

Multidimensional Spectrometry and Mapping

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ABSTRACT: One observes that the early developments in chemistry depended upon the improvement of the balance. Major milestones in chemistry can be related directly to improvements in balance design, precision, and accuracy. In a similar manner, the past three decades have seen dramatic improvements in spectrometers. The development of these instruments has greatly improved our understanding of polymer structure and properties. We discuss our current research in multidimensional spectrometry, imaging, and mapping. How does one determine the structure of molecules? One approach is the infrared and Raman study of the polymer vibrations to understand the structure and interactions so successfully applied by our awardee, Professor Jack Koenig. Historically, in the 1950s, the Perkin–Elmer Corp. introduced an infrared microscope for a limited number of applications. This development stimulated the thought of seeking more information about the microstructure. Today, we have a number of two-dimensional detectors for infrared and Raman studies. However, the expense of this instrumentation tends to limit its utilization. In this article, a new inexpensive approach for mapping molecular structure in polymeric materials is discussed. This new approach includes the combination of interferometers and Hadamard transform techniques to perform multidimensional spectrometry and mapping. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1307–1310, 1998

Key words: Hadamard transform spectrometry; imaging; multiplexing

INTRODUCTION

Hadamard transform spectrometry (HTS) has been of interest to our research group for nearly two decades.^{1–9} Here, HTS is a unique combination of dispersive and multiplexing spectrometries. Similar to a dispersive spectrometer, the radiation from an infrared source is collected and separated into its individual spectral resolution elements by a grating, prism, or other spectra separators such as a linear variable filter. This spectrally separated radiation is collected and focused by a mirror or lens and spatially presented on a focal plane. Unlike a dispersive spectrometer, which possesses a single exit slit, the Ha-

damard transform spectrometer employs a multi-slit array. This optical configuration allows for the simultaneous measurement of a multitude of spectral resolution elements and produces a multiplexing spectrometer. The main direction and focus of our research efforts has been the application of Hadamard transform techniques to visible and near-infrared Raman spectrometry. This article discusses the application of Hadamard transform techniques to chemical mapping.

Previously, photoacoustic spectrometry (PAS) has been demonstrated to be a useful technique in the investigation of solid samples.^{10–12} This depth-profiling ability of PAS has been well documented.^{10,11} Rosencwaig and Gersho¹³ defined a thermal diffusion length as $\mu = (\kappa/pC\Pi f)^{1/2}$, where κ is the thermal conductivity; p , the density; C , the specific heat; and f , the modulation frequency in Hz. It is only the heat generated

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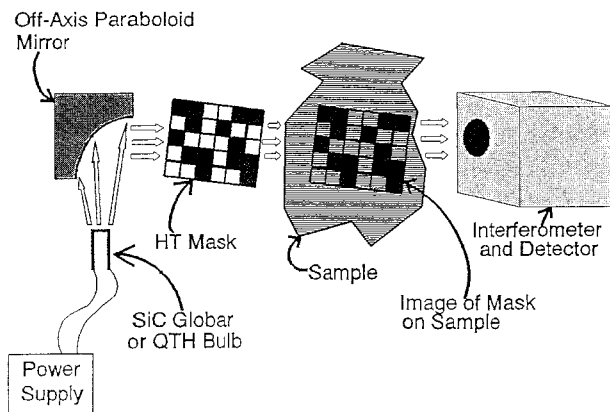


Figure 1 The chemical imaging experiment was conducted in the NIR region with a mechanical 2-D Hadamard encoding mask combined with a Midac™ FTIR spectrometer and source encoding where the “shadow” of the mask falls onto the sample.

within one thermal diffusion length of the sample surface which gives rise to a detectable modulation of the boundary-layer temperature. The thermal diffusion length is inversely dependent on the modulation frequency, so by changing the modulation frequency, the observed depth in a sample may be varied.

Because a finite time is required for the generated heat to flow from the sample into the carrier gas, a phase lag is observed between signals generated at the sample surface and those coming from below the surface. Adams and Kirkbright¹⁴ were among the first to exploit this phenomenon, applying it to the analysis of biological samples in the ultraviolet-visible region. They demonstrated their ability to distinguish between the surface and bulk components.

EXPERIMENTAL

In this experiment, we used a Midac MD2400 series FTIR spectrometer equipped with a quartz window, a CaF₂ beam splitter, and an InSb detector at liquid nitrogen temperatures. The source was a 12 V, 150 W quartz-tungsten-halogen bulb (Osram Longlite part # 64642) and was powered by a variable power supply (DC Power Supply 155, Laser Instruments). The experiments were performed at about 80% of full detector saturation, which for our optical arrangement turned out to correspond to about 6.2 V and 4.5 amps.

The experimental setup is shown in Figure 1. Radiation from the SiC globar or OTH bulb is

collected and collimated by an off-axis paraboloidal reflector (02 POA 19, Melles Griot) through the 2-D encoding mask. Here, the shadow of the mask impinges upon the sample. The interferometer used as the detector yields the encoded spectrum.

