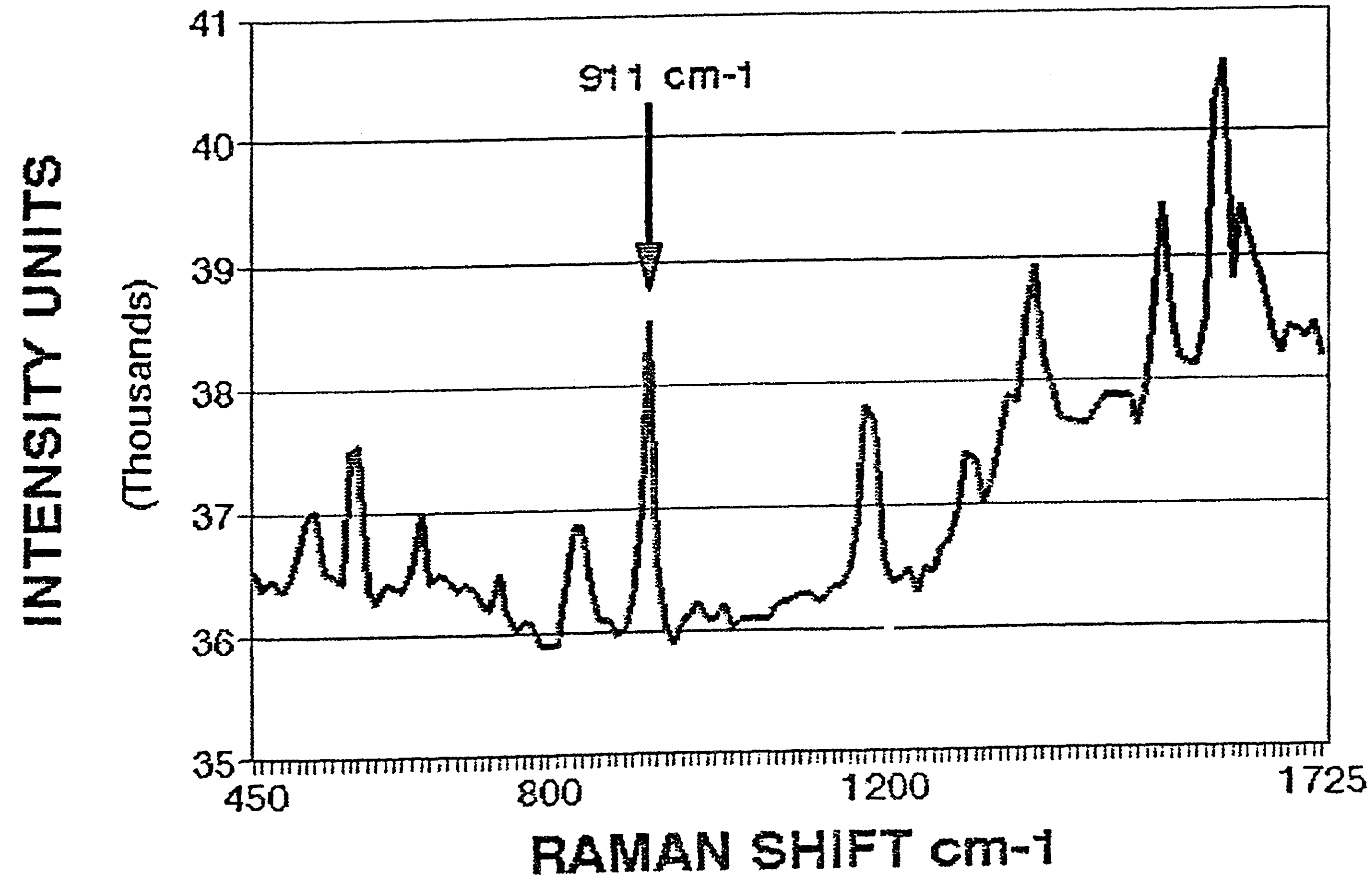


Figure 9. The SERS Raman spectrum of pararosaniline hydrochloride as a spot on a TLC plate.

