Lorillard
TOBACCO COMPANY

**MEMORANDUM**

October 26, 1995

TO: M. A. Sudholt

FROM: A. Prakash

SUBJECT: Menthol Analysis by Near-Infrared Spectroscopy

PROJECT NO.: Q 449 Analytical Support Services

FINDINGS:

Near-infrared spectroscopy can be used for menthol analysis on tobacco as evaluated by the three Near-Infrared (NIR) companies. Further experiments for the on-line evaluation of menthol are proposed.

## Introduction

Near-infrared (NIR) spectroscopy is widely used for the on-line analysis of moisture in tobacco. NIR can also be used to distinguish the different types of tobacco, reducing and total sugars, nicotine alkaloids, total nitrogen, humectants, and menthol. In 1978, Pandeya and coworkers used NIR reflectance spectroscopy to study the nicotine alkaloids in tobacco (1). Pandeya and coworkers (1), and McClure et al. (2) have published their works on the studies of total and reducing sugars by NIR spectroscopy. The amount of stems in a stem and lamina mixture was determined by NIR technique (3). Canon (4) studied the triacetin levels in the cellulose acetate filter rods. A wide variety of applications including menthol (5) have been studied using NIR reflectance spectroscopy.

The quality control department at Lorillard currently analyzes menthol by isolating the menthol from tobacco by distillation with subsequent quantitation by GC with FID detection. This method is labor-intensive and time consuming. The mentholated tobacco is made into cigarettes within a few hours. Hence, a menthol analyzer which can indicate the menthol level on tobacco after being sprayed with menthol, but before making cigarettes would prevent the recalling and reclaiming of cigarettes.

NIR spectroscopy, a nondestructive analysis technique, provides the results at a speed such that the levels of menthol will be known before the menthol cigarettes are made. Three NIR companies, Analytical Spectral Devices, Inc. (Boulder, CO), NIRSystems, A Perstorp Analytical Company (Silver Spring, MD) an

LT Industries, Inc.(Rockville, MD), were chosen to evaluate the feasibility study of menthol on tobacco.

## Experimental

The Kent tobacco blend was used to prepare standard samples for the menthol studies. Barnes and Harper sprayed menthol at various levels ranging from 0.1% to 1.2% on tobacco in the pilot plant to obtain a NIR standard calibration curve for menthol. The moisture on the tobacco was determined by placing a known amount of tobacco in an oven at 100°C for 8 hours. The menthol level on the tobacco was quantitated by GC/FID (6) and the percentage of menthol on the basis of dry weight of tobacco was calculated. The GC/FID menthol results for the standards were provided to the NIR companies so that NIR calibration curves could be established.

The unknown samples are the mentholated tobacco of Newport and Style cigarettes obtained from production in the menthol spray room. The samples were taken from the conveyor belt after the tobacco was sprayed with menthol.

### Calibration and Cross Validation

A first or second derivative transformation was performed on each sample spectrum to remove baseline offset. A Partial Least Square (PLS) calibration was performed on the first or second derivative spectra to eliminate non-homogeneous sample distribution and scattering effects from the samples (8-11). The calibration model was built using the sample spectra and the known concentrations from the GC/FID method. The model is then applied to predict the concentration of each sample. The standard error of calibration is calculated from the predicted model. The calibration plots are presented in Figures 1-4.

A validation step is done to evaluate the performance of the calibration model. Leave-one-out cross validation was used, which means leaving one sample out to build a calibration model and predicting the concentration of the left out sample. The difference between the calibration and cross validation is that the predicted sample is not included in the calibration model. The reason for doing cross validation is to test the model independently. Cross validation plots are presented in Figures 1-4.

### Analytical Spectral Devices, Inc. (ASD)

On-site measurements in the pilot plant were taken with an ASD's FieldSpec portable NIR spectrometer by inserting a fiber optic

reflectance probe into fresh mentholated tobacco samples. The samples were scanned from 1000 nm to 1800 nm.

