

A B S T R A C T S

from the

10th INTERNATIONAL NIRA SYMPOSIUM

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Technicon Science Center
Tarrytown, New York

F O O D A P P L I C A T I O N S S E S S I O N

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INTERACTANCE - A NEW WAY FOR NONDESTRUCTIVE MEASUREMENTS

K. H. Norris, Instrumentation Research Laboratory, Beltsville Agricultural Research Center, USDA, Beltsville, MD 20705

Radiation entering a diffusely scattering sample is propagated throughout the sample by multiple scattering. As the radiation moves through the sample, absorption occurs depending on the absorption properties of the constituents in the sample. Diffuse transmittance and diffuse reflectance measurements are used to characterize the constituents in such samples. However, comparable information can be obtained by illuminating one area of a sample and measuring the radiation emitted by the sample at another area such that the surface reflectance is excluded. We have coined the word INTERACTANCE for this type of measurement. We measure the interaction between the sample and the radiation. Fiber optic bundles provide a convenient tool for the interactance configuration, and the technique is illustrated with measurements on human subjects to measure fat content.

SPECTRAL CHANGES OF WATER ADSORBED ON BIOPOLYMERS

Gabor Kemeny, Technicon Instruments Corporation, 511 Benedict Avenue, Tarrytown, NY 10591 and Dr. David Wetzel, Kansas State University

The spectrum of water is usually considered simple, due to the small number of expected fundamental infrared bonds. In the near-infrared region, however, the presence of the various combined H-bonded species, the complex selection and also the effects of temperature, ionic content and the interaction between the adsorbed molecules all have significant impact on the apparent spectrum of water.

In this study several products - usually occurring in the near-infrared analysis - were treated to result in differing moisture content. The spectrum, the difference spectra and spectral reconstruction reveals many subtle changes that may influence quantitative analysis. The 1940 nm bond of water, most used in simple industrial moisture analysis show significant red-shift, bond broadening, the 1410 nm overtone region shows strong interaction especially with starch. The importance of the 1200 nm ternary combination region to detect the various H-bonded species is also emphasized.

AN EVALUATION OF TECHNICON'S DATA COMMUNICATIONS SOFTWARE,
INFRANET, FOR MAINTENANCE OF NEAR INFRARED CALIBRATIONS

G.R. Anderson & T.N. Tweeten, The Pillsbury Company, Research & Development
Laboratories, 311 Second Street S.E., Minneapolis, MN 55414

Technicon's new data communication software, InfraNet, has been in operation in our laboratory for three months. As Near Infrared (NIR) and InfraNet users, we would like here to address the practical questions:

1. How important is data communication between laboratory and plant for both establishing and maintaining accurate NIR calibrations? More specifically, how many plants and how many products involve NIR analysis? Where is the expertise to establish new calibrations? What training is required as well as what is expected with personnel turnover?
2. What are the strengths and weaknesses of InfraNet after three months experience? What is accomplished by telephone modem with I1NET "up loading" NIR raw data, together with identifying the advantages of I2NET for "down loading" revised calibrations? Where does the new IODAS skew-bias adjust program fit?

The answers of course are not simple nor are all applications of NIR analysis alike. Infranet is designed for centralized technology "hub" organizations as opposed to diversified plant laboratories with individual autonomy. Analysis of similar products in multiple sites also favors an InfraNet approach. Whatever the organization, wherever NIR responsibility resides, this software package should be considered seriously. On balance, we at Pillsbury R&D feel well served by this new data management capability.

EGG SOLIDS DETERMINATION WITH NIR

Keevin Speckman, Director of Technical Services, Wrightco, Incorporated, P.O. Box 428, 206 West Fourth Street, Monticello, MN 55362

Egg processing is a low margin industry handling a highly perishable product. With cost and quality depending closely on solids content, a rapid, accurate analytical method is needed. The NIR has provided this speed and accuracy.

When calibrated to the moisture oven method (AOAC) and with monthly bias adjustments, the system has provided solids analyses on Whole Egg in less than 15 minutes - accurate to within $\pm 0.1\%$ of the standard method. The original calibration established on egg liquid of 17 - 29% solids with 40 duplicate analyses used three wavelengths. Correlation was .997; standard error, .057; index of system error, 55.69; regression F ratio, 64651. Over the seven months of on line use, (>1,000 data points) correlation with the standard method continues $>.990$.