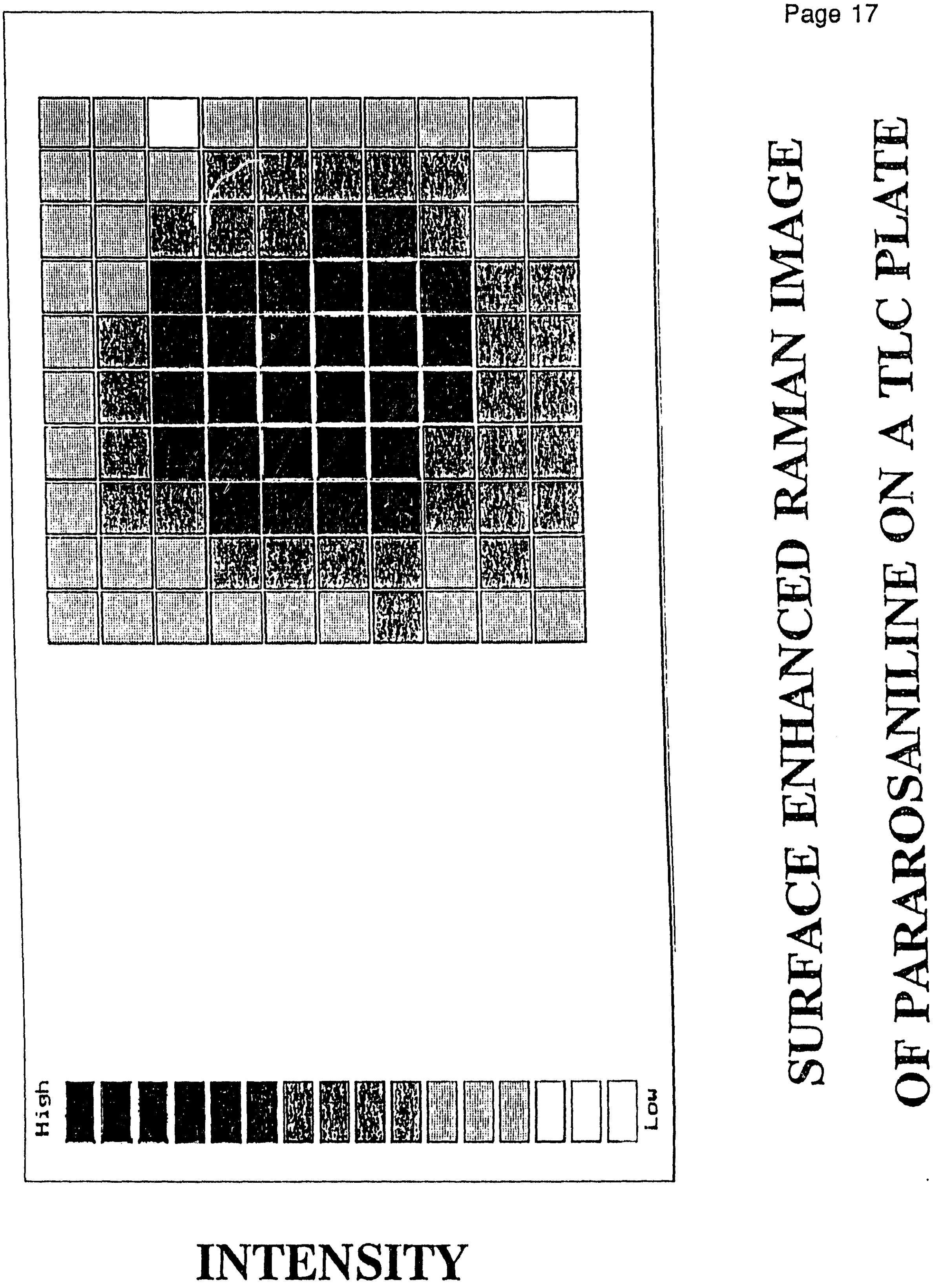


Figure 10. The SERS Raman image of pararosaniline hydrochloride on a TLC plate using a Raman frequency shift of 911 cm^{-1}.

