SEVENTH INTERNATIONAL SYMPOSIUM

ON

NEAR INFRARED REFLECTANCE ANALYSIS (NIRA)

# ABSTRACTS

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## PLENARY SESSION I

FUTURE DIRECTIONS FOR NIRA

Mr. Edward Stark, Principal Scientist,
Technicon Instruments Corporation, Tarrytown, NY

What are the future directions for NIRA? Applications development will continue as the largest area of effort. Expansion to new industries and additional analyses for existing users can be predicted with assurance. Simplification of the calibration process is of prime importance. Better understanding of the fundamentals of the measurement and the sources of problems will lead to improved mathematical techniques. A start has been made using sample selection algorithms to reduce the number of calibration samples required. Reducing the calibration workload while assuring that the calibrations can be readily transferred from the methods development instrument to those used for routine analysis will expand the utility of NIRA.

We have seen the beginning of advanced qualitative analysis with the development of discriminant analysis and spectral reconstruction. The use of these techniques should expand rapidly as more people become familiar with their power. The combination of qualitative and quantitative techniques should provide still greater automation of the analysis.

On-line analysis is on the horizon. Technology and instrumentation development is required to produce on-line measurements meeting the requirements of process control. The environmental and sampling problems must be addressed as well as maintaining the accuracy and precision of the present off-line NIRA measurements. Remote analysis using fiber optics and the power of the NIRA algorithms may be one solution to these problems.

## PLENARY SESSION I (Con't)

### REASONS FOR WAVELENGTH CHOICES

Dr. William Hruschka, Mathematician, U.S.D.A., Beltsville, MD

We Illustrate two extreme situations involving wavelength selection; one in which no spectroscopic knowledge was required, and one in which a careful justification of wavelength choice was advisable.

In the first case, it was desired to select as few samples as possible from a set of 600 forage samples for calibration of NIR data to protein, acid detergent fiber, neutral detergent fiber, lignin, and in vitro dry matter. Two hundred samples, randomly chosen were sufficient when a 60-term linear regression was used on Log 1/R values at 60 evenly-spaced wavelengths in the 1100 to 2500 nm region. Effects of smoothing and extrapolation will be discussed.

In the second case, a calibration for added salt in ham, two different computer search procedures found a calibration to a second derivative in a special location (1806 nm). Here, the effect of salt on the water band could be Isolated from the influence of other components of the ham spectrum. Possible limitations of this application will be discussed.

### AUTOMATED WAVELENGTH AND SAMPLE SELECTION

David Honigs, Professor of Chemistry, Washington University

NIRA has several advantages over more conventional spectrophotometric approaches, not the least of which is the computerized approach to methods development. Because of the present level of automation, NIRA can analyze many sample types where the exact chemistry or spectroscopy of the sample matrix is not known.

Although NIRA methods development is more automated than most analytical techniques, there is a surprisingly large amount of reliance on the user for such areas as wavelength and sample selection. In fact, the first thing that a would-be NIRA user must do is select a series of training samples before turning on the instrument. In this presentation, the reasons for sample and wavelength selection will be discussed along with some potential methods for automating these selection processes.

## PLENARY SESSION I (Con't)

### SAMPLE PREPARATION CONSIDERATIONS

TIS Applications Staff Joint Project

Near Infrared Reflectance Analysis is a convenient means of measuring many solid materials. Unfortunately, some solids do not lend themselves easily to the instrumentation available for the analyses. This paper will present sample preparation techniques for some of the more exotic and difficult samples we have encountered. InfraAlyzer methods have been developed for presentation of such samples as meat, butter, soils, rocks and textile fibers and fabrics. A mathematical means of determining that a sample has been properly prepared and presented to an InfraAlyzer will also be discussed.

### INCREASING THE SENSITIVITY AND SELECTIVITY OF NIRA

Dr. Tomas Hirschfeld, Senior Scientist, Lawrence
Livermore National Laboratory, Liver-more, CA

Near IR reflectance analysis currently requires gram quantity samples in which desirable constituents should exceed the 0.1% level. For well-behaved samples, however, the signal noise in the spectrometer is much lower than noise sources related to the sample's nature or preparation. Since the latter scale with the size of the sample's signal, substantial improvements in these sensitivities are possible using smaller cups or thinner samples. The former method requires piecewise calibration curves to reduce problems due to surface reflection.