HOW TO DO FEASIBILITY STUDIES IN THE NIR

Michael Dzwinczyk, Technicon Instruments Corporation, 511 Benedict Avenue,
Tarrytown, NY 10591

This paper will give the general steps needed to properly do a good feasibility study in NIR. Such considerations as experiment objective, initial information gathering, sources of error, preparation of samples, and interpretation of results, will be discussed. Short-cuts in feasibility work can often lead to misleading or inconclusive results.

Examples of feasibility conducted will be given to point out various methods of analysis. Some warnings and common problems encountered will be useful to anyone who plans to explore the NIR Region for potential applications.

A G R I C U L T U R A L S E S S I O N

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UNIQUE SAMPLE SELECTION, SPECTRAL RECONSTRUCTION, AND NEW TOOLS FOR NIRA
EVALUATION OF FORAGE QUALITY

Jerry J. Workman, Technicon Instruments Corporation, 511 Benedict Avenue,
Tarrytown, NY 10591

NIR spectroscopy has been utilized for research in forage quality evaluation since the late 1970's, and has been in routine use in forage analysis since the early 1980's. To date specific technologies have been vigorously applied to the forage quality application, while other approaches have not received widespread publicity. New techniques, such as unique sample selection, spectral reconstruction, networking, functional group identification methods, discriminant analysis, and chemometric statistics, may lend additional capabilities to those methods currently touted. This paper is an attempt to introduce several of these techniques and to discuss their significance for NIR users.

STUDIES MONITORING NIRS PERFORMANCE FOR QUALITY MEASUREMENTS
IN FORAGES

Dr. William R. Windham, U.S.D.A., Athens, GA ABSTRACT

NOT AVAILABLE AT THIS TIME.

NIR ANALYSIS OF PROTEIN AND ACID DETERGENT FIBER FOR FORAGE CROP
BREEDING

D.I. McGregor and R.E. Howarth, Agriculture Canada Research Station, 10?
Science Crescent, Saskatoon, Saskatchewan S7N 0X2

Herbage of field grown alfalfa, bromegrass, crested wheatgrass and intermediate wheatgrass were freeze-dried, ground through a 2 mm screen in a Wiley mill, subsampled and reground through a 1 mm screen in a cyclone mill. The PICKS spectral selection program was successfully to establish calibration sets. Absorbance data yielded corrected standard errors of performance (SEPC) on the Technicon 500 of 0.61 and 1.10 - 1.93 for protein and ADF, respectively. Comparable SEPC's, 0.65 - 1.24 for protein and 0.81 - 2.36 for ADF, were obtained on the Technicon 400. Use of first derivative data reduced SEPC's for the 500. Storage of the samples for several weeks resulted in a shift of NIR predicted values which could not be attributed to changes in moisture. Study of the genetic variability in protein and ADF of leaves and stems of crested wheatgrass indicated that either the 500 or 400 could be used for genotypic selection.

CORRELATION TRANSFORM SPECTROSCOPY IN FOURIER SPACE: SPECTRAL
SEARCHING AND MATCHING

W. F. McClure, Professor, North Carolina State University, Raleigh, NC 27695

The use of correlation transform spectroscopy to estimate chemical composition from the Near-Infrared spectrum of solid samples is well known and widely used in a multitude of industries; its rate of growth and acceptance has been phenomenal. Intrinsic to correlation transform spectroscopy is its reliance on correlation calibrations which are usually specific to particular products; in other words, the Near-Infrared spectral data is transformed from one type to another and through the use of multilinear regression calibration algorithms are developed to estimate chemical composition. For example, computing nicotine in tobacco requires a different calibration equation for each of the four tobacco types: flue-cured (Virginia), Burley, Maryland, and dark-fired. Research in this laboratory has shown that a program can be written which will identify the tobacco type, select the appropriate calibration equation, and compute the nicotine level with a much higher degree of accuracy than by the indiscriminant use of calibrations. Search, matching, and computation of chemical composition are all carried out in the Fourier domain. Search and matching algorithms will be discussed.

NIR ANALYSIS OF DRY PET FOODS

Ron Crow, Hills Pet Foods, Incorporated

ABSTRACT NOT AVAILABLE AT THIS TIME.