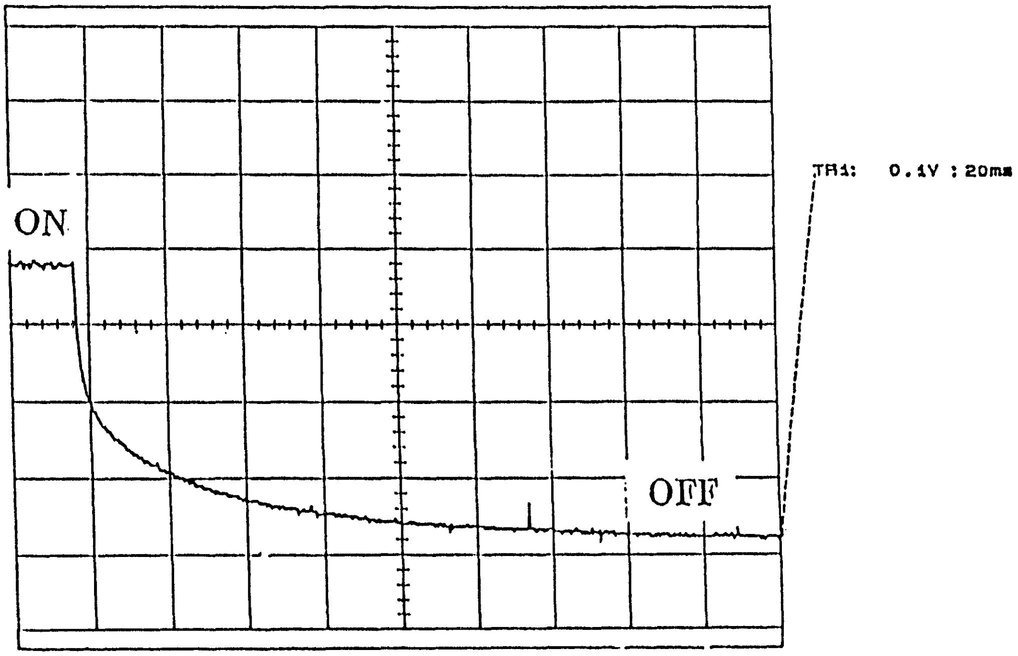
Spex 14018 double monochromator set at a Raman frequency shift of 911 cm^{-1}. We will continue development of SERS Raman imaging of TLC plates with a long term goal of generating a convenient and compact imaging unit for general use with Raman spectrometers. Our next project will be to test an alternate configuration to that in Figure 8 by using an off-axis parabolic mirror with encoding of the source radiation prior to incidence on the sample. Once we establish whether source radiation encoding prior to incidence on the sample or encoding of the scattered radiation from the sample is the better overall arrangement, we will begin to develop the next generation of configurations for SERS Raman imaging.

3. Hadamard Transform Raman Spectrometry. Mr. Edward A. Orr, Mr. John M. Poholarz, Mr. Steven L. Wright, Graduate Students in the Chemistry Department. Mr. J. Lance Porter, Mr. Mark Spinar, Graduate Students in Electrical and Computer Engineering, Professor Joseph V. Paukstelis, Chemistry Department. Professor Stephen A. Dyer, Electrical and Computer Engineering.

