Progress Report for Second Year of Contract
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Hadamard Transform Spectrometry: A New Analytical Technique

by Kansas State University
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Progress Report

March 15, 1989 to November 15, 1989

This progress report contains the following sections:

1. Summary of work
2. Recognition
3. Service
4. Papers published or accepted, chapters and meeting proceedings completed
5. Presentations of work from our laboratory

A few entries in sections 4 and 5 are not directly supported by this contract but are an integral part of the activities of the Fateley/Hammaker research group.

1. Summary of work

The following four projects were expanded during the second year of this three year program.

a. Construction of a stationary interferometer for possible use in the Hadamard transform Raman high performance liquid chromatography (HPLC) experiment.

b. Construction of a dispersive Hadamard transform spectrometer with concave holographic gratings for possible application as a HPLC detector.

c. Investigation of both colloidal-dispersed and polymer-dispersed liquid crystal materials as efficient optical shutters for making improved Hadamard encoding masks.

d. Improvement of the software necessary to recover a spectrum from the Hadamard encoded data.

Part a. (J.D. Tate, graduate student)

The stationary interferometer appears to have important advantages needed for the construction of an instrument with no moving parts. Some desirable features of the stationary interferometer are the following:

(1) No moving parts are required. Since the interferogram is sampled in space and not in the time domain, all apparatus needed for a smooth, perpendicular and reproducible mirror translation (i.e. Michelson interferometer) are eliminated. This means that there are no vibration problems from a moving mirror, thus allowing spectral measurements in harsh environments.

(2) Sampling of the interferogram is fixed by the Hadamard encoding mask; therefore, no sampling device is required to measure mirror displacement and optical retardation, such as the HeNe laser in the conventional FT spectrometer.

(3) A microcomputer can be utilized to perform all necessary data acquisition.

(4) The instrument is small and reasonably inexpensive.

(5) The field of observation should be equal to or greater than that for the Michelson-type interferometer allowing small f/number optical components to be used.

Presently all of the optical components for a stationary interferometer have been assembled and testing has begun. This instrument will be used in the Hadamard transform Raman HPLC experiment and other experiments. This instrument could prove to be useful for remote measurements as well.

Part b (A. P. Bohlke, graduate student; Dr. J. S. White, postdoctoral fellow)