Partial Least Square (PLS) calibration method was used on the first derivative transformation. The standard error of the calibration (SEC) for the predicting model is 0.13% and the standard error of validation is 0.23%.

The one month old samples of the standards and the unknowns were sealed in glass jars. The glass jars were shipped to the ASD labs, so the menthol evaluation could be duplicated like an on-line system. The menthol analyses of the samples were done by GC/FID (7) before shipping. The shipped samples were analyzed by the ASD's FieldSpec portable NIR spectrometer scanning from 1000 nm to 1800 nm using two 50 W DC tungsten halogen lamps. The lamps were placed 14 inches above the tobacco sample. The fiber optic probe, 1 meter long, 57 silica-silica fibers, 110 µm and 220 µm diameter were fixed one inch above the sample. The sampling area was 13 mm diameter. Five reflectance spectra were taken on different areas of each sample and 50 scans were taken for each spectrum scanned at a rate of 0.1 sec/scan.

A Partial Least Square (PLS) calibration was performed on the first-derivative spectra and the laboratory reported menthol values. The standard error of calibration for the six-factor PLS model was 0.02%. The standard error of cross validation is 0.11%.

NIRSystems A Perstorp Analytical Company (Perstorp)

NIRSystems, Inc. Model 5000 monochromator with sample transport attachment was used for the sample analyses. The two months old samples sealed in jars were shipped and analyzed in a reflectance mode in the spectral region, 1100 nm to 2500 nm. The sample was analyzed in a coarse sample cell which provided a 60 $cm^2$ area for sample analysis. The average of the triplicate analyses was used to calculate the second-derivative spectra to minimize baseline drifts.

A Partial Least-Square (PLS) calibration was performed on the second-derivative spectra and the laboratory reported menthol values for the standards. With a three-factor PLS model, the correlation was 0.971 and the standard error of calibration was 0.1%. The standard error of cross validation for two samples is 0.09%.

LT Industries (LT)

A Quantum 1200 Plus Analyzer was used for the analysis of the three months old tobacco samples which were sealed in jars. Each sample weighing 30-50 gms in a sample cup, was scanned from 1200

nm to 2400 nm three times. Each sample was scanned three times and the average was processed with the second derivative math transformation to eliminate non-homogeneous sample distribution and scattering effects from the samples.

A calibration model for menthol concentration was derived with the Partial Least Squares (PLS) algorithm. With a three-factor PLS model, the correlation coefficient was 0.93 and the standard error of calibration was 0.065%. The standard error of cross validation was 0.178%.

**Results and Discussion**

Portable NIR Analysis

The results of the Analytical Spectral Devices, Inc. on site study using a fiber optic reflectance probe immersed in the tobacco sample for the freshly mentholated tobacco are shown in Table I. The sample being nonhomogeneous from particle to particle, and the small area viewed by the probe immersed in the sample produced a relative standard deviation of 23% for the Newport blend and 26% for the Style menthol blend.

Laboratory NIR Analysis

The results of the one month old tobacco samples analyzed similar to an on-line process by ASD are presented in Table II. The relative standard deviation for the Style menthol blend is 22%. The results obtained for the Style menthol is twice as expected.

The reflectance cell measurements of menthol by Perstorp are summarized in Table II. The relative standard deviation for the Newport blend is 1% and for the Style menthol blend is 14%.

Table II summarizes the results of the reflectance cell measurements of menthol by LT industries. The relative standard deviations for the Newport and the Style menthol blends are 9% and 2%, respectively.

The menthol results for the unknown samples by NIR were all higher than the expected values. One of the reasons may be due to the difference in the tobacco blends used for the standard calibration and the unknowns. Two samples for each unknown were taken. The relative standard deviation can be improved by sampling more than twice at definite intervals during the menthol spraying process. The studies done in the laboratories suggest that the NIR menthol analyses on tobacco are feasible.