Optical improvements can also be used to reduce sampling requirements. In existing instruments, microfocussing cups can reduce sample requirements 20-50-fold, and in redesigned instruments, further gains will be possible by replacing integrating spheres with ellipsoidal mirror systems.

The sensitivity of the method can also be increased by wetting the sample with "shift reagents" which will also enhance the selectivity of the method.

## AGRICULTURAL SESSION

### ROUTINE FORAGE ANALYSIS USING NIRA: CALIBRATIONS AND PERFORMANCE DATA

Jerome J. Workman, Jr.*, and Shirley A. Dieterman**, *Biochem Consultants, North Mankato, MN, **Watkins, Inc., Winona, MN

A turret-mounted discrete filter near infrared reflectance spectrometer was evaluated for routine and rapid nondestructive forage analysis. The instrument was utilized over a four-year period, and near infrared reflectance analysis (NIRA) calibrations were tested by standard wet laboratory methods and compared to NIRA estimates. The analyses were determined for hay, haylage, and corn silage. Hay and haylage samples were composed of legume, grass, and legume-grass mixtures. Standard deviations for laboratory versus NIRA estimates are included.

Over the four-year period hay standard deviations were (±1.09%, N=132) for crude protein; (±2.80%, N=97) for acid detergent fiber; (±0.29%, N=88) for calcium; (±0.06%, N = 90) for phosphorus. Haylage standard deviations were (±1.20%, N = 95) for crude protein; (±2.54%, N=102) for acid detergent fiber; (±0.34%, N=81) for calcium; and (±0.07%, N = 72) for phosphorus. Most recent corn silage standard deviations were (±1.16%, N=25) for crude protein; (±1.89%, N=21) for acid detergent fiber; and (±0.10%, N=26) for calcium.

Single NIRA estimate standard deviations for protein, fiber, calcium, and phosphorus were compared to single wet laboratory analyses standard deviations for nine commercial forage laboratories. Coefficients of variability for the NIRA estimates were found to be equivalent to those of between laboratory analyses for all forage types tested.

### SOME APPLICATIONS OF NIRA IN THE UK MILLING AND BAKING INDUSTRY

Dr. Brian Osborne, Principal Scientific Officer,
FHBRA, Chorley Woods, Watford, Hertfordshire, UK

Practical NIRA calibrations for the analysis of wheat, flour, doughs and baked goods have been devised. All of these have an acceptable degree of accuracy for industrial purposes and none, except the determination of protein in wheat, requires any sample pretreatment. In addition, calibrations for protein and moisture in wheat and flour have been shown to be stable with respect to time and transferable between instruments.

## NIRA IN COMPOUND FEED PRODUCTION

Mr. U. C. Vercauteren, Cehave N.V., Veghel, Netherlands

Compound feed is an industry, which especially in Europe uses a lot of grain-replacing raw materials coming from all over the world.

Therefore it is essential to have a sound knowledge of values and behavior, so that optimum mixtures can be created. The InfraAlyzer is used for analyzing raw materials as well as finished products.

The analyses are made in the ungrinded original matter by using 19 filters as a standard. To develop the system, a know-how of product qualities and common lab practice is necessary. With the InfraAlyzer it is also possible to analyze technological parameters and also very small parameters such as aflatoxins, carotene and lysine.

## WHEAT HARDNESS DETERMINATION

Gordon L. Rubenthaler, Director Western Wheat Quality Lab., Pullman, WA.

