

Additions and Corrections

Freeze-Quench Resonance Raman Spectroscopic Evidence for an Fe–CO Adduct during Acetyl-CoA Synthesis and Ni Involvement in CO Oxidation by Carbon Monoxide Dehydrogenase from *Clostridium thermoaceticum* [*J. Am. Chem. Soc.* **1995**, *117*, 2653–2654]. DI QIU, MANOJ KUMAR, STEPHEN W. RAGSDALE, AND THOMAS G. SPIRO*

JA9754214

S0002-7863(97)05421-8

Raman and Infrared Spectroscopy of Cyanide-Inhibited CO Dehydrogenase/Acetyl-CoA Synthase from *Clostridium thermoaceticum*: Evidence for Bimetallic Enzymatic CO Oxidation [*J. Am. Chem. Soc.* **1996**, *118*, 10429–10435]. DI QIU, MANOJ KUMAR, STEPHEN W. RAGSDALE, AND THOMAS G. SPIRO*

JA975422W

S0002-7863(97)05422-X

Characterization of a Diiron(III) Peroxo Intermediate in the Reaction Cycle of Methane Monooxygenase Hydroxylase from *Methylococcus capsulatus* (Bath) [*J. Am. Chem. Soc.* **1995**, *117*, 4997–4998]. KATHERINE E. LIU, ANN M. VALENTINE, DI QIU, DALE E. EDMONDSON, EVAN H. APPELMAN, THOMAS G. SPIRO,* AND STEPHEN J. LIPPARD*

JA975423O

S0002-7863(97)05423-1

The resonance Raman spectra reported in these three papers have been found to be unreliable and to consist mainly of artifacts. However, the non-Raman data [specifically the IR spectra of the CODH cyanide adduct in the second paper [Figure 4], and the kinetic absorption data for MMO in the third [Figure 1]] are reliable. We are confident that all the samples were properly prepared and contained the reaction intermediates under investigation. However, we have been unable to reproduce the Raman spectra with fresh samples, and judge the published spectra to be artifacts resulting from electronic processing of the data.

This retraction affects our conclusions about the role of Ni in center C of CODH and about the metal[s] to which CO or CN[−] binds, since these conclusions rested heavily on the reported isotope sensitivity of signals which are now considered spurious.

In the case of MMO, there is little doubt about the formation of a peroxide adduct in the H_{peroxo} intermediate, from many other lines of evidence, but the O–O stretching frequency is now in question.

Computer Software Reviews

Un-Scan-It. Silk Scientific: P.O. Box 533, Orem, Utah 84059. Telephone 801-377-6978. Fax: 801-378-5474

Un-Scan-It is a program designed to digitize scanned images such as gels or graphs and then to convert the intensity values into an x,y representation. This program is very user-friendly and can be mastered in merely 1–2 h. The help menus are very informative and provide the user with a quick alternative to using the manual. In addition, the manual is easy to follow and provides a full explanation of the menu options.

Un-Scan-It was tested for its ability to digitize a gel image and to integrate the area under the resulting intensity peaks. The program has three modes for digitizing gels. One mode has an autolane selector that is supposed to automatically select the lanes for the user. Unfortunately, the sensitivity of this option seems to be very poor because even on the highest sensitivity reading, the autolane selector failed to distinguish between the various lanes and instead selected the entire gel as one lane. The second mode allows the user to choose his/her lanes manually. Again, this is very straightforward and is simplified by the copy option, which allows the user to copy a selected box and move it to the next desired region. Finally, the third mode for gel digitization allows the user to digitize by segment instead of by lane. This option can be useful, for example, if a lane on the gel is not straight, making it difficult to fit all the bands into one selection box. One of the features under the digitizing menu includes calibration, which is particularly useful for analysis of gels with high background. Also, Un-Scan-It is versatile in the type of gel it can analyze. The user simply selects either negative image type for agarose gels or positive image type for gels with dark bands.