On-Line Menthol Analyses

The objective of this project is to obtain an on-line NIR system for menthol analysis. An on-line evaluation of the samples by

the Process Analyzers will be different from the laboratory evaluation of the menthol samples. In the on-line process, the NIR measurements are continuously analyzed on the moving tobacco samples and the samples are freshly sprayed with menthol solutions.

Potential Errors Involved in an On-line NIR Analysis Using the Current Production Set-Up

In the menthol process, the depth of the tobacco on the conveyor belt is different, and also, the tobacco is moving at a great speed on the conveyor belt. These factors may have an effect on the NIR readings and could present problems. Modifications of the production set up may be necessary, such as, (a) placing a levelling bar on the top of the belt to make it a smooth surface and (b) channeling a small amount of sample at the end of the conveyor belt to a belt where NIR analysis can be done.

**Conclusion**

An on-line NIR evaluation of menthol on tobacco should be studied to understand the system and to answer the unsolved questions. The Perstorp Analytical company and LT industries will perform an on-line menthol evaluation for a month in the production area at a cost of $ 5,000. The on-line evaluation will also involve obtaining a standard calibration for each tobacco blend to be analyzed. Each calibration will require preparing and analyzing tobacco samples with menthol concentrations ranging from 0.01% to 1%. If, an on-line menthol NIR processor is not feasible, as an alternative, a bench top or a portable NIR spectrometer should be purchased to analyze the menthol on tobacco before cigarettes are made.

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**Table I**

**Results of the Freshly Mentholated Tobacco by Reflectance Probe**

| Sample | Expected Menthol | | Menthol(GC/FID) | Menthol(NIR) |
|---|---|---|---|---|
| Unknown 1 | Newport | 0.367% | 0.419% | 0.664% |
| Unknown 2 | Newport | 0.367% | 0.412% | 0.475% |
| Unknown 3 | Style | 0.55 % | 0.632% | 0.701% |
| Unknown 4 | Style | 0.55 % | 0.645% | 1.017% |

**Table II**

**Results of the Laboratory Analyses of Mentholated Tobacco Samples****

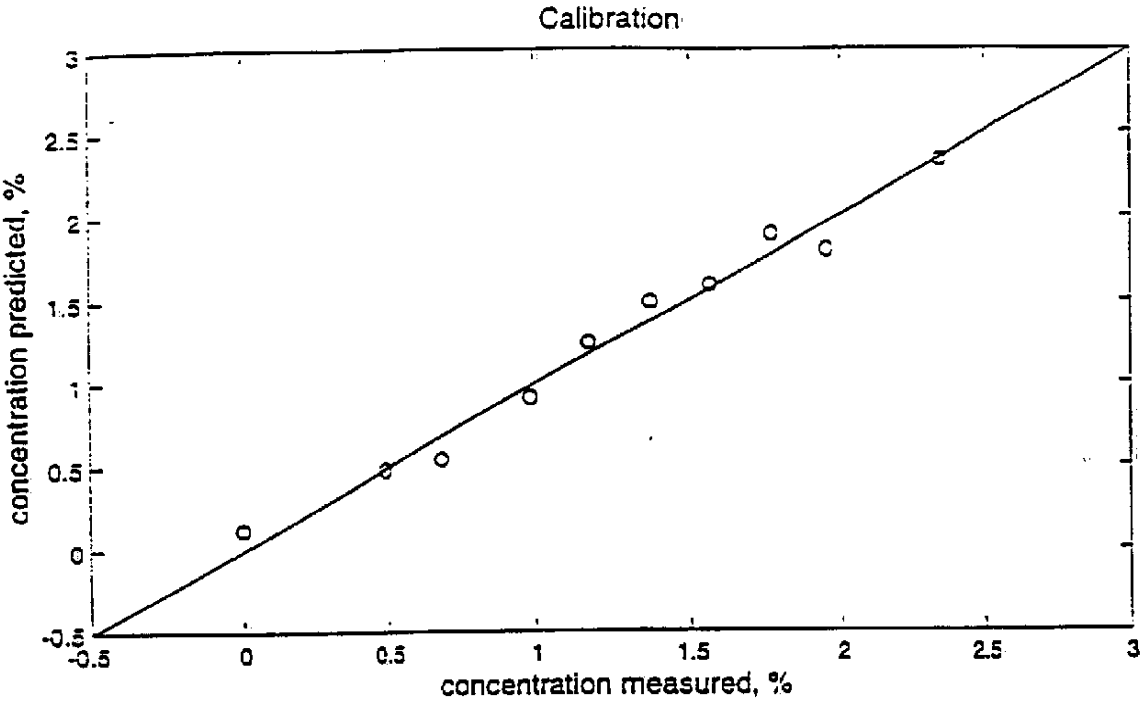
| Sample | Expected Menthol | | GC/FID | ASD(Simulated On-Line) | Reflectance Cell Perstorp | LT |
|---|---|---|---|---|---|---|
| Unknown 1 | Newport | 0.367% | 0.299% | 0.27% | 0.559% | 0.426% |
| ,, ,, 2 | Newport | 0.367% | 0.320% | 0.87%* | 0.568% | 0.376% |
| Unknown 3 | Style | 0.55 % | 0.411% | 0.94% | 0.660% | 0.812% |
| ,, ,, 4 | Style | 0.55 % | 0.416% | 1.28% | 0.800% | 0.838% |