PROGRESS IN ON-LINE NIRA MONITORING

Dr. David Wetzel, Kansas State University

On line spectroscopic measurement of granular materials presents a challenge in terms of both sample transport and optical consideration. Even when operating with the sample in an optical contact mode as described, small compositional differences require data averaging to find actual, rather than perceived, changes in flowing stock. Defining matrix compositional range, matrix physical range as well as analyte range for one monitor point on a production system represents the customization required for success. Multiple concentric or exclusive calibration and appropriate schemes will assist in maximizing the usefulness of NIRA monitoring from a customized installation.

INDUSTRIAL PROCESS SESSION

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PROGRESS TOWARDS THE ON-LINE CONTROL OF ORGANIC SYNTHESIS USING
NIRA

M. Leach, Kingston Polytechnic, U.K.

NIRA research at Kingston Polytechnic is involved with exploring the utility of InfraAnalyzer 400's as tools for examining the progress of chemical reactions with real time multi-component analyses. A number of systems have been examined:

1. A simple titration, involving ethanolamine and hydrochloric acid, has been followed, with NIRA giving molar concentrations of the free amine and the amine hydrochloride during the course of the reaction. A rational has been developed to eliminate cross correlation of constituents.
2. A 50L solvent recovery still (acetone/water system) with a peristaltic pump allowing the InfraAnalyzer 400 to work in an on-line mode has been developed. The InfraAnalyzer 400 down-loads log values to a BBC micro-computer, which acts as a process controller, initiating analyses, calculating molar concentrations, timing the pump action, and setting the reflux ratio of the still.
3. The self contained InfraAnalyzer 400/BBC/pump is being used to follow the course of preparative organic reactions. Work is proceeding on the esterification of acetic acid and 1-butanol (with azeotropic removal of water).

SPECTRAL LIBRARIES AS A KNOWLEDGE SOURCE - FACT OR FICTION?

Mr. Ken J. Leiper, Central Analytical Services Manager, Glaxo Operations UK Limited, Bernard Castle

While from the spectroscopists viewpoint the renewed interest in the Near Infrared region of the spectrum is due to improved instrumentation and data processing, it is the minimal requirement for sample treatment prior to analysis which is promoting the analytical chemists' general level of interest in the technique.

However, the establishment of the Near Infrared region as a viable information source would not have been possible without the development of a reliable means of sample preparation/presentation.

Interestingly, it has been the inability to control sample preparation as a variable which has proven to be a major constraint in developing the full potential of spectral data bases in the mid infrared.

This paper will review the current status of NIRA developments being undertaken in our laboratories, particularly factors relating to instrument selection and software developed to meet our primary objective of replacing conventional identification testing on incoming raw materials by NIRA, which has also allowed the compilation of an extensive near infrared database. Those areas of future use of this database will also be discussed.

NIRA POTENTIAL FOR THE PROCESS MONITORING OF HEATSET TEMPERATURE

James E. Rogers, Analytical Specialist, Monsanto Fibers & Intermediates Company, P.O. Box 12830, Pensacola, FL 32575

In previous heatset temperature (HST) evaluations, a majority of the work has been on "model-prediction" evaluations, where the NIRA technique measured the effective HST of heatset griegge nylon carpet samples that had been heatset at different temperatures. A two-part program was implemented to evaluate the NIRA methodology for its capability in monitoring HST in a process control mode. Several nylon 6,6 griegge, Suessen heatset carpet yarn sets, in which the samples had been heatset at different HSTs, were obtained from one source. The Technicon 400TX InfraAnalyzer and Pensacola HST calibration equation did accurately measure the effective HST of these model-prediction samples. Having verified the calibration equation's ability to monitor HST differences in the model-prediction samples, two large lots of routine Suessen (6 tunnels/machine) headset yarns were measured on the 400TX. The NIRA methodology successfully monitored the effective HST of both lots, with no values outside of the established ± 5 C limit (tunnel, the control tunnel). The NIRA methodology also detected the known slight HST differences between Suessen tunnels.