The digitized data are displayed as an intensity plot, and peaks can be selected for analysis. The peak find sensitivity seemed to be low, and it was unclear if it could be adjusted. This made the analysis more time consuming, as peaks had to be selected by hand and baselines adjusted for each individual peak. The data corresponding to each band are then displayed and a hardcopy can be printed. The location of each band is designated by a number, but the program does not allow a printout of the gel image with the numbers positioned on it. This is a slight inconvenience because he/she must make a note of which number corresponds to which band. Furthermore, the intensity plots

which are generated by digitization also cannot be printed and must be saved as x,y data and printed from the graphics option in the program. Besides being able to compare pixel intensities between gel bands, this program has a very useful molecular weight option that automatically determines the molecular weights based on standard values input by the user. This feature eliminates the need for graphing a standard curve in a separate graphing program.

Un-Scan-It also allows the user to graph the digitized data in an x,y format. It is only in this mode that the x,y image can be printed. The area under the peaks can be easily obtained and is yet another way the user can compare the band intensities on a gel. Individual data points can be changed or new ones added, but this program does not allow for changes to be made simultaneously to all the points. This operation would be useful, for example, when several lanes have to be normalized with respect to each other. Another drawback is that two x,y data sets cannot be overlaid. Again, this would be useful when comparisons between several lanes are being made. To manipulate the full data set or to obtain an overlay, the x,y values must be loaded into a separate spreadsheet or graphing program. A larger capacity for data manipulation within this graphing mode would enhance this program, but it certainly is clear that the program was not designed for this purpose. Unlike other image programs, Un-Scan-It makes an earnest effort to combine the digitizing and graphical modes within the same program.

Although this review focused mainly on the use of Un-Scan-It to digitize and analyze gel images, it is clear that this program could be used for other purposes as well. This user-friendly program would be useful for both academic and industrial applications, and with the exception of a few minor drawbacks mentioned above, it does exactly what it is designed to do. It is copyright protected, and information regarding backup policy is provided. It is not clear whether or not this program is also available for Macintosh computers, which would greatly increase its usefulness in academics where often only Macintosh computers are available.

Pamela J. Carter and H. Holden Thorp,
University of North Carolina

JA975906S

S0002-7863(97)05906-4

Book Reviews

Detergents in the Environment. (Surfactant Science Series, Volume 65). Edited by Milan Johann Schwuger (Institute of Applied Physical Chemistry, Research Center Jülich GmbH, Jülich, Germany). Marcel Dekker: New York, 1996. 336 pp. \$145.00. ISBN 0-8247-9396-X.

The focus of this monograph on detergents in the environment is somewhat narrower than the title suggests. The editor aims to describe the physicochemical fate of important detergent components in the environment, explicitly excluding biodegradation. The book succeeds reasonably well in this mission, dealing mostly with standard detergent chemistry as related to interactions with soil and water. In keeping with the affiliations of the contributors, the case studies quoted largely revolve around scenarios in Germany. The references are sufficiently up to date to preserve relevance, although little material published during the last 3 years is included. Unfortunately, the book's ease of access is marred by a poor index.

The four sections of the book deal with surfactants, zeolites, polycarboxylates, and complexing agents, respectively. The first chapter of section I, written by Franz Malz, discusses surfactant loading of surface waters and provides a historical overview of detergent usage in Germany during the last 35 years. In the second chapter, Erwin Klumpp and Milan Schwuger describe the interactions of surfactants in soil, focusing on the sorption of different classes of surfactant onto clay minerals. In the third and longest chapter of section I, Gerd Kloster discusses the determination of detergents in the environment. After a somewhat superfluous introduction, a useful description of titrimetric and colorimetric techniques is presented. This is followed by a brief exposé of electrochemical methods and a slightly longer segment on

spectroscopic techniques, including UV, IR, NMR, and MS. The emphasis of the chapter is on chromatography, with a discussion of HPLC that provides a wealth of practical information. GC is given good coverage, while SFC and electrophoretic methods are briefly mentioned. As the references run only through 1992, these last two techniques may not have been given their full due. The next portion of the chapter deals with isolation and preconcentration procedures, providing a good overview of extraction, sublation, and chromatographic technologies. The last pages of the chapter present a similar, albeit shorter, description of analytical procedures for complexing agents.