The indirect measurements of the properties of wheat which characterize its physical hardness (texture) have centered around methods to estimate the particle size of ground grain or the power/ time to grind it. While particle size of the granulated wheat meal has long been recognized as a key influencing factor in determining other constituents, such as protein in wheat by NIRA, new evidence suggests there is more than particle size involved in the NIRA prediction of hardness. Wheats differing in kernel hardness were ground and separated into eight particle size groups and scanned. The absorbance shifts dramatically from a low level with the coarsest material (overs, 350$\mu$ screen) progressively increasing to a peak at about the 100$\mu$ size range and then declining as the material got finer. In all size groups the absorbance values were distinctly ordered as those observed in the parent whole meals, i.e., the soft textured wheats were consistently lower than the medium and hard texture wheats. The NIRA determined differences between the soft and hard wheats are therefore thought to: be either chemical in nature or other physical properties such as shape, since particle size is removed. A mathematical summation of absorption of the separated parts was found to correlate to .99 with the absorption of the parent whole meals.

## APPLICATION OF NEAR INFRARED REFLECTANCE SPECTROSCOPY (NIR) FOR THE EVALUATION OF FORAGE SAMPLES

E.V. Valdes, L.G. Young and J.R. Winch, Departments of Animal & Poultry Science and Crop Science, University of Guelph, Guelph, Ontario

Calibrations for forages (hay, haylage, corn silage) were developed to estimate forage quality by Near Infrared Reflectance Spectroscopy (NIR). Parameters studied included crude protein (CP), add detergent fiber (ADF), calcium (Ca) and phosphorus (P). A calibration for haylage also included parameters such as neutral detergent fiber (NDF), acid detergent fiber insoluble nitrogen (ADF-N) and in vitro dry matter digestibility (DMD). The coefficients of determination (r?) of the prediction equations for CP ranged from 0.91 to 0.96 while $r^2$ values for ADF ranged from 0.21 to 0.92. With the exception of hay and haylage in the calibration set samples, the $r^2$ values for Ca and P were low. The calibrations predicted the quality parameters for forage samples with standard errors (SEP) of ±0.4 to 1.1% for CP, ±1.4 to 2.5% for ADF, 0.07 to 0.40% for Ca and 0.03 to 0.05% for P. Coefficients of determination ($r^2$) and SEP for NDF, ADF-N and PMD for haylage samples were: 0.76, 2.3; 0.58, 0.03 and 0.45, 3.8, respectively.

Calibration for physical properties of grass samples (timothy, bromegrass and orchardgrass) representing different stages of maturity were developed and included calibrations for density (D), water retention (UR), solubility (S) and packed volume (PV). The $r^2$ and SEP values for D, UR, S and PV for the calibration set samples were: 0.63, 18; 0.69, 40; 0.55, 1.4; 0.61, 3.6 and for the prediction set 0.55, 24; 0.55, 56; 0.42, 1.7; 0.54, 4.8 respectively.

## APPLICATIONS OF NIRA FOR PHOSPHATE ROCK ANALYSIS IN THE FERTILIZER INDUSTRY

Mr. William Hall, Chief Chemist, Estech, Inc.,
Bartow, FL

Monitoring of phosphate rock flotation is done using NIRA methods for rapid analysis of wet un-ground phosphate rock ores. Data from in-plant testing of the InfraAlyzer 400 monitoring trends of analysis of grab samples in a plant process control environment was collected and compared against a laboratory reference method. Six sites were monitored for phosphorus as $Ca_3(PO_4)_2$ or BPL. The coarse sized circuit (-14 +150 mesh) and the fine circuit (-28 +150 mesh) were monitored for BPL of incoming product (Feed), finished product (Concentrate) and waste (Tailings). The trend data provided by timely in-plant analysis will improve reaction time to changes in incoming product and ore characteristics.

## AGRICULTURAL SESSION (Con't)

### USE OF NIRA IN ANIMAL FEED ANALYSIS

Mr. Phillip Randall, Senior Scientist, RHM Research Centre, High Wycombe, Buckinghamshire, England

A Technicon InfraAlyzer 500 has been used to derive calibrations for animal feeds. These are now used on an InfraAlyzer 300 in an animal feed mill.

Moisture, oil, protein and for some materials, crude fibre, *are* now routinely measured by this technique. Data is used in raw material and process control.

Standard errors of calibration and prediction are presented.