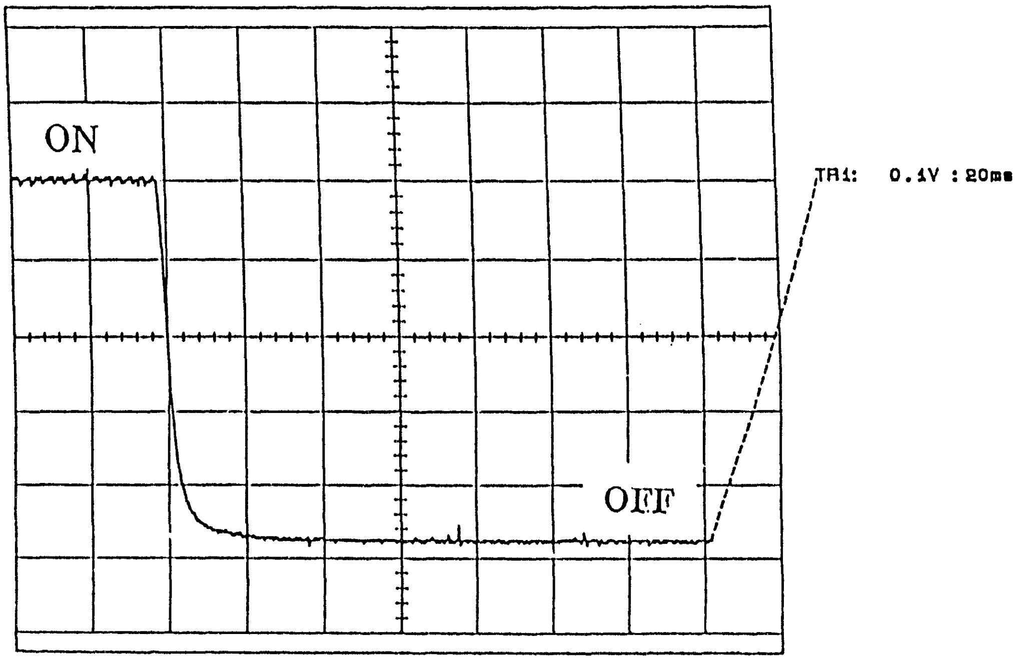
Plans for the continued development of our Hadamard transform Raman spectrometer were presented in last year's progress report. These plans included the introduction of a modified second generation stationary Hadamard encoding mask based on a polymer dispersed liquid crystal (PDLC) material with on board heaters to allow for faster switching times and the development of new and faster detection system electronics based on the Motorola DSP 56001 digital signal processor. Also included in last year's progress report were plans to develop a new Hadamard transform spectrometer for the near infrared (NIR) spectral region. The development of this new

Hadamard transform spectrometer has been discontinued in this project as others are now doing related work with funding independent of this contract Substantial progress has been made in the development of the new detection system electronics based on the Motorola DSP 56001 digital signal processor and completion of the project appears near. Problems with commercial components appear to have been solved and the software appears to be complete or nearly complete. The Hadamard encoding masks with on board heaters have been obtained and tested and should decrease our data acquisition time by a factor of 4.

The time required for the PDLC stationary Hadamard encoding mask to switch from the "ON" state to the "OFF" state is not as short as we would like. If the mask is forced to run faster than this specification, artifacts appear in the spectra. Figure 11 presents oscilloscope traces for the detector response when the mask is switched from the "ON" state to the "OFF" state at 24°C and 40°C. The improvement at 40°C is apparent as the curve falls much more sharply and the change in signal is also somewhat larger (i.e. better contrast leading to better signal-to-noise ratio other things being equal). Figure 12 shows the emission spectra of a mercury pen lamp for mask operation with a 50 millisecond (ms) delay between encodements at temperatures of 24°C, 30°C, 35°C, and 40°C. We use the mercury pen lamp spectra rather than Raman spectra because the sharper lines make the artifact easier to recognize. Figure 13 contains the emission spectra of a mercury pen lamp at 40°C for delay times between mask encodements of 20 ms, 30 ms, 40 ms, 50 ms, 75 ms, and 80 ms. Based on these results we have



MASK SWITCHING TIME @ 24° C



MASK SWITCHING TIME @ 40° C

Figure 11. Oscilloscope traces for the detector response when the mask is switched from the"ON" state to the"OFF" state at 24°C and 40°C.

