Fourier, Hadamard, and Hilbert Transforms in Chemistry

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**Dedicated
to
the Memory of
Willis H. Flygare**

PREFACE

In virtually all types of experiments in which a response is analyzed as a function of frequency (e.g., a spectrum), transform techniques can significantly improve data acquisition and/or data reduction. Research-level nuclear magnetic resonance and infra-red spectra are already obtained almost exclusively by Fourier transform methods, because Fourier transform NMR and IR spectrometers have been commercially available since the late 1960's. Similar transform techniques are equally valuable (but less well-known) for a wide range of other chemical applications for which commercial instruments are only now becoming available: for example, the first commercial Fourier transform mass spectrometer was introduced this year (1981) by Nicolet Instrument Corporation. The purpose of this volume is to acquaint practicing chemists with the basis, advantages, and applications of Fourier, Hadamard, and Hilbert transforms in chemistry. For almost all chapters, the author is the investigator who was the first to apply such methods in that field.

The basis and advantages of transform techniques are described in Chapter 1. Many of these aspects were understood and first applied by infrared astronomers in the 1950's, in order to improve the otherwise unacceptably poor signal-to-noise ratio of their spectra. However, the computations required to reduce the data were painfully slow, and required a large computer. In 1965, Cooley and Tukey published a fast Fourier transform algorithm that reduced the computation time by a factor of $N/\log(N)$, making it possible to transform data sets of useful size (say, 8192 points) in an acceptably short time (about 10 sec for 8192 points, compared to about 6 hours with the conventional algorithm). On-line FT computations could thus be done by a minicomputer. Moreover, analog-to-digital converters with suitable speed (50,000 words/sec) and accuracy (12-bit per word) were available, and commercial stand-alone FT-IR and FT-NMR spectrometers were produced within 3 years.

Application of transform methods to other experiments required additional theoretical and/or technical developments, and thus occurred later. For example, FT-rotational spectrometry (first demonstrated in 1974) used the same pulse excitation as FT-NMR, but required a much wider spectral range and thus faster analog-to-digital converters (e.g., 100 MHz at 1 bit per word). Different excitation

waveforms were necessary for FT ion cyclotron resonance mass spectrometry (frequency-sweep, 1973), FT faradaic admittance (pseudo-random noise, 1977), and FT dielectric relaxation (voltage step, 1975). Two-dimensional FT NMR (1975) and the conceptually similar FT ENDOR experiment (1972) required significant theoretical groundwork. FT mu spin resonance analysis (the mu atom is a very light isotope of the hydrogen atom) followed very soon after wide use of the μ SR technique itself (ca. 1975). Hadamard transform methods were developed independently (again, first for IR applications) about 1968. Hilbert transform techniques were first applied to spectroscopy (in this case for NMR) in 1978.

Chapter 1 (Marshall) presents a general basis for describing the advantages of Fourier, Hadamard, and Hilbert transform techniques in acquisition of data, enhancement of desired spectral features (e.g., signal-to-noise or resolution), and suppression of instrumental artifacts (deconvolution of imperfect excitation). The next three chapters introduce general aspects of these three transform types. Chapter 2 (Sloane) describes the construction and properties of Hadamard "codes", which are perhaps the conceptually simplest "multiplex" spectrometric method. Chapter 3 (Dumoulin & Levy) contains practical details in applying the fast Fourier transform algorithm to large data sets using a computer with limited memory. Chapter 4 (Marshall) provides the first review of applications for the "DISPA" (dispersion versus absorption) data reduction based on the Hilbert transform, as a means for identifying and distinguishing between spectral line-broadening mechanisms.

The succeeding chapters are loosely organized in order of increasing frequency of the spectrum of interest. Beginning at low frequency (0-2 MHz), Chapter 5 (Comisarow) describes the FT mass spectrometry technique, and gives some very recent applications showing the advantages of the technique for unraveling complex mass spectra at high ionic masses. At somewhat higher radiofrequency, Chapter 6 (Klainer et al.) reviews the state of the art in development and applications of FT nuclear quadrupole resonance spectrometers, and suggests a number of areas for immediate future work. Chapter 7 (Cole & Winsor) gives a history of advances in time-domain reflectometry as a source of dielectric relaxation data, including a review of all detection methods in current use. Chapter 8 (Flygare) is a comprehensive treatment of the theory and experimental complications of FT rotational spectroscopy--this technique appears especially promising for spectra of weakly associated van der Waals molecules.

Chapter 9 (Morris) critically compares the advantages of the principal two-dimensional FT-NMR experiments, and includes a comprehensive literature survey through mid-1980. Chapter 10 (Mims) gives a brief review of the somewhat parallel development of electron spin echo FT spectroscopy. Chapter 11 (Dalal) critically compares the

advantages of the "double-resonance" approach of Chapter 10 and direct FT-NMR for radicals containing quadrupolar nuclei. Chapter 12 introduces FT methods in mu spin resonance spectrometry, an area new to many chemists, but with implications important in the study of isotope effects. Chapter 13 (de Haseth) reviews the continuing development of the FT-IR technique, including the new areas of photo-acoustic spectroscopy, gas- and liquid-chromatography/FT-IR, and silicon impurity determinations. Chapter 14 (Nordstrom) extends interferometric detection to the optical frequency range, with proposed applications in atomic absorption spectroscopy.

The remaining two chapters offer somewhat different approaches. Chapter 15 (Smith) details various possible pseudorandom sequences as spectral sources over the frequency range used for a.c. polarography, and gives several applications of this quite new technique. The final Chapter 16 (McCreery & Rossi) describes a new FT technique which was first published (by those authors) this year (1981), in which Fourier transformation of the pattern of light diffracted near the edge of an electrode is used to discover the concentration profile of electroactive species very near to the electrode.

This volume is a successor to "Transform Techniques in Chemistry", edited by Peter R. Griffiths three years ago (Plenum, 1978). Since virtually all the work described in the present volume has been produced in just those intervening three years, the accelerating increase in use of transform techniques by chemists is obvious. Future directions are expected to include more uses of hard-wired fast Fourier transform processors (a 1024-point FFT can now be performed in about 15 millisec), array processors (especially for two-dimensional Fourier transforms), and use of other excitation waveforms (e.g., pseudo-random excitation in FT mass spectrometry). The market share of FT-spectrometers can be expected to increase in all areas in which commercial FT-instruments are available.

The editor wishes to thank all various contributors for providing authoritative, up-to-date, critical summaries of the state of the art in various transform techniques. The manuscripts were converted to their present form by Alan Marshall and Dixie Fisher. Finally, this volume is dedicated in recognition of the late Professor W. H. Flygare, who contributed his own comprehensive chapter at a time when he was already very ill.

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