Near-Infrared Spectroscopy in Agriculture

Co-Editors
Craig A. Roberts
Jerry Workman, Jr.
James B. Reeves III

Managing Editor: Lisa Al-Amoodi

Number 44 in the series
AGRONOMY

American Society of Agronomy, Inc.
Crop Science Society of America, Inc.
Soil Science Society of America, Inc.
Publishers
Madison, Wisconsin, USA

2004

American Society of Agronomy, Inc.
Crop Science Society of America, Inc.
Soil Science Society of America, Inc.
677 South Segoe Road, Madison, WI 53711-1086 USA

ISBN: 0-89118-155-5

Library of Congress Control Number:

Printed in the United States of America.

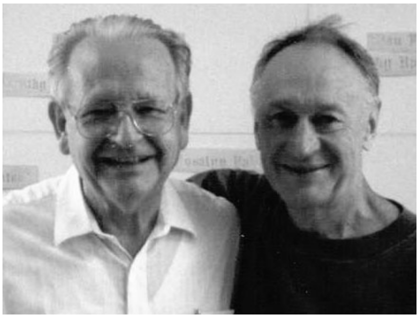
CONTENTS

SECTION C—NIR APPLICATIONS IN ANALYSIS OF FOOD CROPS

SECTION D—NIR APPLICATIONS IN ANALYSIS OF PROCESSED FOODS

SECTION E—NIR APPLICATIONS IN ANALYSIS OF NON-FOOD AGRICULTURAL PRODUCTS

DEDICATION



Near-Infrared Spectroscopy in Agriculture is dedicated to Phil Williams and Karl Norris. Collectively, they made this technology usable, especially in agricultural applications. Individually, each has his own list of contributions and achievements.

Karl Norris was the first to demonstrate that NIR spectral data could be measured on samples such as ground grains. His real contribution was the incorporation of computers to interpret data that could predict composition. This contribution, while it appears intuitive in our time, was innovative 40 years ago, long before desktop computers existed. The coupling of computers with spectrophotometers for statistical interpretation of spectra has facilitated the subdiscipline now known as chemometrics. In addition to working with small grains, Norris worked with other agricultural products. He collaborated with coworkers at the Instrumentation Research Laboratory at the USDA, Beltsville, MD to predict moisture in soybean and fat content in milk. This work involved both design of instruments operating in the NIR region and development of software to process the data. Because of this work, as well as the applied collaboration with Williams, many people consider Karl Norris the unofficial father of modern NIR spectroscopy.

Phil Williams was the applied equivalent of Norris. He was first ever to apply NIR technology to large-scale, real-world testing of a commercial commodity. In his search for a method rapid enough to test railway carloads of wheat at the time of unloading, Williams acquired one of the first NIR instruments ever built. His commitment to analytical precision, supported by the engineers of what was then the Neotec Corporation, resulted in replacement of the traditional Kjeldahl method by an automated NIR system for the protein segregation program. Within only four years, all testing—about 600,000 samples per year—was carried out at terminal elevators. Williams' subsequent work has been aimed at resolving problems associated with application of NIR technology to grain handling, with particular emphasis on electronic grading. In the field of plant breeding, Williams has concentrated on development of calibration models for the prediction of functionality, as well as composition. Over the past 32 years his research on evaluation of new instruments has been of significant benefit to several instrument manufacturing companies.

Though Williams and Norris have both retired from their original positions, they remain active in the field of NIR spectroscopy. They continue to help jump-start new analytical laboratories, mentor young spectroscopists, and field questions to almost anyone searching for an answer. As a result of their substantial contributions, they have both received prestigious awards. Today, Williams and Norris are household names, often mentioned together because of their synergistic effect in spawning, then documenting, a growing technology.