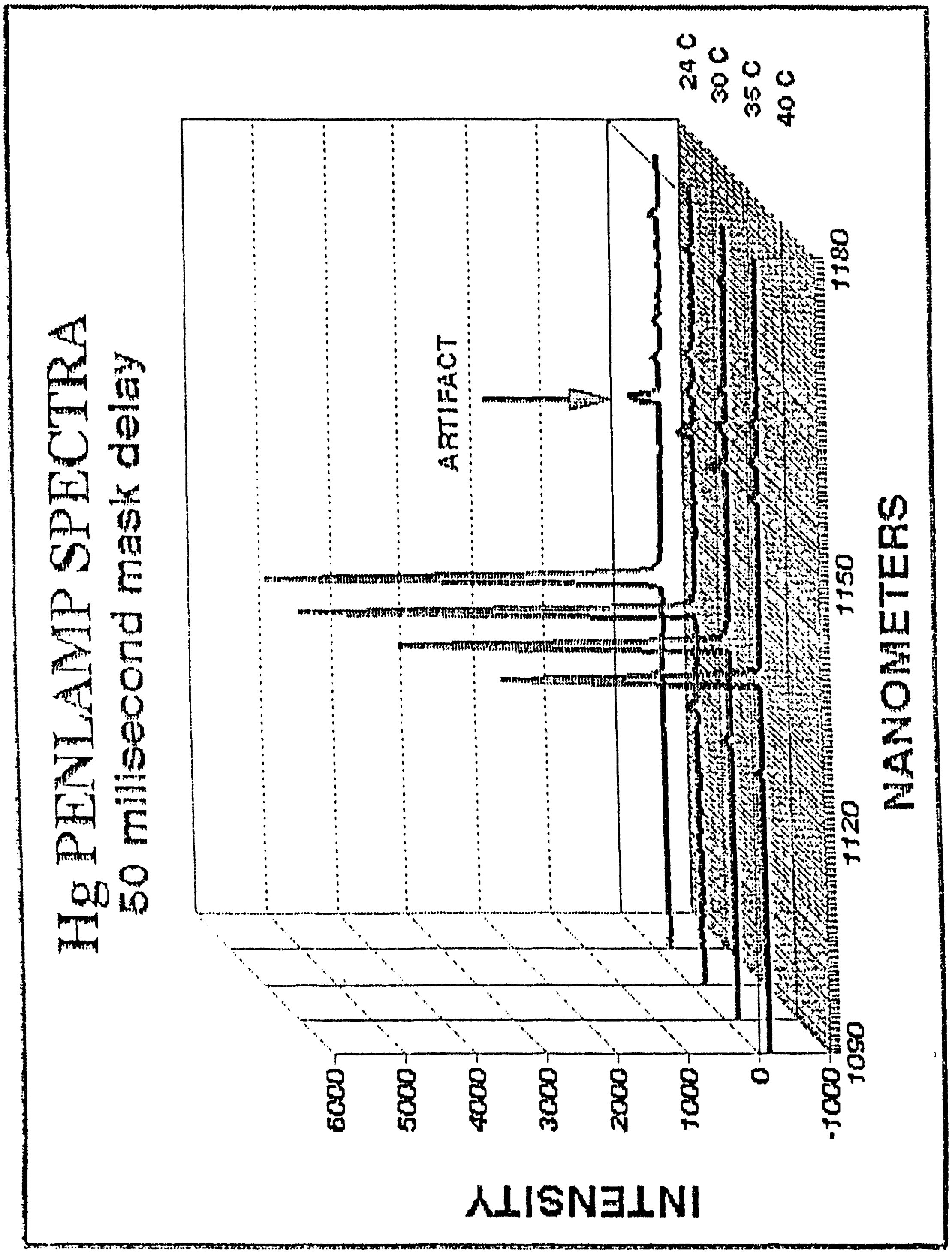


Figure 12. The emission spectrum of a mercury pen lamp for mask operation with a 50 ms delay between encodements at temperatures of 24°C, 30°C, 35°C, and 40°C.