The remainder of the book (slightly more than one-third) deals with detergent builders and co-builders, including zeolites, polycarboxylates, and nitrioloacetates. It begins with section II, contributed by Claus Kurzendörfer, Peter Kuhm, and Josef Steber, which is entirely devoted to zeolites. The coverage offered is inordinately extensive, including historical and structural details, environmental effects in different matrices, analyses, and effects on heavy metal distribution. A total of 146 references are quoted, but few are dated beyond 1990.

Section III, incorporating Chapters 5–8, deals with polycarboxylates (PCAs). The first chapter in this section, written by Dieter Kissling, provides a brief overview of these co-builders, addressing their role in detergent formulations. In Chapter 6 Angelika Bartelt, Ulrich Schröder, and Dieter Horn discuss the trace analysis of PCAs in water, providing many useful details on titrimetric procedures. Chapter 7, by Jean-Marie Séquaris, is the first that deals with environmental aspects of PCAs and appears to be somewhat out of sequence. It offers good discussion of PCA interactions, with emphasis on metal ion removal by these

polymers. Chapter 8, by Inge Langbein, complements Chapter 7 well, focusing on the biological effects of PCA.

Section IV, entitled Complexing Acids, comprises two chapters—one on nitrioloacetic acid and one on EDTA. In the former, Dieter Kissling and Ulrich Kaluza give a comprehensive account of NTA, including extensive data on its occurrence in the Rhine Basin. In the last chapter, Fritz Frimmel presents a similar discussion on EDTA. In keeping with the expansive history of this complexing agent, the only items of recent vintage in this chapter are the regional data.

This monograph provides a compilation of some useful information for practitioners in environmental analysis and remediation. Readers may not find all they expect, but the material covered provides a view not offered by other texts on the subject.

Ray von Wandruszka, *University of Idaho*

JA965783W

S0002-7863(96)05783-6

Attenuated Total Reflectance Spectroscopy of Polymers: Theory and Practice. Polymer Surfaces and Interfaces Series. By Marek W. Urban (North Dakota State University). American Chemical Society: Washington, DC, 1996. xvi + 215 pp. \$99.95. ISBN 0-8412-3348-9.

This volume is part of the Polymer Surfaces and Interfaces Series published by ACS. However, because at least two-thirds of the book deals with ATR theory and analysis, this volume belongs in the company of books such as Harrick's *Internal Reflection Spectroscopy* and Griffiths' *Fourier Transform Infrared Spectrometry*, whose foremost objective is to familiarize the reader with an analytical and instrumental methodology. The book's audience stated in the preface is those interested in entering the field of surface ATR spectroscopy. However, as ATR is inherently a surface method, and as the book addresses all of the issues critical to its effective use, I believe that the first two sections, if not the entire book, not only are essential reading for newcomers to ATR but should serve as a refresher and/or reference for more experienced ATR users.

The book is divided into three sections: Section I. Principles and Basic Concepts, Section II. Quantitative ATR Spectroscopy, and Section III. Selected Applications. The first section contains four chapters. In general, these four chapters are arranged in a sensible order, although I thought that coming upon the historical perspective at the beginning of Chapter 3 was a bit disorienting. It should have been presented earlier (in Chapter 1, for example) and should have been longer, containing a more detailed review of previous (significant) ATR literature. Chapter 1 reviews light's interaction with matter, the various IR sampling techniques, general background for reflection and refraction of light, and multiple reflectance effects in ATR. Chapter 2 derives the equation for the reflectance using an expression for exponential decay of the evanescent wave in the sample. Chapter 3 discusses the interactions of polarized light with ATR crystal and sample and presents mathematical relations for these interactions. Chapter 4 provides illustrations of the differences that arise in spectra of the same IR spectral bands taken with transmission (absorbance) vs ATR techniques when the spectra contain strong IR bands and/or bands with small separations. Spectra of polymers are used to illustrate these effects.

The second part of the book (Section II, Chapters 5 and 6) is devoted to presenting methods for correcting these effects, thus leading to the ability to use ATR to obtain quantitative information about polymers. Chapter 5 presents the Kramers–Kronig transforms, while Chapter 6 shows how these and the Fresnel equations are used in three different methods for correcting ATR spectra, Bertie–Eysel algorithm, Dignam–Mamiche–Afara algorithm, and Urban–Huang algorithm. The strengths and weaknesses of these three algorithms are discussed and illustrated. The ability of the Urban–Huang method for correcting distortions for both weak and strong spectral bands is emphasized. Chapter 7 presents methods for obtaining surface depth profile spectra of nonhomogeneous samples from spectra taken at different incidence angles (and therefore penetration depths). The methods use reflectivity values for surface slices and embedded loops to calculate the band intensities in those slices. The optical constants (n and k) which are input into the calculation are from the Urban–Huang KKT algorithm.