Following the success of the feed mill work, NIRA studies were then carried out on mixed animal feed diets for laboratory animals. "Ash", crude fibre, moisture, oil and protein calibrations were derived for the range of ten different animal diets routinely analyzed by our analytical department. Eight diets conformed to a "standard" calibration. The remaining two diets had been heat treated and required separate calibrations.

The calibrations may be used in a scanning role to identify suspect diets for standard analytical analyses, but require further work before they are suitable for certifying specifications.

## PLENARY SESSION II

### ON-LINE MONITORING FOR CONTROL OF PROCESS

Dr. David Wetzel, Professor, Kansas State University Manhattan, KS

A sampling system for near-infrared reflectance Measurement of granular material transported through 3-inch aluminum spouting has been designed, fabricated and tested for ground homogenous and heterogeneous samples. The system allows diffuse reflectance measurement at preprogrammed wavelengths with a vertically mounted Technicon InfraAlyzer 400 sensing head equipped with extended cables. The design will accommodate stop flow operation or monitoring under continuous controlled motion through a gravity filled sample loop. Application of this particular on-line monitoring is targeted for routing control of a particular subprocess effluent to improve the efficiency of the overall processing. Wavelength selection with off line use of an InfraAlyzer 500 in the incremental wavelength and filter transform mode has produced a calibration capable of monitoring the quality parameter variation upon which the control of routing is based. A particular flour milling application illustrates the utility of the system.

### INDICATOR VARIABLES: HOW TO USE THEM

Dr. Donald Burns, Technicon Instruments Corporation, Tarrytown, New York

In Near Infrared Reflectance Analysis (NIRA) the instrument/computer combination "learns" what is significant in a so-called "teaching set" of samples so that it can later be used to analyze unknown samples of the same type. It can do this rapidly (usually in 15-30 seconds), non-destructively, on several constituents simultaneously, and often with little or no sample preparation.

Sometimes samples contain more differences than meet the eye. Even when there is only a single constituent, there may be differences due to more than one operator, more than one kind of sample treatment (such as drying time or temperature), more than one particle size, etc. One can quantitate the effect of these additional factors by including information about them during the calibration procedure. This "extra" information is entered as a so-called "indicator variable", and is a route to better analyses, easier sample handling, and a means of identifying subtle interactions in a process or procedure.

The use of Indicator variables will be illustrated with a real-world analytical problem, the experimental design to solve it, the individual steps undertaken, and the intermediate results.

## PLENARY SESSION II (Con't)

ADVANCES IN FTIR

Dr. Fred McClure, Professor, Department of
Biological Engineering, North Carolina State University.

Fourier anal/sis of near infrared spectra offers several advantages to NIRA users. Fourier coefficients can be used directly in calibrations for measuring chemical composition with equal "robustness" as conventional NIRA math. Magnetic storage requirements for wavelength data can be reduced by 97% by transformation to Fourier space. Computation times for developing calibration equations are curtailed by 97X since only the first eleven Fourier coefficients are used for measuring chemical composition. Derivative enhancements of calibrations can be achieved in Fourier space. Results of analyses pertaining to tobacco, forages and mice will be given.

## DAIRY/MEAT/FOOD SESSION

### THE UNIVERSALITY OF NIRA FOR THE ANALYSIS OF DAIRY PRODUCTS

Mr. William C. Green, Dairy Chemist, State of California, Sacramento, CA

The determination of constituents for dairy products by NIRA such as fat, protein, lactose, and moisture is quite feasible and challenging. Reducing two days analysis time to thirty minutes is an accomplishment.

As California's payment for producer milk is on fat and solids-non-fat, the direction has been on the analysis of fluid milk. Correlation coefficients of 0.99 for fat and protein and 0.87 for lactose were obtained when compared with the chemical analyses. Sterile milk is used daily to adjust the $F_0$ bias.

With the solids drawer, the effort has been with non-fat dry milk and cottage cheese. Analysis time with the powder of 13 seconds for fat and moisture vs. 90 minutes and 18 hours respectively for the chemical analysis is encouraging. With cottage cheese the direction is in recognizing and controlling the variables such as sample preparation, temperature and additives.