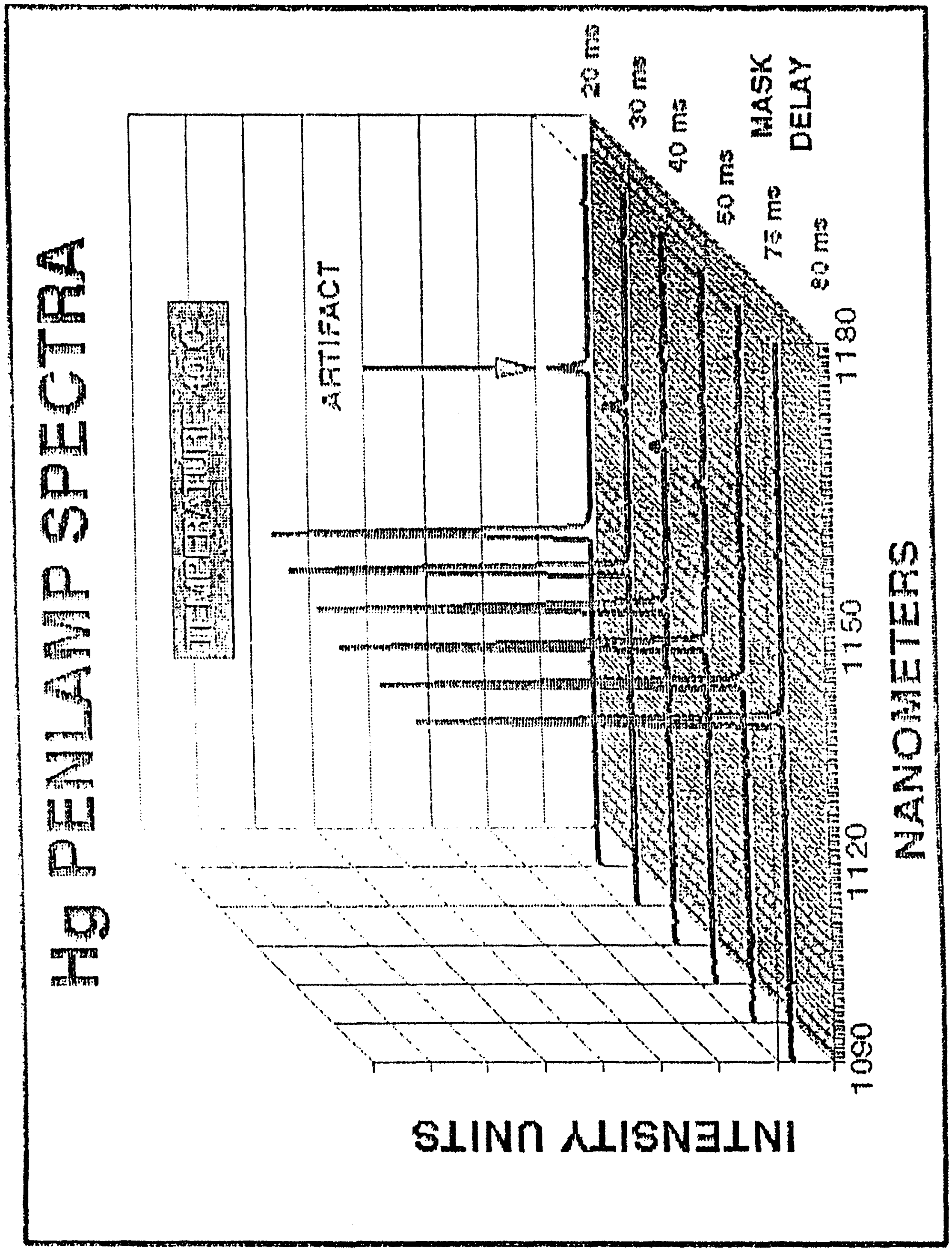


Figure 13. The emission spectrum of a mercury penlamp at 40°C for delay times between mask encodements of 20 ms, 30 ms, 40 ms, 50 ms, 75 ms, and 80 ms.

adopted 40°C and 80 ms as our new standard operating conditions for our PDLC stationary Hadamard encoding masks with on board heaters. The published spectra ("A New Stationary Hadamard Encoding Mask for Near-Infrared Hadamard Transform Raman Spectrometry," A. P Bohlke, J. M. Jarvis, J. S. White, J. D. Tate, J. V. Paukstelis, R. M. Hammaker, and W. G. Fateley, J. Molec. Struct., 247, 392-303 (1991)) presented at the 1990 Workshop on Advanced Laser Technology for Chemical measurements were obtained in 3.2 minutes but with the new standard operating conditions we estimate those spectra could be obtained in 45 seconds.