* Outside the model
** Samples were sealed in the jars for 1-3 months

ASD INC.

ASD, Inc.

**Fresh Menthol Samples**



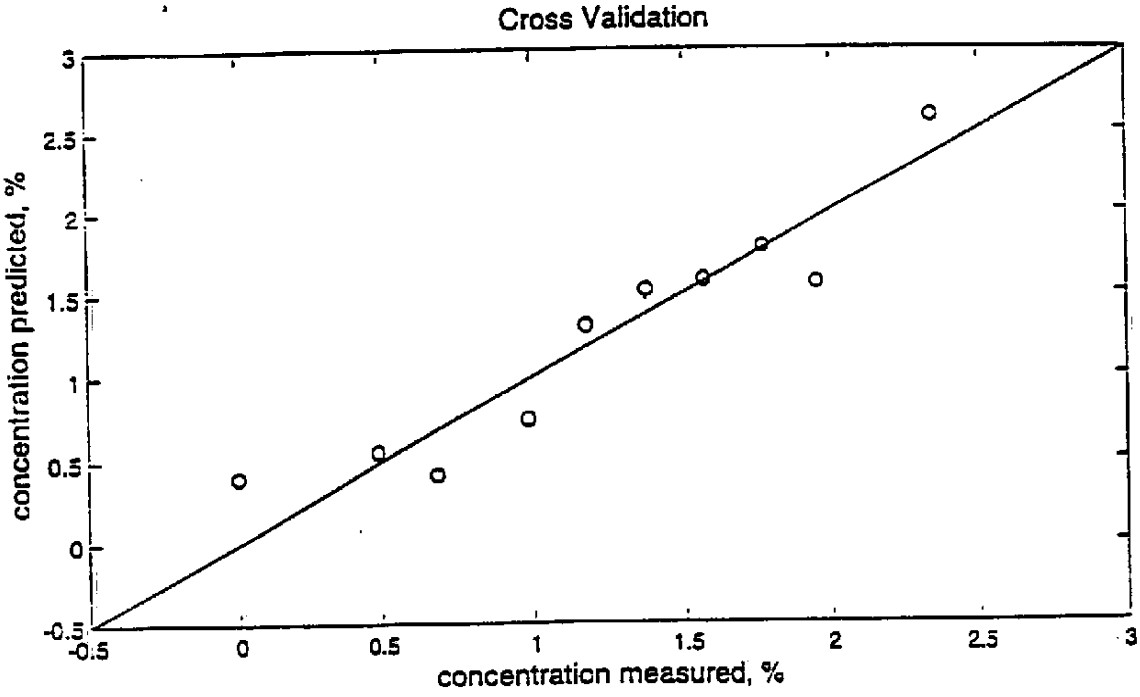