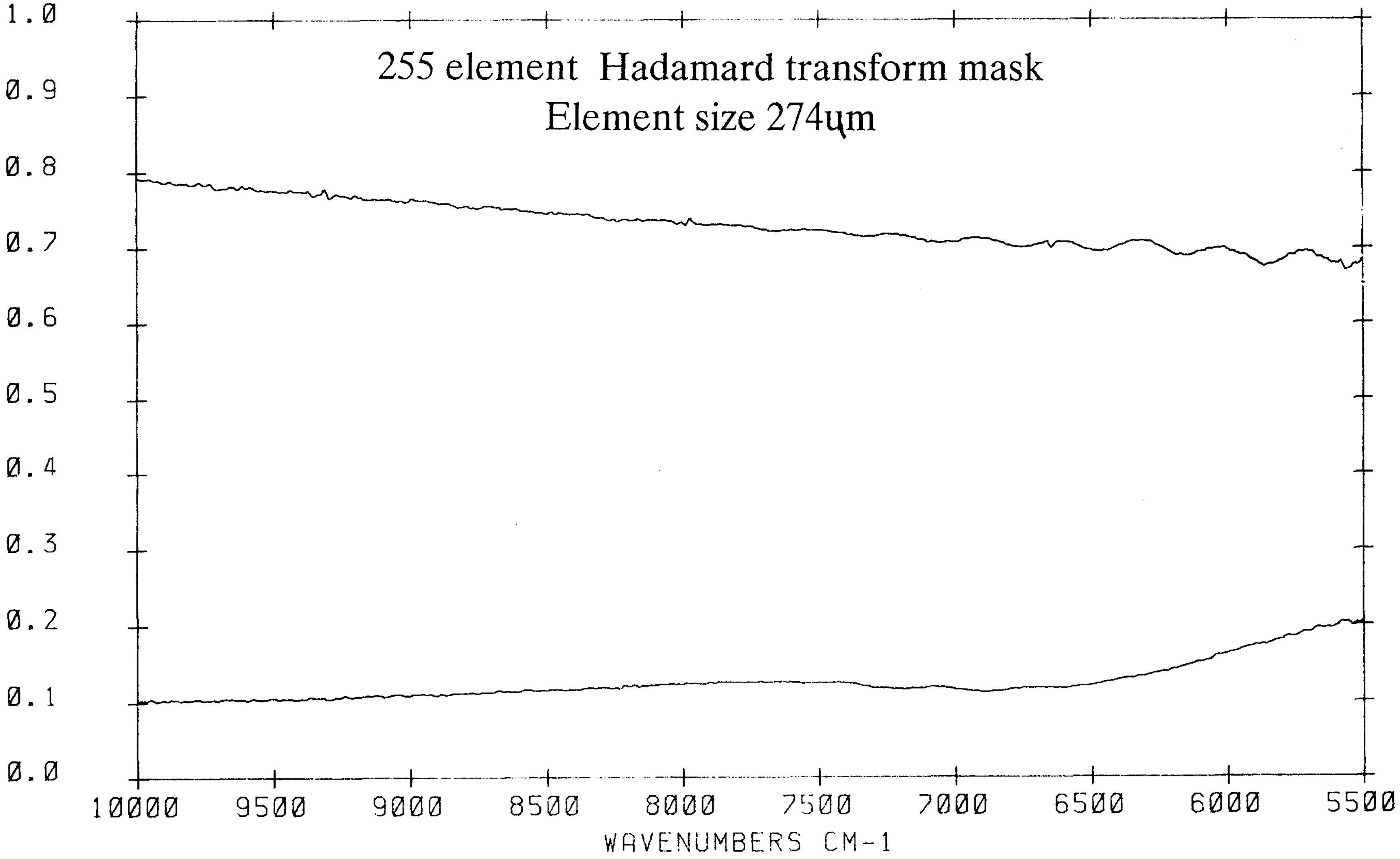
Dispersive optics still play an important role in the construction of Hadamard transform spectrometers. The use of a Jarrell-Ash dispersive instrument led to our initial breakthrough in Hadamard transform spectrometry. However, the large number of optical surfaces in this instrument are a source of reflection losses of radiation and make alignment very difficult. This instrument also suffers from a throughput disadvantage because it uses relatively slow f/8.7 optics. Recently, Instruments SA Inc. (ISA) has donated four concave holographic gratings to be used in the new visible (VIS) and near-infrared (NIR) spectrometers under construction. The use of the concave holographic grating greatly simplifies the optical system with consequent reduction in the number of optical surfaces which results in a corresponding ease in alignment. The throughput will also improve by more than a factor of 16 as these gratings use f/2 introduction optics. This situation is ideal, as the input f/number matches that of a very common fiber optic bundle, thus simplifying alignment even further. The design of this new concave holographic grating dispersive spectrometer has been completed. It is our intent to compare the stationary interferometer and concave holographic grating dispersive spectrometer. Both instruments will use the same source, Hadamard mask, and detector during comparative testing. One purpose of this experiment is to find the best instrument for use in recording the Raman scattering in the HPLC experiment.

Part c (Dr. J. S. White, postdoctoral fellow; J. M. Jarvis, graduate student)

Of great importance to our research programs is the Hadamard encoding mask. We feel we have made great improvements during the past six months in the mask for use in the near-infrared spectral region. To illustrate the improved qualities of the mask, let us start the discussion by defining the efficiency of the Hadamard encoding mask as ΔT, which is the effective contrast difference between the transmissive and opaque states of the mask (i.e. ΔT is equal to the fraction of radiation passing through the shutter during its <u>open</u> cycle <u>minus</u> the fraction of radiation passing through the shutter during its <u>closed</u> cycle). ΔT is directly related to the signal-to-noise ratio of our system. The liquid crystal mask employed in previous research had low values of ΔT (e.g. 0.15 or less) in the near-infrared spectral region (a perfect mask would have ΔT=1). Nevertheless, we were able to obtain near-infrared Hadamard transform Raman spectra with these low ΔT values for a Hadamard encoding mask with 127 spectral resolution elements. Our new Hadamard encoding masks, constructed from colloidal-dispersed liquid crystal material, have values of ΔT ranging from 0.48 to 0.70 in the near-infrared spectral region and also contain 255 spectral resolution elements (double the number of the masks used previously). Spectra showing near-infrared transmission values of the new Hadamard encoding mask in the <u>open</u> and <u>closed</u> cycles appear in Figure 1. The collidal-dispersed liquid crystal uses diffuse scattering to generate an opaque condition (the bottom transmission curve in Figure 1). When an external voltage is applied to this mask, the mask loses its diffuse scattering property and becomes relatively transparent to visible and near-infrared radiation (the top transmission curve in Figure 1). An important characteristic of these new collidal-dispersed liquid crystal materials is the elimination of polarizing films previously employed. The removal of two polarizing films and the better optical properties of the collidal-dispersed liquid crystal material has significantly increased the value of ΔT. These masks have been constructed by a commercial supplier and the electrical drivers have been built by Mr. John M. Jarvis, a graduate student. Mr. Jarvis's electrical drivers controlling the individual elements of the mask have proven to work very successfully in recent testing. The test involves reliability, switching speed and optical shutter efficiency.

