Transform Techniques in Chemistry

Edited by Peter R. Griffiths

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Preface

The application of the Fourier transform is being seen to an increasing extent in all branches of chemistry, but it is in the area of chemical analysis that the greatest activity is taking place. Fourier transform infrared and nuclear magnetic resonance spectrometry are already routine methods for obtaining high-sensitivity IR and NMR spectra. Analogous methods are now being developed for mass spectrometry (Fourier transform ion cyclotron resonance spectrometry) and microwave spectroscopy, and Fourier transform techniques have been successfully applied in several areas of electrochemistry. In addition the fast Fourier transform algorithm has been used for smoothing, interpolation, and more efficient storage of data, and has been studied as a potential method for more efficient identification of samples using pattern recognition techniques.

Linear transforms have also been shown to be useful in analytical chemistry. Probably the most important of these is the Hadamard transform, which has been applied in alternative methods for obtaining IR and NMR data at high sensitivity. Even though *measurements* involving this algorithm will probably not be applied as universally as their Fourier transform analogs, in the area of pattern recognition application of the Hadamard transform will in all probability prove more important than application of the Fourier transform.

In this book, distinguished investigators in the various fields mentioned above have written on their area of expertise at a level that should be understandable to graduate analytical chemists and to the advanced undergraduate, as well as the professional maintaining and updating research skills. It is hoped that the similarities between the various spectroscopic and data manipulation techniques will become evident throughout the book. We have omitted treatment of crystallographic applications because they seem outside the mainstream of analytical interests.

After a brief look at the history of transform techniques in chemistry and an editorial forecast of their applications in the future (Chapter 1), the mathematical basis of the Fourier transform is introduced by Charles Foskett of Digilab, Inc., in Chapter 2. In Chapter 3, Alan Marshall and Melvin Comisarow of the University of British Columbia discuss the foundation of multiplex methods in spectroscopy, showing the origin of the advantages of instruments that do not measure a spectrum directly, but rather generate a signal that is related to the spectrum through the Fourier or Hadamard transform. In Chapter 4, James Cooper of Tufts University discusses the nature of the data-handling and computer capabilities required for on-line Fourier transform spectrometry.

The next six chapters describe the theory, instrumentation, and applications of several different types of multiplex spectroscopy. In Chapters 5 and 6 the editor describes Fourier transform infrared spectrometry, and in Chapter 7 Martin Harwit of Cornell University describes Hadamard transform infrared spectrometry, including how this technique may be used to multiplex information both spectrally and spatially. In Chapter 8, Thomas Farrar of the National Science Foundation introduces Fourier transform–NMR spectrometry, and some of the more recent advances in this subject are described in the subsequent chapter (Chapter 9) by James Cooper. In Chapter 10, the nature of Fourier transform ion cyclotron resonance spectrometry is introduced by Melvin Comisarow.

Several of the more important applications of the Fourier transform in data processing are discussed in Chapter 11 by John Lephardt of Philip Morris U.S.A., and in Chapter 12, the application of transform techniques in pattern recognition is described by Charles Wilkins of the University of Nebraska and Peter Jurs of Pennsylvania State University. Chapter 13, by Russell Larsen of the University of Nevada at Reno, describes potential applications of binary transforms for very rapid data processing; to a greater extent than the previous chapters, this represents a look into the future and is written to a slightly more advanced audience than the earlier chapters. We believe it represents an important new transform technique of the future and merits a more advanced treatment since there is little readily available reference material on this subject. Finally, the editor has summarized the applications of the Fourier transform in electrochemistry in a chapter that illustrates not only the sensitivity advantage obtained through acquiring data at several frequencies simultaneously but also shows how the information content of different types of electrochemical data may be enhanced by the application of the Fourier transform independently of the manner in which the data were acquired.

That a volume such as this may be compiled is a tribute to the many pioneers in all the areas covered in this book. The fact that so many of the techniques that are described here are now available in the market place is similarly a tribute to the individuals and companies who had faith that transform techniques were of sufficient value to be developed commercially. On a more personal level, the editor and many of the authors would like to thank the various agencies that, in such timely fashion, supported their research and the many co-workers without whose cooperation and hard work many of the results described in this book would not have been found. Finally, the secretarial assistance so valuable in preparing the manuscripts of these chapters is gratefully acknowledged.

Peter R. Griffiths

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Chapter 1

Transform Techniques in Chemistry: Past, Present, and Future

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1.1. THE PAST

1.1.1. Optical Spectroscopy

Although the use of transform techniques in analytical chemistry and applied spectroscopy has only become widespread in the past five years, the history of this subject can be traced back to the middle of the nineteenth century when the effect of the interference of light was first used to derive spectroscopic information. In 1862, Fizeau(1) used Newton's rings to show that the yellow sodium radiation was a doublet whose separation was 1/980 of their average wavelength. At the end of the century Michelson designed the *interferometer*, which now bears his name.(2,3) The initial uses of this instrument for spectroscopic purposes concerned the determination of spectral profiles through the use of the visibility technique,(4) which is essentially a study of the envelope of what we now call the *interferogram*. Rayleigh(5) pointed out that a unique spectral distribution cannot be found from the visibility curve itself, and the Fourier transform of the interferogram is needed to calculate the spectrum unequivocally.