APPLICATION OF NIRA IN THE TOILETRIES INDUSTRY

Priscilla L. Walling, Group Leader, Advanced Spectroscopy, Helene Curtis, Incorporated, 4401 W. North Avenue, Chicago, IL 60639

The quality control of incoming raw material detergents for use in shampoos is both costly and time consuming. Several daily shipments of synthetic liquid detergents such as the lauryl sulfate salts must meet specifications range before they are accepted. These sales are mixtures of predominately C12 sulfated matter containing varying amounts of unsulfated lauryl alcohol, sodium sulfate as well as bleaching agents and preservatives. Wet chemical and instrumental analysis for %solids, %active detergent %sulfate, %moisture and %benzoic acid take several hours to perform. The feasibility of using NIRA as a substitute for the traditional methods has been investigated. The results will be presented.

The feasibility of using NIRA as a control device for the continuous process of shampoo has also been investigated. In order to identify possible pumping malfunctions in the feeder streams of raw materials, several key constituents must be analyzed. The correlation of traditional analyses for these constituents with NIRA should allow continuous on-line sampling of the process. Preliminary results of this study will be presented.

CHEMICAL INTERMEDIATE PROCESS ANALYSIS VIA NIRA

Barbara B. Zinck, Noramco of Delaware Incorporated/First State Chemical Company,
500 Old Swedes Landing Road, Wilmington, DE 19801

NIRA was selected as a secondary method to analyze the powder intermediate of a chemical process. The original intent was to use the NIRA as a "black box" with testing performed by chemical operators during nights and weekends when lab coverage was not available for the primary method.

However, once the NIRA was in daily operation a better understanding of the intermediate and process was realized. After testing many samples by NIRA, it was determined that the chemical intermediate was not homogeneous. Those results took a few hours by NIRA, but would have taken days with the primary method. The larger sample size needed for the NIRA was in some cases a more representative sample and thus a more accurate result than the primary method but still not indicative of the entire batch.

As a result of the lack of homogeneity of the chemical intermediate, the intermediate was put into solution to start the final chemical process. As soon as the intermediate was dissolved, but before the remaining raw materials were initiated the reaction were added, the batch was sampled and assayed for the content of the chemical intermediate. This necessitated using a liquid drawer. Even though this work is ongoing, the results are promising.

REAL TIME PROCESS ANALYSIS KEY TO PROFITABLE MANUFACTURING

Neil Cahill, Vice President, Manufacturing Technology, Institute of Textile Technology, Charlottesville, VA

When asking a production manager what performance measures indicate whether a manufacturing operation is "effectively" controlled or not, the responses are usually such things as low off-quality, high productivity or low cost. But are these the measures of manufacturing effectiveness or are they the "rewards" for having been effective? The fact is they are the rewards and not the measures of manufacturing control effectiveness.

It is essential to define how to measure control effectiveness, especially for high-speed production systems. One key was uncovered recently in a plant survey to determine how much of the total performance losses in textile manufacturing was directly related to the occurrence of malfunction in the manufacturing process. The performance losses measured were such things as machine stoppage, quality defects, and process efficiency.

The results were not surprising; of the total performance losses incurred in these textile plants, only about 25 percent was in fact related to the actual occurrences of a process malfunction, while the remaining 75 percent of the losses was due to delay in reacting to these problems. It is response delay which is a decisive key to improving manufacturing effectiveness.

In manufacturing there are three flow networks operating which influence control delay. These are: (1) Defect Flow Network, (2) Information Flow Network, and (3) Decision Flow Network.

Manufacturing consist of a series of separate processes which are physically linked to each other by the flow of material. This movement of material acts as a coupling which carries defects from process to process. For this reason it is called the Defect Flow Network. The second network is Information Flow. This determines how quickly management is made aware that a malfunction even exist. And finally, there is the Decision Flow Network which determines how rapidly management can diagnose and take action.

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Neil Cahill

Within these networks are the sources of delay. But, it must be recognized that the real measure of delay is not time, but the number of defects generated during that time. Consequently, time by itself is not an adequate measure of control effectiveness. However, by combining delay time with the rate at which defects flow from the process, we now know the total number of defects generated after a malfunction has occurred. And more importantly, this effectiveness is expressed in terms of delay time, and delay is management controllable.

As has always been the case, management is responsible for manufacturing control effectiveness and that will be as important a technology decision facing management as selecting the "right" production machine.