FOREWORD

Near-infrared (NIR) spectroscopy is a remarkably versatile and robust analytical methodology. Its nondestructive nature, fast analysis time, and relative ease of use has led to the development of many applications in a broad array of agricultural fields. The evolution and widespread application of NIR spectroscopy in the past several decades is one of the great success stories in analytical technology development. From the humble beginnings of fixed-filter instruments and simple calibrations to the scanning monochromators and advanced chemometrics of today, the technology has undergone an astonishing transformation. Key to this achievement was the rapid development of the microprocessor and the advanced analytical software it made possible. Today, NIR spectroscopy is widely used to detect and quantify an almost unending list of analytes in a host of agricultural and food products.

This volume provides monographic coverage of the use of NIR spectroscopy in agriculture. It begins with a section on fundamental principles of NIR spectroscopy, including chapters on instrumentation and sample preparation. This is followed by a comprehensive section on advanced chemometrics for qualitative and quantitative NIR analysis. The remaining three sections describe NIR applications for analysis of food crops, processed foods, and other agricultural products and byproducts. The chapters are authored by a who's who list of the leading experts in the design, calibration, and application of NIR spectroscopy. The book is truly international in scope with contributing authors from around the world.

Our thanks to the feasibility committee, editors, authors, reviewers, and staff that worked diligently to make this outstanding volume available. They have created an exceptional reference, that will serve as a leading source and definitive authority on NIR spectroscopy in agriculture for many years to come.

KENNETH J. MOORE
President
Crop Science Society of America

LOWELL E. MOSER
President
American Society of Agronomy

J. THOMAS SIMS
President
Soil Science Society of America

PREFACE

Near-infrared (NIR) spectroscopy is fast becoming a preferred method of routine analysis, especially in agriculture. Its growing popularity is due to its accuracy and efficiency of process. As an empirical procedure, NIR spectroscopy differs from standard spectroscopy; it does not require a full understanding of the physical relationships between spectral data and chemical functional groups. Instead, NIR spectroscopy is based on mathematical relationships between spectra and reference data. Once a mathematical relationship is established, the NIR spectrophotometer collects spectra and predicts analysis, thereby expediting rapid, large-scale processing of samples. The repeatability and accuracy of predicted data are monitored through an array of blind validation protocols.

Because of its empirical approach and indirect analysis, NIR spectroscopy sometimes attracts criticism. In many ways, it is a technology comparable to cryptanalysis during World War II—it "had an aura of sorcery, but the basis was highly scientific."[1] Criticism of NIR spectroscopy as a bench-top analytical tool is most common among theoretical researchers, who strain to understand the same principles they readily accept in remote sensing. Among practitioners, however, criticism is rare. In fact, practitioners have come to appreciate the inherent advantages of NIR spectroscopy, such as nondestructive sampling, reduced dependence on chemical reagents, and simultaneous quantification of constituents.

Near-Infrared Spectroscopy in Agriculture highlights the practical use of NIR technology during its first forty years in international agriculture. The book was requested by a feasibility committee of the Agronomy Society of America, who commissioned the work and cosponsored it with the Crop Science Society of America and the Soil Science Society of America.

Near-Infrared Spectroscopy in Agriculture is organized into five sections. The first two sections present the fundamentals of spectroscopy and chemometrics. These two sections were simplified as much as possible at the request of the editors because this book targets a broad scientific audience rather than a narrow group of spectroscopists and statisticians. The last three sections are applied and give this book a clear niche among other NIR publications. These applied sections detail the use of NIR analysis in crop production, food processing, and non-food agriculture. Chapters in the applied sections are generally comprehensive, and they include standardized tables of applications for ease of reference.

The editors would like to express their appreciation to all authors, reviewers, and editors of these chapters, as well as the editors of ASA, CSSA, and SSSA for their commitment and hard work in producing this book. We thank the Managing Editor, Lisa Al-Amoodi. We would also like to thank certain colleagues who helped us in the early stages of this work. Specifically, we are grateful to Ian Murray and Chris Scotter, who helped us identify international authors with various specializations in NIR application. We owe a special word of gratitude to authors Roberto Giangiacomo, Tiziana Cattaneo, Stephen Delwiche, Trish Townsend, and Michael Hammersley; these authors submitted their chapters early in the process and pro-

[1] Stevenson, W. 1976. A man called intrepid. Harcourt, Brace, Jovanovich, New York.

vided their colleagues with excellent examples of content and composition. Finally, we are grateful to Jerry Nelson, who offered a steady stream of reliable advice through the entire publication process.