Part d (Prof. J. V. Paukstelis, Department of Chemistry and Prof. S. A. Dyer, Department of Electrical and Computer Engineering)

New software recently developed to perform the fast Hadamard transform has been tested and found to be successful. Data collection, coaddition of data, and data presentation software have been greatly improved with the help of Professor Joseph V. Paukstelis, Department of Chemistry. In addition, Professor Stephen A. Dyer and coworkers, Department of Electrical



Transmission characteristics of a
Colloidal Dispersed Liquid Crystal Optical Shutter
Array

255 element Hadamard transform mask
Element size 274µm

Figure 1

and Computer Engineering, have developed new spectral-recovery methods specific for Hadamard transform spectrometry employing liquid crystal technology in stationary masks. Their work includes a general theoretical analysis of and procedure to correct for the effect of mask nonideality (deviation from 100% transmission in the transparent state and 0% transmission in the opaque state) on the spectral recovery process. Papers on spectral-recovery have been published in Applied Spectroscopy in 1989. The spectral recovery alogrithms take a small amount of computer time and yield greater precision in the measured transmission values in the spectrum. A simplified summary of the method follows:

1) All elements of the mask are held in the opaque position (closed). Approximately ten measurements are made at the detector. This procedure records noise upon the detector and "other" light intensities.
2) Each element of the mask is opened individually and a measurement of the transmission of each element is made for the transparent state (open). A matrix which reflects the "mask defects" is constructed from these data.
3) In the spectral recovery manipulations the mask defect information and other data are applied appropriately to correct the output spectrum for nonidealities of the mask to reconstruct the input spectrum correctly. The measurements in 1) and 2) only need to be made once for a particular mask.

The procedure for spectral recovery is important in maintaining good analytical precision in the measurements made by the Hadamard transform spectrometer.

2. Recognition

The principal investigator was named a University Distinguished Professor in 1989. The principal investigator was a visiting Professor at the University of Utah for the Spring Quarter of 1989.

3. Service

Editor-in-Chief, Applied Spectroscopy, 1974-present

Organization Committee, European Congress on Molecular Spectroscopy, 1980-present

Society for Applied Spectroscopy, tour speaker, 1989

4. Papers published or accepted, chapters and meeting proceedings completed

1. "Near-Infrared Hadamard Transform Raman Spectrometry," A. P. Bohlke, J. D. Tate, J. S. White, J. V. Paukstelis, R. M. Hammaker, and W. G. Fateley, J. Molec. Struct., 200, 000 (1989). Special issue dedicated to Prof. Bryce Crawford, Jr.

2. "Near-Infrared Hadamard Transform Raman Spectrometry," A. P. Bohlke, R. M. Hammaker, and W. G. Fateley, Proceedings of the 7th International Conference on Fourier Transform Spectroscopy, June 19-23, 1989, SPIE Proceedings, in press.

3. "Stationary Hadamard Transform Interferometer," J. D. Tate, R. M. Hammaker, and W. G. Fateley, Proceedings of the 7th International Conference on Fourier Transform Spectroscopy, June 19-23, 1989, SPIE Proceedings, in press.

4. "Instrumentation Needs for Hadamard Transform Spectrometry (HTS)," J. S. White, R. M. Hammaker, and W. G. Fateley, Proceedings of the 7th International Conference on Fourier Transform Spectroscopy, June 19-23, 1989, SPIE Proceedings, in press.

5. "Hadamard Transform Spectroscopy: Teaching Old Monochromators New Tricks," R. M. Hammaker, W. G. Fateley, and D. C. Tilotta, Spectroscopy International, 1(2) 10-23 (1989); R. M. Hammaker and W. G. Fateley postscript in following issue Spectroscopy International 1(3) 000 (1989).