FUNDAMENTALS OF HEAT HISTORY MEASUREMENT OF POLYESTER YARN USING
NIRA

Subhas Ghosh, Institute of Technology, Charlottesville, VA 22902

Near Infrared Reflectance Spectroscopy has been used to determine heat history of poly(ethylene terephthalate). X-ray diffraction study, thermal stress analysis, and fiber density measurements were also conducted to estimate the structural and morphological changes of PET due to annealing. A five-wavelengths regression model was selected to measure the heat-set temperature of polyester yarns. The coefficient of determination was $R^2 = 0.97$, with Standard Error of Prediction (SEP) = 1.2 C. Degree of crystallinity of PET increased with heat-set temperature, which was evident in the structural studies. The intensity of NIR absorptions at selected wavelengths was found to be very sensitive to the development of order in PET, and thus lends itself extremely well to the measurement of crystallinity and heat history of the polymer.

CONSIDERATIONS IN THE APPLICATION OF NIRA FOR THE ANALYSIS OF
PHARMACEUTICALS

Richard G. Whitfield, The Upjohn Company, Kalamazoo, MI

Near Infrared Reflectance Analysis (NIRA) has been shown to be a useful technique for rapid quantitative analysis of mixtures. In particular, applications involving the determination of moisture and protein in solids substances have been well documented. The promise of minimal sample preparation and inherent speed of NIRA makes it attractive for pharmaceutical analysis. In addition, NIRA is more readily adapted to on-line analysis than more traditional analysis techniques.

The issues pertaining to the application of this technique for the analysis of pharmaceutical products concern both the quantitative accuracy and -precision and the qualitative strength of the technique as compared to current methods of analysis. The development of the algorithms for pharmaceutical applications will be reviewed. The emphasis of this discussion will be on the above issues and the techniques for evaluating these algorithms.

NIRA FOR DISCRIMINANT ANALYSIS OF POLYMERS FOR SUSTAINED RELEASE FORMULATIONS

Robert L. Sharp & Richard G. Whitfield, The Upjohn Company, Kalamazoo, MI 49001

A Near Infrared Reflectance Analysis (NIRA) method has been developed for the identification of Hydroxypropylmethylcellulose (HPMC) and Sodium-Carboxymethylcellulose (CMC). The identification of these raw materials can be completed in minutes with no sample preparation required. It is intended for this method to replace the current wet chemical identification tests of these materials.

Sample spectra were identified using a discriminate analysis technique based on Mahalanobis distance (MD). A maximum MD or upper control limit (UCL) was determined to quality samples for positive identification. For a test set consisting of samples of like identity to the training set samples, all samples were positively identified.

Mahalanobis distance determination is shown to segregate between the spectra of other cellulose derivative materials, samples of different particle size and samples of different apparent viscosity. This ensures selectivity of the method toward only those samples identical to those which composed the training set.

THE DISCRIMINANT ANALYSIS OF PURE LIQUIDS

Emil W. Ciurczak, Sandoz Corporation, East Hanover, NJ

The use of Mahalanobis distances for discriminant analyses has been reported for both complex natural products (wheat, soy meal, etc.) and pure granular substances (barbiturates, lactose, sugars, etc.). In all cases the materials have been solids. In this paper I will address pure liquids.

Using the "European" liquid cell, samples of simple alcohols were used as a model system. 95% ethanol (USP), alcohol SD30 (denatured), methanol, and isopropanol were chosen for this test.

Contrary to expectations, the lack of interference from non-homogeneity and particle size variations hinders rather than helps the DISCRIM program. The Mahalanobis distances between group means soars to as high as 5000 which seemed well at first, but minor variations in temperature or as little as .05% water caused the failure of the identity test. Distances from the appropriate group mean were as high as 180-300 M.D.'s.

Examination of the plotted data showed that the groups were nearly identical with the group means themselves. That is the "normal" ellipses had degenerated to points.

A degree of ruggedness was built into the equation via two methods.

1. The absorbances at the chosen wavelengths were modified using the EDIT program, and the equation regenerated.
2. Minute quantities of impurities potentially present in the alcohols were added (e.g. acetone, water, and methylamine in methanol) and the samples used in a new equation.

The results of these experiments will be reported and their implications reviewed.