We hope this work will benefit all those interested in efficient analysis of agricultural products.

CRAIG A. ROBERTS
University of Missouri
Columbia, Missouri

JERRY WORKMAN, JR.
Argose Inc.
Waltham, Massachusetts

JAMES B. REEVES III
USDA-ARS
Beltsville, Maryland

CONTRIBUTORS

Judy Abbott	USDA-ARS, Produce Quality and Safety Laboratory, BARC-West, 10300 Baltimore Ave., Beltsville, MD 20705, USA
John Antoniszyn	Canadian Grain Commission, Grain Research Laboratory, 1404 - 303 Main Street, Winnipeg, MB R3C 3G8, Canada
Eyal Ben-Dor	Remote Sensing/GIS Laboratory, Dep. of Geography, Tel-Aviv University, P.O. Box 39040, Ramat Aviv, Tel-Aviv 69978, Israel
Tiziana M.P. Cattaneo	Istituto Sperimentale Lattiero Caseario, Via Lombardo, 11, 26900 Lodi, Italy
Ian Cowe	37 Broughton Way, Osbaldwick, York YO10 3BG, UK
Daniel Cozzolino	The Australian Wine Research Inst., Waite Road, Urrbrae, P.O. Box 197, Glen Osmond, SA 5064, Australia; formerly, INIA La Estanzuela, Animal Nutrition Laboratory, Colonia, Uruguay
Bob Dambergs	The Australian Wine Research Inst., Waite Road, Urrbrae, P.O. Box 197, Glen Osmond, SA 5064, Australia
Stephen Delwiche	USDA-ARS, Instrumentation & Sensing Laboratory, Bldg. 303, BARC-East, 10300 Baltimore, Ave., Beltsville, MD 20705-2350, USA
Gerard Downey	Teagasc, The National Food Center, Astown, Dublin 15, Republic of Ireland
James Duckworth	Galactic Industries Corp., 395 Main Street, Salem, NH 03079, USA
Dan Dyer	Renessen, LLC, 3000 Lakeside Drive, Suite 300S, Bannockburn, IL 60015, USA
Michael Esler	The Australian Wine Research Inst., Waite Road, Urrbrae, P.O. Box 197, Glen Osmond, SA 5064, Australia; currently: Bureau International des Poids et Mesures, Sevres, France
Peter Flinn	Agriculture Victoria, Pastoral & Veterinary Institute, Private Bag 105, Hamilton, Victoria 3300, Australia
Juan García-Olmo	ETSIAM, University of Cordoba, Apdo. 3048, 14080 Cordoba, Spain
Ana Garrido-Varo	ETSIAM, University of Cordoba, Apdo. 3048, 14080 Cordoba, Spain
Roberto Giangiacomo	Istituto Sperimentale Lattiero Caseario, Via Lombardo, 11, 26900 Lodi, Italy

Mark Gishen The Australian Wine Research Inst., Waite Road, Urrbrae, P.O. Box 197, Glen Osmond, SA 5064, Australia

Michael Hammersley 2/19d Dyers Pass Road, Cashmere, Christchurch 2, New Zealand

Kjell Ivar Hildrum MATFORSK, Osloveien 1, N-1432 Ås, Norway

Sumio Kawano National Food Research Institute, 2-1-12 Kannondai, Tsukuba 305-8642, Japan

Sandra Kays USDA-ARS, Quality Assessment Research Unit, Richard B. Russell Agric. Research Center, P.O. Box 5677, Athens, GA 30604-5677, USA

Richard Kramer Applied Chemometrics, 77 Beach Street, Sharon, MA 02067, USA

Diane Malley PDK Projects, Inc., 365 Wildwood Park, Winnipeg, MB R3T 0E7, Canada

Howard Mark Mark Electronics, 21 Terrace Avenue, Suffern, NY 10901, USA

Paul Martin #2-12 McGillivray Place, Winnipeg, MB R3T 1N4, Canada

Sam Millar Campden and Chorleywood Food Research Association, Chipping Campden, Gloucestershire, GL55 6LD, UK