**Figure 1**

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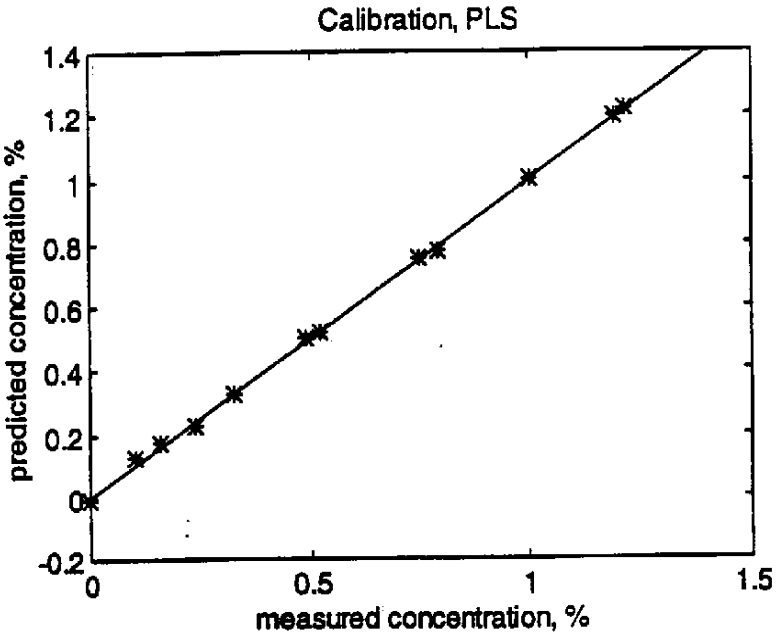
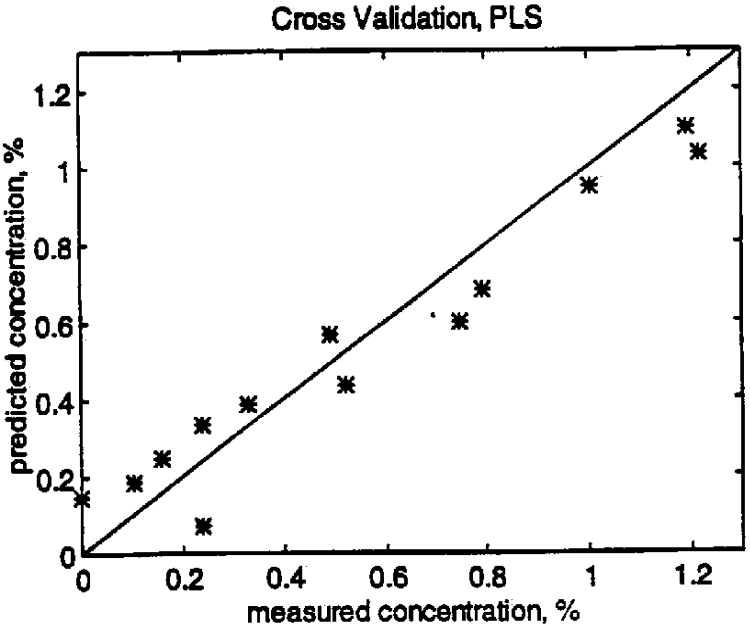
ASD INC.