The 2-D mechanical mask is constructed from metal, 5000s of an inch thick, employing a proprietary procedure (Towne Technologies Inc., Somerville, NJ). The art work for this mask was prepared by Microphase Inc. (Colorado Springs, CO). The mask consists of a 15 × 17-array of pixels, each being 540 μm × 540 μm with a 30-μm spacer between each pixel. The pixels are either “off” or “on” and groups of 15 × 17 or 255 pixels are used to change the illumination of the test area of the sample. The array is moved, one row at a time, by a translation stage so that the sample can be measured with a sequence of encodements. The matrix used the 255 different encodements was a Simplex-255 matrix. Each pixel of the mask can be considered to be an “unknown.” Thus, one needs 255 equations to solve for the 255 unknowns of the mask. This is done by collecting a conventional FT-NIR spectrum at the 255 different encodement patterns of the 2-D encoding mask. A fast Hadamard transform is performed on these 255 “equations,” and the result is 255 spectra of the sample in the shadow of the 255 pixels of the mask on the sample. Details of both the matrix and the fast Hadamard transform can be found in Sloane and Harwit.¹⁷ Software written here at Kansas State University was used to process the experimental data.

Two different samples were used to demonstrate the FT-NIR-HT spectroscopy. The first sample is designed to demonstrate that the FT-NIR-HT experiment can spatially resolve components that have overlapping bands. This sample consists of three different plastics from common products that were readily available in the laboratory. These three plastics are a blue filter from an old U.S. Army flashlight, a brown piece of laboratory safety goggles, and a white piece from the case in which a backup diskette came. The arrangement was the placement of each sample in a different position.

The second sample consisted of two small pieces of clear Scotch tape on top of a glass microscope slide. This sample is meant to demonstrate how this technique could be used to image impurities of heterogeneities in the samples.

DATA AND RESULTS

Conventional FT-NIR spectra were collected for this sample. These spectra were collected at an 8 cm^{-1} spectral resolution and 32 coadditions. The spectra are overlaid on each other to show how the bands of the three spectra overlap in the region around 5700 cm^{-1} .

A conventional FT-NIR spectrum of the entire sample, instead of one component at a time, shows how the bands of the three components of the samples are convoluted. The FT-NIR-HT experiment was then performed using this sample where the locations of pixels 47, 58, and 137 of the 2-D encoding mask are examined. The spectra of the sample of pixels 47, 58, and 137 were recorded. These three spectra are plotted and show no similar absorptions. One finds that the HT-FT-NIR process was able to separate spatially the spectra of the different components of the sample.

To demonstrate that this technique is capable of imaging what would be analogous to small impurities in a sample, the sample that consisted of two small pieces of clear "packing" tape on a glass microscope slide was also analyzed. A conventional single-beam FT-NIR spectrum of a large piece of the tape was collected as a reference spectrum. The observed bands between about 5100 and 5500 cm^{-1} were identified as water bands. The only bands that are attributed to the absorption by the tape are those between about 4100 and 4300 cm^{-1} . A conventional single-beam FT-NIR spectrum of the actual sample of the two small pieces of tape on the glass slide clearly demonstrated that the bands due to the absorption of radiation by the tape are not visible. Again, it should be possible to perform the FT-NIR-HT experiment and obtain good spectra of the two small pieces of tape.

Since we have 255 spectra of different regions of the sample, we should be able to construct chemical images of the sample. Using the single-beam HT-FT-NIR spectra and plotting the area of the bands between about 4200 and 4300 cm^{-1} versus the pixel position resulted in the chemical image. It is easy to see from the image we obtained that we were successful in imaging the two small pieces of tape in the sample.

Lastly, the multiplex advantage of the 2-D Hadamard encoding mask was observed. One pixel of the mask was allowed to pass radiation and a conventional FT-NIR single-beam spectrum of the sample was collected. If 254 more

spectra were obtained in the same manner, then these spectra could be used to construct chemical images of the sample. We did this to demonstrate the multiplex advantage. However, instead of collecting a spectrum through one pixel at a time (a raster scan), we collected spectra through encode-ment patterns of the pixels. Each encode-ment pattern has 128 pixels open at a time. Most importantly, we have more light on the detector at a time and we are able to realize a multiplex advantage. This advantage was observed by comparing the spectrum of the sample collected as a raster scan with a spectrum of the same size area of the sample collected in the FT-NIR-HT manner.

CONCLUSIONS

It is clear from this work that it is possible to combine a 2-D Hadamard encoding mask with an NIR FTIR spectrometer. This combination gives 255 NIR spectra of the sample. The 255 spectra correspond to the areas on the sample where the shadows of the 255 pixels of the 2-D mask were formed. The spectra that are obtained are identical to spectra that would be obtained by collecting a conventional FT-NIR spectrum through a single pixel of the mask, except that the FT-NIR-HT spectra has a higher SNR.

Also, several different designs for encoding masks are being considered. We hope that in the near future we will have an inexpensive and easy-to-use FTIR attachment to market.

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