Development work on cheddar cheese has been initiated.

### AN EVALUATION OF THE TECHNICON INFRAALYZER 400 FOR THE RAPID MEASUREMENT OF VARIOUS CONSTITUENTS IN FOOD PRODUCTS

H.L. Watson, Staff Chemist, Procter *t* Gamble Company, Cincinnati, OH

A general evaluation of the Technicon 400 InfraAlyzer was done to determine the potential applicability of near infrared reflectance analysis to the measurement of various components in food products. The instrument was calibrated on samples of products in which the concentration of the specific component of interest had been measured by a standard method of analysis. Calibration of the InfraAlyzer was also done on samples of a product matrix to which known amounts of the component to be measured had been added. The applications developed were the analysis of iodine values of hardened soybean oil, % monoglycerides in shortening, % propylene glycol monoesters of palmitate and stearate in shortening, % fat in potato chips, % fat in cake mix and the % moisture in baked products. Other promising applications evaluated were the analysis of fat-protein-moisture in peanut meal and the sugar-flour-fat ratios in cake mix blends.

## 5000 PROTEIN ANALYSIS PER DAY USING A MODIFIED INFRAALYZER 400

Jean B. Stalnaker, Agriculture Lab Technician, Kansas State University, Manhattan, KS

Using a specifically designed sample compartment, rapid sample loading and removal is possible. This unit requires a modification in the position of the InfraAlyzer 400 optical head. The improved efficiency of the total system will be presented.

## DETERMINATION OF COLLAGEN IN BEEF USING NEAR-INFRARED REFLECTANCE SPECTROSCOPY

G.H. Lee, Graduate Student and D.G. Olson, Professor Iowa State University, Ames, IA

Collagen is the principal protein in meat connective tissue. Collagen solubilizes during heating and solidifies during cooling. These properties can result in the formation of unstable meat emulsions if collagen levels are too high. Most least-cost formulations of emulsion meat products have a maximum collagen level as a restraint to prevent formation of unstable emulsions. The collagen levels in raw meat material however are only estimated based on average values because the determination of collagen requires considerable time (over 24 hours) and specialized equipment not normally found in meat company quality control laboratories. Since estimated collagen levels are generally higher than actual values to provide a margin of safety in formulation stability, many emulsion type products are formulated with more expensive meat materials than are needed if actual collagen values were known. Rapid determination of collagen in beef using near-infrared reflectance spectroscopy through Technicon's InfraAlyzer 400 has been investigated. Nineteen beef samples with varying amounts of collagen were prepared and measured via the InfraAlyzer and hydroxyproline. The multiple correlation coefficient ($R^2$) was 0.8815. Preliminary tests showed no significant ($p<.01$) difference between predicted values and hydroxyproline assay values.

# PHARMACEUTICAL/TEXTILE SESSION

## QUALITATIVE ANALYSIS OF PHARMACEUTICAL RAW MATERIALS VIA NEAR INFRA-REO REFLECTANCE (NIRA) SPECTROSCOPY

Emil W. Ciurczak, Instrumentation/Chromatology
Specialist, Sandoz Inc., East Hanover, NJ

A rapid and specific Method of doing identity testing of incoming raw Materials has been sought for some time. Time consuming infra-red scans and non-specific color tests have been the commonly used means of identity testing. NIRA provides just the rapid and precise Methodology sought.

A newly developed discriminant analysis program was used for several families of raw Materials:

1. Chemically similar, as represented by barbiturates, (i.e., phenobarbital, pentobarbital, butalbital, etc.).
2. Chemically varied; but produced in the same plant, (i.e., aspirin, fumaric acid, etc.).

A third class would involve materials produced at a plant where many chemicals are manufactured. The sheer number (i.e., 200-300) would tend to overwhelm any program. In this instance, selected materials are chosen for comparison. An example is caffeine, where theophylline and theobromine were chosen as the most likely to be mistaken for the caffeine.

Examples of each group will be discussed along with the Methodology involved.