A Month Old Menthol Samples



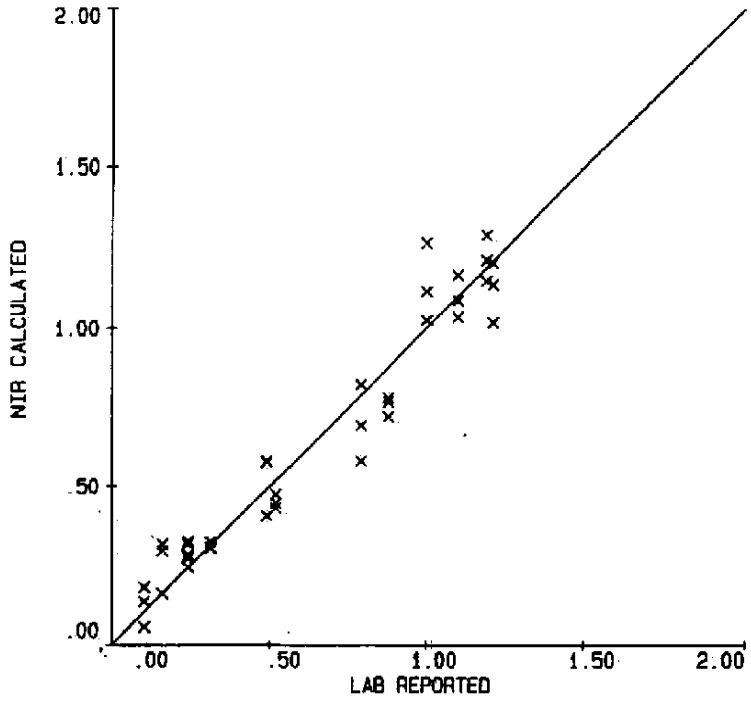




Prediction results of PLS calibration and cross validation

Figure 2

Perstorp Analytical Company

Two Months Old Menthol Samples




Cross Validation, PLS