The third section of the book presents applications including polymer surface (Chapter 8) and in situ (Chapter 9) systems. The examples presented are very informative, illustrating effects discussed in earlier

chapters. A wide range of problems relevant to the polymer scientist is presented. This should send a message to the polymer chemist not already using ATR about the technique's potential usefulness for solving his (or her) problems.

The book is generally easy to read with sufficient text to explain the complex mathematical expressions, helpful flowcharts diagramming the procedures for depth profile analysis, clear figures, and pictures of various instrumental setups. I was impressed by the way the book first presents a "problem" with ATR (the last topic in Chapter 2 is called Problems with ATR and Chapter 4 begins with a discussion of frequency shifts produced by optical dispersion), not shying away from a discussion of difficulties with the technique, yet presents a step-by-step approach to solving them. The topics are covered in-depth while keeping the presentation short and to the point. But of course, since *ATR Spectroscopy of Polymers* addresses only a single IR sampling mode, the task is easier than that involved in a book such as Griffiths' *FTIR Spectrometry*.

Amy S. Glass, *University of Dayton*

JA965804M

S0002-7863(96)05804-0

The Maillard Reaction: Consequences for the Chemical and Life Sciences. Edited by R. Ikan (Hebrew University of Jerusalem, Israel). Wiley: New York, 1996. xii + 214 pp. \$89.95. ISBN 0-471-96300-3.

The Maillard reaction is a complex degradative reaction involving a series of reactions, starting with the initial interaction of a carbonyl compound (usually a reducing sugar) and an amino group (often an amino group of an amino acid or a protein). For many years, the reaction was of interest to food chemists, interested in the generation of food flavors and the browning of certain foods during their processing. However, during the last decade, interest in the Maillard reaction has increased significantly, as a result of findings which have shown that it proceeds in living systems. The *in vivo* Maillard reaction appears to be related to protein modifications as a function of age and to have implications in diabetic complications and cataract formation, along with a host of other protein-related issues.

Despite a number of conference books available on the subject, this book is the first attempt to develop a broad but concise overview of the Maillard reaction with an emphasis on the latest developments over the past 15 years (up to 1995). This book examines the importance of the Maillard reaction in foods, nutrition, and health related aspects, as well as the effects of other parameters thought to affect the overall reaction. Its nine chapters, each of which is a short critical review, are written by established specialists in the field. The editor contributed to the first chapter, which is devoted to geochemical aspects of the Maillard reaction. The remainder of the book space is evenly distributed between two major areas, namely the Maillard reaction as it relates to foods (four chapters) and *in vivo* reactions (four chapters). The chapters are not logically arranged nor necessarily connected to one another, and the small size of the volume enables only a restricted presentation of the material. However, the chapters are well referenced and a number of important classes of Maillard reaction products are discussed, including insoluble polymeric melanoidins which are produced during soil formation, Maillard reaction products as oxygen scavengers, and low-molecular-weight products, as well as food aroma constituents and mutagens. The remainder of the chapters deal with advanced glycation end-products (AGEs) on proteins and nucleic acids and their possible reaction role in pathogenesis. The potential role of oxygen in the Maillard is also discussed, which is of particular value, since this represents a contributor that has attracted considerable interest in recent years.

In summary, this book is a good effort at describing the broad scope of the reaction, and is reasonably current in its approach. The book will be a good addition to the libraries of specialists, as well as to scientists who are simply curious about the role and scope of the Maillard reaction and with terms that are commonly in use in this field, such as "nonenzymatic browning", "glycation", and "AGE formation", all of which will gradually be finding their way into standard textbooks in biochemistry, nutrition, and clinical chemistry.

Milton S. Feather and Valeri V. Mossine,
University of Missouri—Columbia

JA965800H

S0002-7863(96)05800-3