The actual calculation of a digital Fourier transform was beyond the technical resources available at the turn of the century and, in a remarkable

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attempt to circumvent this limitation, Michelson developed a harmonic synthesizer that was designed to output the Fourier transform of an input signal. This was an 80-channel device consisting of 80 gears driving 80 wheels to rotate at speeds proportional to the integers 1 through 80. Each wheel rocked a lever, which in turn generated a simple harmonic motion in an adjustable arm. Each arm was linked by springs to an axle, and the composite motion of all 80 arms moved a pen. There is no doubt that this was the first Fourier transform computer; however, there is no record of Michelson ever using this device to obtain a spectrum from an optical signal. He did successfully reinvert synthetic signals, which in itself is a remarkable feat since it was achieved more than 40 years before the same operation was performed on a digital computer.

Michelson was able to show that the red Balmer line of hydrogen is a doublet and that the red line of cadmium is exceptionally narrow. He proposed this line as a wavelength calibrant, and it was used as the standard of length until 1960, when it was supplanted by the orange line of krypton produced by a lamp operating at the triple point of nitrogen. He also showed that the green line of natural mercury is a complicated multiplet, which he was unable to resolve completely with his 80-channel harmonic synthesizer.

The first true interferogram was published by Rubens and Wood in 1911(6); they were investigating the far-infrared radiation emitted by a Welsbach mantle, and chose to use an interferometer because a quartz prism with sufficient dispersion absorbed too much of the incident radiation. They did not use a Michelson interferometer, but rather one that worked using the same principles as the Newton's rings apparatus employed by Fizeau.(1) Rubens and his co-workers, in this and subsequent work, guessed a spectral distribution, calculated the Fourier transform, and then adjusted the estimate to try to make the calculated and observed interferograms match. No reason was ever given why this method was preferred to direct Fourier transformation. In Rubens' work the multiplex gain (*vide infra*) was realized, but there is no evidence that it was ever appreciated.

Several refinements and applications of interferometry were made in the next forty years, but it remained a tool for high-resolution spectroscopy until Jacquinot in France and Fellgett in England recognized two important advantages of interferometers for the measurement of spectra. Jacquinot(7,8) recognized that the optical energy *throughput* (the product of the area and solid angle of a beam at its focus) of a Michelson interferometer used for spectroscopy is greater than that of a monochromator used for spectral measurements at the same resolution. Fellgett(9) not only published the first numerically transformed interferogram, but also recognized that an interferometer gave a fundamental advantage over a scanning monochromator, that of *multiplexing* the spectral information. The multiplex, or Fellgett, advantage is the basis for several types of spectrochemical and electrochemical methods described in this book.

The gain in signal-to-noise ratio resulting from the application of the multiplex principle may be appreciated intuitively on the basis that the signal integrates in direct proportion to T, the time of observation, whereas the noise integrates in proportion to $T^{1/2}$. If a total observation time T is available for the exploration of M spectral elements, they may be investigated sequentially or simultaneously, provided that, in the latter case, they may be *decoded* at the end of the measurement. In sequential investigations, each element is observed for an average time T/M, with a noise level proportional to $(T/M)^{1/2}$, so that the signal-to-noise ratio is proportional to $(T/M)^{1/2}$. In the simultaneous investigation, each element is observed for a time T, and the signal-to-noise ratio is proportional to $T^{1/2}$, indicating a gain of $M^{1/2}$ over the sequential case. For spectra measured with equal signal-to-noise ratios on each type of spectrometer, the observation time required for the sequential measurement is M times longer than the simultaneous measurement.

The time, effort, and cost involved in decoding the spectral information from the output of a multiplex spectrometer was a principal reason for the reluctance of chemists to use multiplex methods for infrared spectroscopy, especially in view of the fact that most infrared spectrochemical data could be obtained using a scanning monochromator (albeit at less than the optimum signal-to-noise ratio). Only those scientists who could not obtain acceptable spectra using a monochromator because of the weakness of their sources had a strong interest in developing multiplex methods. It is therefore not surprising that many of the pioneers of Fourier transform infrared (FT–IR) spectrometry were astronomers and far-infrared spectroscopists. Connes and Mertz, who led the development of high-resolution and rapid-scanning low-resolution interferometers, respectively, are both astronomical spectroscopists. Gebbie and Strong, who pioneered the development of Michelson and lamellar grating interferometers, respectively, were both interested in far-infrared measurements. The first Michelson interferometer sold commercially was designed for measurements in the far-infrared region.

It is surprising that, despite the simplicity of Michelson interferometers designed for far-infrared spectroscopy, the first commercial instrument (manufactured by Research and Industrial Instruments Corporation in England) was not delivered until 1964, well over a decade after Jacquinot and Fellgett showed the fundamental advantages of this type of instrument. Since that time, the number of FT–IR spectrometers has steadily increased. The development of the fast Fourier transform (FFT) algorithm has substantially reduced the time to compute a spectrum, to the point that it is rarely the rate-limiting step in spectroscopic measurements. The development of small, relatively inexpensive data systems has greatly increased the flexibility and ease with which these instruments can be used. Now that the advantages of FT–IR spectrometry are becoming appreciated by chemical spectroscopists, several new applications for infrared spectroscopy are finally being used routinely in the analytical laboratory.