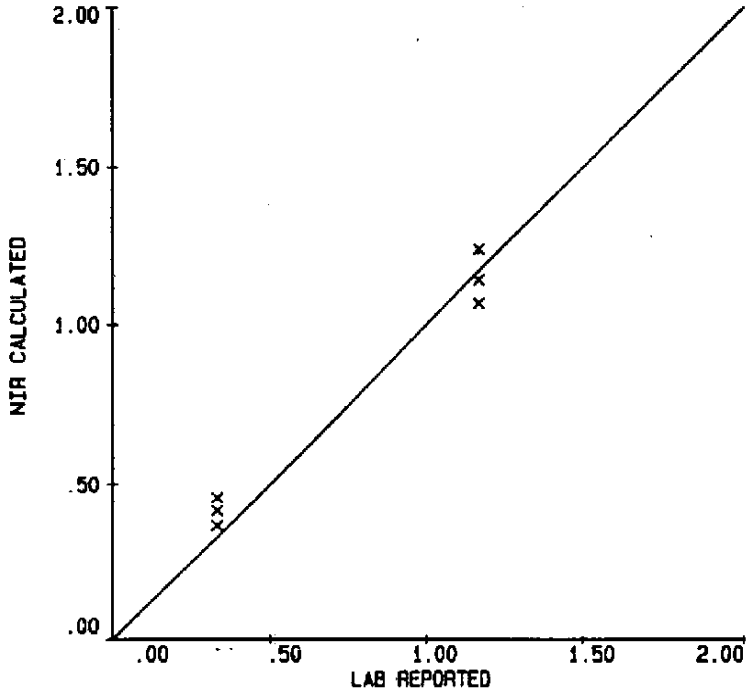



Figure 3

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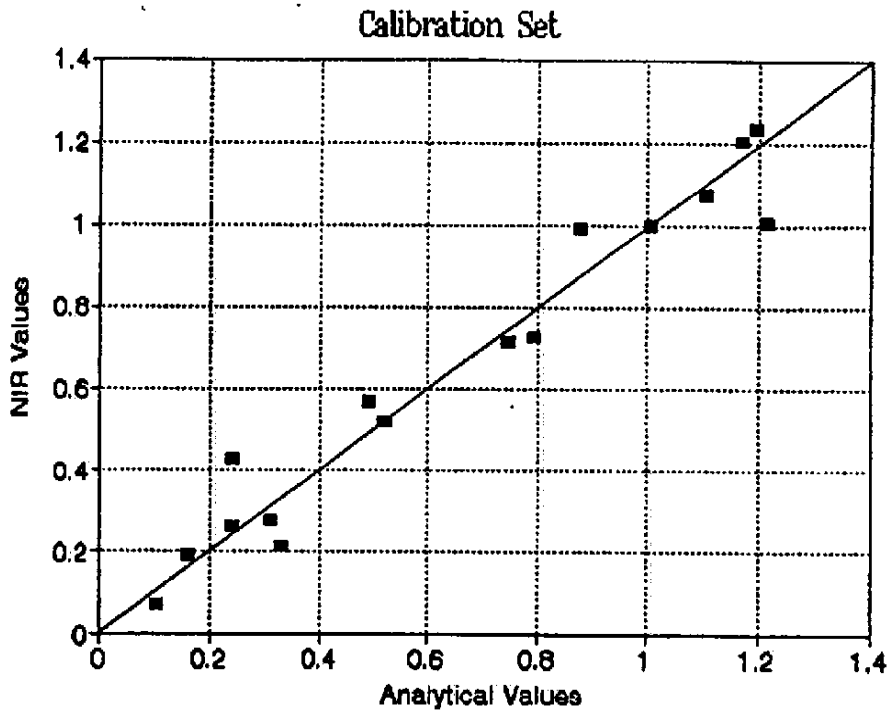
LT Industries

Three Months Old Menthol Samples



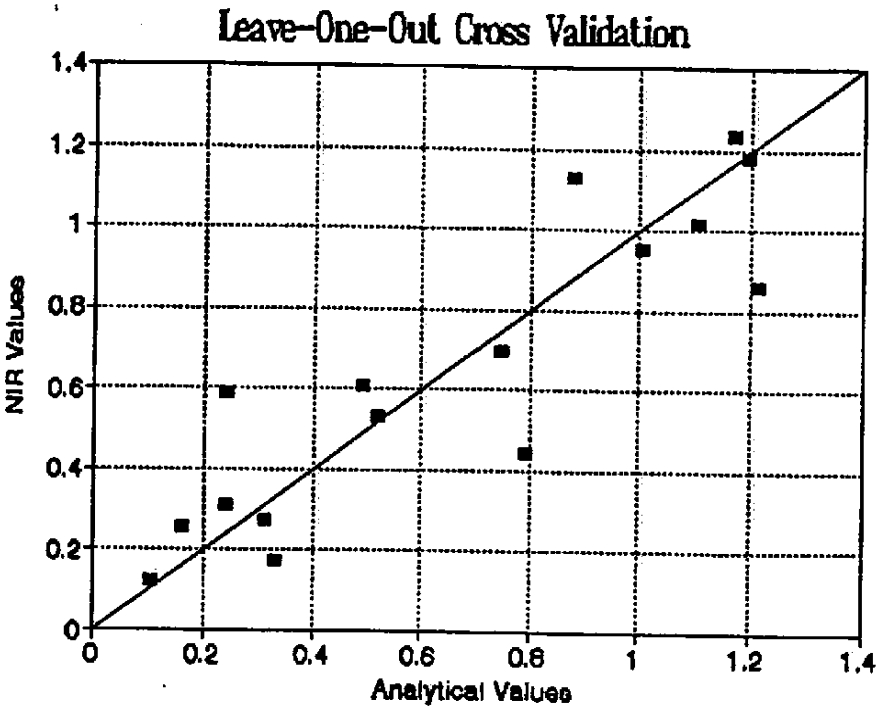




Figure 4