Joseph Montalvo USDA-ARS Southern Regional Res Ctr, 1100 Robert E. Lee Boulevard, Bldg. 001, Rm. 3025, New Orleans, LA 70179-0687, USA

W.L. Cap Munday Sydco Technical Sales, 1706 Justin Drive, Gambrills, MD 21054, USA

Ian Murray SAC, Ferguson Bldg., Craibstone Estate, Bucksburn, Aberdeen AB21 9YA, Scotland

Maria Dolores Pérez-Marín ETSIAM, University of Cordoba, Apdo. 3048, 14080 Cordoba, Spain

Craig Roberts Agronomy Dep., 214 Waters Hall, University of Missouri, Columbia, MO 65211, USA

James Reeves USDA-ARS, Animal & Natural Resources Institute, BARC-East, Bldg. 306, Rm. 101, Beltsville, MD 20705, USA

Laurence Schimleck D.B. Warnell School of Forest Resources, The University of Georgia, 4-330, Athens, GA, 30602-2152, USA

Hartwig Schulz Federal Centre for Breeding Research on Cultivated Plants, Institute of Plant Analysis, 22/23, D-06484 Quedlinburg, Germany

Chris Scotter Campden and Chorleywood Food Research Association, Chipping Campden, Gloucestershire, GL55 6LD, UK

Reiji Sekiguchi Japan Food Research Laboratory, Shibuya, Tokyo 151-0062, Japan

John Shenk Infrasoft International, 109 Sellers Lane, Port Matilda, PA 16870, USA

David Slaughter Biological & Agric. Engineering, University of California, One Shields Ave., Davis, CA 95616, USA

Jerry Stuth Dep. of RLEM, Animal Industries Bldg., Texas A&M University, College Station, TX 77843-2126, USA

Trisha Townsend 74 Greendale Avenue, Avonhead, Christchurch 8004, New Zealand

Masami Ueno University of the Ruykyus, Okinawa 903 -0213, Japan

Terri Von Hoven USDA-ARS Southern Regional Res Ctr, 1100 Robert E. Lee Boulevard, 001, Rm. 3025, New Orleans, LA 70179-0687, USA

Mark Westerhaus Infrasoft International, 109 Sellers Lane, Port Matilda, PA 16870, USA

Phil Williams PDK Grain, 365 Wildwood Park, Winnipeg, MB R3T 0E7, Canada

Jerome Workman Argose Inc., 230 Second Avenue, Waltham, MA 02451, USA

Charles M. Zapf McCormick & Company, Inc., Technical Center, 202 Wight Avenue, Hunt Valley, MD 21031-1066, USA

Conversion Factors for SI and non-SI Units

Conversion Factors for SI and non-SI Units

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 non-SI Units	To convert Column 2 into Column 1, multiply by
		Length	
0.621	kilometer, km (10^3 m)	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
3.28	meter, m	foot, ft	0.304
1.0	micrometer, µm (10^{-6} m)	micron, µ	1.0
3.94×10^{-2}	millimeter, mm (10^{-3} m)	inch, in	25.4
10	nanometer, nm (10^{-9} m)	Angstrom, Å	0.1
		Area	
2.47	hectare, ha	acre	0.405
247	square kilometer, km^2 (10^3 m)^2	acre	4.05×10^{-3}
0.386	square kilometer, km^2 (10^3 m)^2	square mile, mi^2	2.590
2.47×10^{-4}	square meter, m^2	acre	4.05×10^3
10.76	square meter, m^2	square foot, ft^2	9.29×10^{-2}
1.55×10^{-3}	square millimeter, mm^2 (10^{-3} m)^2	square inch, in^2	645
		Volume	
9.73×10^{-3}	cubic meter, m^3	acre-inch	102.8
35.3	cubic meter, m^3	cubic foot, ft^3	2.83×10^{-2}
6.10×10^4	cubic meter, m^3	cubic inch, in^3	1.64×10^{-5}
2.84×10^{-2}	liter, L (10^{-3} m^3)	bushel, bu	35.24
1.057	liter, L (10^{-3} m^3)	quart (liquid), qt	0.946
3.53×10^{-2}	liter, L (10^{-3} m^3)	cubic foot, ft^3	28.3
0.265	liter, L (10^{-3} m^3)	gallon	3.78
33.78	liter, L (10^{-3} m^3)	ounce (fluid), oz	2.96×10^{-2}
2.11	liter, L (10^{-3} m^3)	pint (fluid), pt	0.473