6. "Hadamard Transform Spectrometry: Application to Biological Systems, A Review," A. P. Bohlke, D. Lin-Vien, R. M. Hammaker, and W. G. Fateley, chapter in Spectroscopy of Inorganic Bioactivators, Theory and Applications - Chemistry, Physics, Biology, and Medicine, NATO ASI Series C Vol. 280, proceedings of NATO Advanced Study Institute held at Loutraki, Greece, August 20-29, 1988, Edited by Theo Theophanides, Kluwer Academic Publishers, Boston, pp. 159-189 (1989).

7. "A Fast Spectrum-Recovery Method for Hadamard-Transform Spectrometers Having Non-Ideal Masks," S. A. Dyer, B. K. Harms, J. B. Park, T. W. Johnson, and R. A. Dyer, Applied Spectroscopy, 43 435 (1989).

8. "An Efficient Method for Recovering the Optimal Unbiased Linear Spectrum-Estimate from Hadamard Transform Spectrometers Having Nonideal Masks," T. W. Johnson, J. B. Park, S. A. Dyer, B. K. Harms, and R. A. Dyer, Applied Spectroscopy, 43, 746 (1989).

9. "Evaluation of a Mobile FT-IR System for Rapid VOC Determination: I. Preliminary Qualitative and Quantitative Calibration Results," M. L. Spartz, M. R. Witkowski, J. H. Fateley, J. M. Jarvis, J. S. White, J. V. Paukstelis, R. M. Hammaker, W. G. Fateley, R. E. Carter, M. Thomas, D. D. Lane, G. A Marotz, B. J. Fairless, T. Holloway, J. L. Hudson, and D. F. Gurka, American Environmental Laboratory 2(11) 000 (1989).

10. "Development of a Mobile Laboratory System for On-Site Analyses of Atmospheric Volatile Organic Compounds Using FT-IR." M. L. Spartz, M. R. Witkowski, J. H. Fateley, R. M. Hammaker, W. G. Fateley, R. E. Carter, M. Thomas, D. D. Lane, G. A. Marotz, B. J. Fairless, J. Helvig, and J. Hudson, Proceedings of the Fifth Annual Waste Testing and Quality Assurance Symposium, Washington, D.C., July 24-28, 1989.

11. "A Mobile FT-IR to Measure On-Site Emissions of Volatile Organic Compounds (VOC), M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, and W. G. Fateley, Proceedings of the 7th International Conference on Fourier Transform Spectroscopy June 19-23, 1989, SPIE Proceedings, in press.

12. "Design and Calibration of a Mobile Laboratory for On-Site Measurements of Volatile Organic Compounds (VOC) Using Fourier Transform Infrared Spectrometry (FT-IR)," M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, and W. G. Fateley, Proceedings of the Conference on Hazardous Waste Research, Kansas State University, May 23-24, 1989.

5. Presentations of DOE work from our laboratory

23 March - 15 June 1989	Visiting Professor, University of Utah in Salt Lake City, UT
14 April 1989	Lecture, District VII of EPA in Kansas City, KS
21-23 April 1989	Lecture, Meeting of Society for Applied Spectroscopy in Lake Arrowhead, CA
9-11 May 1989	DOE Workshop on Advanced Laser Technology for Chemical Measurements, Argonne National Laboratory in Argonne, IL
14-18 May 1989	Lectures, Fisk Institute in Nashville, TN
18-23 June 1989	7th International Conference on Fourier Transform Spectroscopy, George Mason University in Fairfax, VA, 3 posters
26-27 June 1989	Lecture, Shell Development Company in Houston, TX
31 July - 2 August 1989	Rocky Mountain Meeting in Denver, CO, invited lecture
6-8 August 1989	Process Control Session, Instrument Society of America (ISA) in Lake Geneva, NY, invited lecture
8-11 August 1989	Gordon Conference on Analytical Chemistry, New Hampton School, discussion leader and invited poster
14 August 1989	Lecture, Waters Associate in Boston, MA
15 August 1989	Lecture, EIC Electron Industry in Boston, MA

20-25 August 1989	Lectures, Spectroscopy Conference, University of Helsinki, in Helsinki, Finland
7 September 1989	Talk presented to Rotary Club in Manhattan, KS
13-15 September 1989	Present First Prof. Velmer Fassel Lecture at Iowa State University in Ames, IA
24-28 September 1989	Eastern Analytical Symposium in New York, NY, two invited papers
1-5 October 1989	16th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) in Chicago, IL, invited paper