Another area of past effort has been in signal processing and additional efforts here are desirable. There are two problems in the signal processing area: (1) signal recovery made desirable by imperfections in the mask material (i.e. the "ON" state is not perfectly transparent and the "OFF" state is not perfectly opaque) and (2) elimination or reduction of artifacts generated by switching the mask encodements too fast (i.e. using a shorter delay time than the 80 ms adopted for the masks with on board heaters). Our collaborators in Electrical and Computer Engineering (Professor Stephen A. Dyer and his faculty colleagues and their students) have treated the first problem and a summary of these efforts is now in print. ("Hadamard Methods in Signal Recovery", S. A. Dyer, R. M. Hammaker, and W. G. Fateley, Computer-Enhanced Analytical Spectroscopy, Vol. 3, edited by P. C. Jurs, Plenum, New York, pp. 31-67 (1992).) However, all their demonstrations used simulations and the experimental characterization of each mask element (i.e. transmittance in the "ON" state and in the "OFF" state) has not been done and used as a final test of their procedures. Our group has developed a procedure to approach the second problem and our colleagues in Electrical and Computer Engineering have improved on our procedure. However, the improved procedure has been tested by simulation but not yet incorporated into our operating system and tested on experimental data. Thus, additional effort is required to complete and bring together all the new developments for our Hadamard transform Raman (HT-Raman) spectrometer and demonstrate the improved capabilities that should be achievable.

4. Work on the Growth of VO_2(s) Crystals for Hadamard Masking Material. Mr. Edward A. Orr, Graduate Student in the Chemistry Department.

The synthesis of vanadium (IV)-tetra-isopropoxide for use in dip coating of a substrate was described in last year's progress report as were our efforts to prepare and clean the substrate. We have been unsuccessful in obtaining satisfactory coatings of vanadium dioxide (VO_2) by this method and have suspended our efforts. With funding independent of this contract, we now have an outside investigator pursuing a sputtering technique to prepare VO_2 films on appropriate substrates. The desirable properties of VO_2 film as a Hadamard masking material (described in our original proposal and last year's progress report) motivate us to continue the efforts to develop a Hadamard encoding mask using VO_2 as the switching material.

5. Publications arising from this project.

The following publications have appeared or are scheduled to appear during 1992.

"Hadamard Methods in Signal Recovery," S. A . Dyer, R. M. Hammaker, and W. G. Fateley, <u>Computer-Enhanced Analytical Spectroscopy</u>, <u>Vol. 3</u>, Edited by P. C. Jurs, Plenum, New York, pp. 31-67 (1992).

"Near-Infrared Hadmard Transform Raman Spectrometry - A Progress Report," S. L. Wright, J. L. Porter, J. D. Tate, E. A. Orr, J. V. Paukstelis, R. . Hammaker, and W. G.

Fateley, Thirteenth International Conference on Raman Spectroscopy, proceedings of the Thirteenth International Conference on Raman Spectroscopy, Würzburg, Germany, August 31-September 4, 1992, Edited by W. Kiefer, M. Cardona, G. Schaack, F. W. Schneider, and H. W. Schrötter, John Wiley and Sons, New York, pp. 1092-1093 (1992).

"Hadamard Transform Raman Spectrometry, Past, Present, and Future," W. G. Fateley, R. M. Hammaker, J. V. Paukstelis, A. P. Bohlke, A. N. Mortensen, J. L. Porter, E. A. Orr, J. D. Tate, and S. L. Wright, Thirteenth International Conference on Raman Spectroscopy, proceedings of the Thirteenth International Conference on Raman Spectroscopy, Würzburg, Germany, August 31-September 4, 1992, Edited by W. Kiefer, M. Cardona, G. Schaack, F. W. Schneider, and H. W. Schrötter, John Wiley and Sons, New York, pp. 1114-1115 (1992).

"A Stationary Hadamard Transform Interferometer," J. D. Tate, B. Curnutte, Jr., J. V. Paukstelis, R. M. Hammaker, and W. G. Fateley, Chapter in Advances in Near IR Measurements, Vol. 1, Edited by G. Patonay, JAI Press, Inc., Greenwich, CT, pp 000-000 (1992).

6. Talks presented on this work.

The following presentations were made or are scheduled to be made during 1992

January

Society for Applied Spectroscopy Lecture Tour
Southern California Station
University of Utah (Intermountain Section)

March

43rd Pittsburgh Conference on Analytical Chemistry
and Applied Spectroscopy - one contributed paper

May

40th Annual Fisk Infrared Institute

September

13th International Conference of Raman
Spectroscopy - one invited paper and one poster

October

American Chemical Society Lecture Tour
Brigham Young University
Utah State University
DOE Workshop: Advanced Laser Technology for Chemical Measurements

November

University of Arizona
31st Eastern Analytical Symposium - one invited paper

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