		Mass	
2.20×10^{-3}	gram, g (10^{-3} kg)	pound, lb	454
3.52×10^{-2}	gram, g (10^{-3} kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454
0.01	kilogram, kg	quintal (metric), q	100
1.10×10^{-3}	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907
		Yield and Rate	
0.893	kilogram per hectare, kg ha^{-1}	pound per acre, lb $acre^{-1}$	1.12
7.77×10^{-2}	kilogram per cubic meter, kg m^{-3}	pound per bushel, lb bu^{-1}	12.87
1.49×10^{-2}	kilogram per hectare, kg ha^{-1}	bushel per acre, 60 lb	67.19
1.59×10^{-2}	kilogram per hectare, kg ha^{-1}	bushel per acre, 56 lb	62.71
1.86×10^{-2}	kilogram per hectare, kg ha^{-1}	bushel per acre, 48 lb	53.75
0.107	liter per hectare, L ha^{-1}	gallon per acre	9.35
893	tonne per hectare, t ha^{-1}	pound per acre, lb $acre^{-1}$	1.12×10^{-3}
893	megagram per hectare, Mg ha^{-1}	pound per acre, lb $acre^{-1}$	1.12×10^{-3}
0.446	megagram per hectare, Mg ha^{-1}	ton (2000 lb) per acre, ton $acre^{-1}$	2.24
2.24	meter per second, m s^{-1}	mile per hour	0.447
		Specific Surface	
10	square meter per kilogram, m^2 kg^{-1}	square centimeter per gram, cm^2 g^{-1}	0.1
1000	square meter per kilogram, m^2 kg^{-1}	square millimeter per gram, mm^2 g^{-1}	0.001
		Density	
1.00	megagram per cubic meter, Mg m^{-3}	gram per cubic centimeter, g cm^{-3}	1.00
		Pressure	
9.90	megapascal, MPa (10^6 Pa)	atmosphere	0.101
10	megapascal, MPa (10^6 Pa)	bar	0.1
2.09×10^{-2}	pascal, Pa	pound per square foot, lb ft^{-2}	47.9
1.45×10^{-4}	pascal, Pa	pound per square inch, lb in^{-2}	6.90×10^3

(continued on next page)

Conversion Factors for SI and non-SI Units

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 non-SI Units	To convert Column 2 into Column 1, multiply by
		Temperature	
1.00 (K – 273)	kelvin, K	Celsius, °C	1.00 (°C + 273)
(9/5 °C) + 32	Celsius, °C	Fahrenheit, °F	5/9 (°F – 32)
		Energy, Work, Quantity of Heat	
9.52×10^{-4}	joule, J	British thermal unit, Btu	1.05×10^{3}
0.239	joule, J	calorie, cal	4.19
10^{7}	joule, J	erg	10^{-7}
0.735	joule, J	foot-pound	1.36
2.387×10^{-5}	joule per square meter, J m^{-2}	calorie per square centimeter (langley)	4.19×10^{4}
10^{5}	newton, N	dyne	10^{-5}
1.43×10^{-3}	watt per square meter, W m^{-2}	calorie per square centimeter minute (irradiance), cal cm^{-2} min^{-1}	698
		Transpiration and Photosynthesis	
3.60×10^{-2}	milligram per square meter second, mg m^{-2} s^{-1}	gram per square decimeter hour, g dm^{-2} h^{-1}	27.8
5.56×10^{-3}	milligram (H_2O) per square meter second, mg m^{-2} s^{-1}	micromole (H_2O) per square centimeter second, µmol cm^{-2} s^{-1}	180
10^{-4}	milligram per square meter second, mg m^{-2} s^{-1}	milligram per square centimeter second, mg cm^{-2} s^{-1}	10^{4}
35.97	milligram per square meter second, mg m^{-2} s^{-1}	milligram per square decimeter hour, mg dm^{-2} h^{-1}	2.78×10^{-2}
		Plane Angle	
57.3	radian, rad	degrees (angle), °	1.75×10^{-2}