## NIRA IN RAW WOOL TESTING

M.J. Hammersley, S. L. Ranford and V.C. Patrick,
Wool Research Organization of New Zealand

Clean wool is a major export from New Zealand. The product is normally certified for moisture content and residual grease levels and recent work has shown that NIRA may be used for this purpose with considerable economic benefit anticipated. The particular characteristics of wool have necessitated the development of special sub-sampling and sample handling techniques with corresponding changes in the software.

Whilst moisture content measurement proved easy, successful residual grease determinations were made only after considerable refinement of the manual method and careful structuring of the calibration population.

The first in-plant trials were started in June 1984.

## NEAR INFRARED ANALYZER: A CONTROL TOOL TO DETECT HEAT-SET VARIATION

Nicolette F. Rainey, Mr. Subhas Ghosh, Institute of Textile Technology, Charlottesville, VA

Carpet yarns are heat-set to impart yarn bulk through controlled shrinkage, and to stabilize the yarn throughout further processing and finishing. Heat treatments modify the molecular structure and morphology of the yarn which affects the dyeing and other physical characteristics of the yarn. Small changes in set temperatures can alter the properties of individual yarns such that visible carpet streaks may occur, creating off-quality products. There is currently no quick method to determine a yarn's heat history and thus assist in process control. Near Infrared Reflectance Analysis (NIRA) promises to be a tool which in seconds can detect heat-set differences in yarns. An evaluation of this technique included comparisons with conventional but complex methods of X-Ray Diffraction and thermomechanical Analysis. Results indicated that NIRA was sensing the changes in a fiber's internal structure, which change with rising temperatures, and that is compatible with conventional techniques. The advantages are speed and ease of operation.

## APPLICATION OF NIRA IN THE TEXTILE INDUSTRY ANALYSIS OF COTTON-POLYESTER BLEND YARNS

Wayne C. Tincher, Professor, School of Textile Engineering, Georgia Institute of Technology, Atlanta, GA

Conventional analysis of blended yarns for fiber components is *a* difficult and time consuming procedure. As a demonstration of the applicability of NIRA to typical textile problems, a series of cotton-polyester blend yarns (30 samples over a range from 75% cotton, *25%* polyester to 25% cotton, 75% polyester) were prepared. These were analyzed by the conventional gravimetric procedures and investigated by NIRA. Multiple regression analysis showed that a combination of reflectances at 546, 1650 and 1790 nm was highly correlated with the *per*cent cotton in the yarn samples (r = 0.9985).

The calibration equation from the multiple regression analysis was used to analyze 10 cotton-polyester blend yarns. Excellent correlation (SEP = 0.8523) was obtained between the NIRA and the conventional analysis.

A brief investigation of sample preparation techniques for textile material was also conducted as part of this study.

## PHARMACEUTICAL/TEXTILE SESSION (Con't)

### SPECIFIC APPLICATIONS *Of* NIRA IN THE TEXTILE INDUSTRY

Dr. James E. Rodgers, Analytical Specialist, Monsanto Company, Pensacola, FL

Near Infrared reflectance analysis (NIRA) has gained Increasing use and importance in the textile Industry, especially in the measurement and Monitoring of selected physical and chemical properties of textile yarns. The Moisture level (percent $H_2O$), finish on fiber (OOY), and carpet heat-set temperature (HST) properties of various nylon 6,6 yarns were evaluated by NIRA using the Technicon 400TX InfraAlyzer, and the NIRA values obtained were compared to the values obtained by the routine/standard measurement techniques. For the selected yarn samples, the 400TX did accurately measure the percent $H_2O$ and OOY levels. The standard errors of prediction, SEP, were very good, and the Method precisions appear to be significantly better than those precisions of the routine percent $H_20$ and OOY methods. On selected griege and dyed carpet yarn samples, the 400TX did accurately Measure the HST for Superba and Sussen heatset griege yarns and for Suessen heatset dyed yarns. The SEPs for both the griege and dyed yarn systems were very good over a wide temperature range, and the results were comparable to those obtained by various thermal techniques.