Electrical Conductivity, Electricity, and Magnetism			
10	siemen per meter, S m^{-1}	millimho per centimeter, mmho cm^{-1}	0.1
10^4	tesla, T	gauss, G	10^{-4}
Water Measurement			
9.73×10^{-3}	cubic meter, m^3	acre-inch, acre-in	102.8
9.81×10^{-3}	cubic meter per hour, m^3 h^{-1}	cubic foot per second, ft^3 s^{-1}	101.9
4.40	cubic meter per hour, m^3 h−1	U.S. gallon per minute, gal min^{-1}	0.227
8.11	hectare meter, ha m	acre-foot, acre-ft	0.123
97.28	hectare meter, ha m	acre-inch, acre-in	1.03×10^{-2}
8.1×10^{-2}	hectare centimeter, ha cm	acre-foot, acre-ft	12.33
Concentrations			
1	centimole per kilogram, cmol kg^{-1}	milliequivalent per 100 grams, meq 100 g^{-1}	1
0.1	gram per kilogram, g kg^{-1}	percent, %	10
1	milligram per kilogram, mg kg^{-1}	parts per million, ppm	1
Radioactivity			
2.7×10^{-11}	becquerel, Bq	curie, Ci	3.7×10^{10}
2.7×10^{-2}	becquerel per kilogram, Bq kg^{-1}	picocurie per gram, pCi g^{-1}	37
100	gray, Gy (absorbed dose)	rad, rd	0.01
100	sievert, Sv (equivalent dose)	rem (roentgen equivalent man)	0.01
Plant Nutrient Conversion			
	Elemental	***Oxide***	
2.29	P	P_2O_5	0.437
1.20	K	K_2O	0.830
1.39	Ca	CaO	0.715
1.66	Mg	MgO	0.602

Introduction to Spectroscopy in Food and Agriculture Industries using DLPÂ® Technology. Email. Analyzing Agricultural Crop and Soil using Near-Infrared (NIR) Spectroscopy. Play Video. Play.Â This presentation by the DLP Advanced Light Control Group concentrates on near-infrared spectroscopy applications in the agriculture industry. In the agriculture industry, NIR spectroscopy is a useful technique to monitor and assess quality of crops by reporting soil nutrient content, such as nitrogen, phosphorus, and organic matter indication, soil fertility and its contaminants, and soil moisture content. Also, NIR spectroscopy can be used to find optimal harvest times of crops by measuring crops ripeness. Near-infrared spectroscopy (NIRS) is a spectroscopic method that uses the near-infrared region of the electromagnetic spectrum (from 780 nm to 2500 nm). Typical applications include medical and physiological diagnostics and research including blood sugar, pulse oximetry, functional neuroimaging, sports medicine, elite sports training, ergonomics, rehabilitation, neonatal research, brain computer interface, urology (bladder contraction), and neurology (neurovascular coupling). There are also Near-Infrared Spectroscopy (NIRS) is the most rapidly developing and the most noticeable spectrographic technique in the 90's (the last century). Its principle and characteristics were explained in this paper, and the development of NIRS instrumentation, the methodology of spectrum pre-processing, as well as the chemical metrology were also introduced. The anthors mainly summarized the applications to agriculture and food, especially in-line analysis methods, which have been used in production procedure by fiber optics. The authors analyzed the NIRS application status in China, and made t