Near-Infrared Spectroscopic Analysis of Deterioration Indices of Soybeans for Process Control in Oil Milling Plant[1]

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The feasibility of near-infrared (NIR) spectroscopy was examined for analyzing quality criteria or deterioration indices of soybeans, such as the nitrogen solubility index (NSI), acid value, digestibility and percentage germination, as well as the contents of their major constituents (moisture, oil and total nitrogen). Because all the criteria are closely related to yield and quality of the final product, their rapid analysis is required for process control in the oil milling plant. NIR diffuse-reflectance spectra were measured on ground samples in an InfraAlyzer 500 (Bran+Luebbe Co., Norderstedt, Germany). As for the major constituents, the standard errors of prediction (SEP) were 0.34% (moisture), 0.24% (oil) and 0.067% (total nitrogen). These results show the ability of NIR for analyzing these parameters, as many researchers reported previously. As for the other quality criteria, the SEP values were 2.40 (NSI), 5.58 (digestibility), 0.29 (acid value) and 15.27 (germination percentage). Further, NIR analysis for some of these criteria of the extracted residue and defatted soybeans was also examined, and almost the same level of SEP values was obtained. Although it is still necessary to improve the accuracy, we concluded that the NIR method has the feasibility to measure quality criteria for the purpose of process control in the plant in place of the time-consuming chemical analyses that are conventionally used.

KEY WORDS: Analysis, defatted soybeans, deterioration index, digestibility, near-infrared, NSI, oil milling process, process control, soybeans, spectroscopy.

Recently, near-infrared (NIR) spectroscopy has been recognized as a powerful analytical technique for rapid determination of various constituents in many commodities (1–3). As for soybeans, NIR has been mainly applied in the analysis of the major constituents and has also been adopted as the official analytical method (1). However, application of the NIR method would also be desirable in the analysis of other quality criteria or deterioration indices, such as nitrogen solubility index (NSI), acid value (AV) and digestibility. There have been few reports on these criteria. Further, use of the NIR method has been demanded for the analysis of not only the raw materials but also of the intermediate and final products for process control in the food industry.

Figure 1 shows the oil milling process in the plant. Raw soybeans are selected, dried, crushed, heated and oil-extracted with organic solvent. Crude oil and extracted residue are then obtained. The extracted residue is further processed to defatted soybeans. The left side of the figure shows the stream of the oil component of the soybeans, and the right side shows that of the protein and carbohydrate component in the plant. In this study, NIR analysis of the following materials is presented: the soybeans, the extracted residues after removing the oil, and the defatted soybeans, i.e., the materials outlined in bold in Figure 1 (they are the raw material, the intermediate product and the final product, respectively). However, the defatted soybeans also become the starting material for further processing, such as the production of soybean protein concentrate. In this study, the feasibility of the NIR method for process control in the soybean oil milling plant was examined for analyzing quality criteria, such as NSI, AV, digestibility and germination percentage, in addition to the contents of the major constituents. All these criteria are closely related to the yield and quality of the products in the plant. NSI and digestibility are the indices of protein quality and are related to the processing availability of the final products; for example, they are related to the yield and quality of tofu (soybean curd). AV is a deterioration index of oil. Germination percentage is a deterioration index of the quality of the raw material.

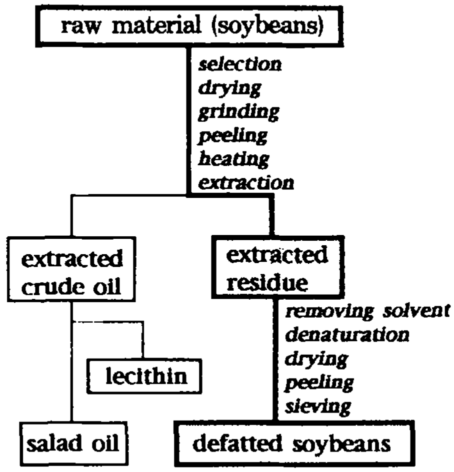

FIG. 1. Oil milling process of soybeans. Areas outlined in bold are the samples analyzed in this study.

MATERIALS AND METHODS

Materials. Each set, composed of three kinds of samples (soybeans, extracted residues and defatted soybeans) was collected once a week in the oil milling plant for two years. In total, 93 sets were collected. The raw materials from which oil was to be extracted were imported mainly from the United States and Brazil.

Chemical measurements. Moisture content was measured by an oven drying method (130°C, 3 h) (4), oil content was measured by the Soxhlet method (4), and total nitrogen content was determined by the Kjeldahl method (4). NSI was measured as follows: Samples were extracted with water, total nitrogen of the fraction was determined by Kjeldahl method, and the ratio of its total nitrogen content to that of the starting material was calculated (4).

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Digestibility was measured as follows: Samples were autoclaved for 20 min and were then incubated at 43°C for two weeks with an enzyme solution (2% taka-diastase; Sankyo Co., Tokyo, Japan). Then, the total nitrogen content of the filtered material was measured, and its ratio to that of the whole was calculated (4). AV was determined by titration with 0.1N KOH solution for the extracted oil from the samples, and the obtained values were converted to the necessary amount of KOH (in mg) for 1 g of the sample to be neutralized (4). Germination percentage was measured by growing 50 grains for days under practical conditions and confirming germination. The ratio of germinating individuals was then calculated (4).

Physical measurements. Samples were ground in a ultracentrifuge mill (Retsch Co., Düsseldorf, Germany), packed in sealed bags, and stored at 0°C until measurements were begun. Samples were moved to the analytical room and were kept at room temperature before starting measurements. Their NIR diffuse reflectance spectra were measured with an InfraAlyzer 500 (Bran+Luebbe Co., Norderstedt, Germany) after the samples were packed in the standard sample cup.

Statistical analysis. Fifty-six samples were used to establish the calibration equations for estimation of the contents of the constituents and the quality indices. With 37 independent samples, the performance of those multiple regression equations obtained were evaluated by predicting these criteria. The default conditions were used for calculating the first and second derivative spectra. Multiple linear regression analysis (MLRA) was carried out by means of IDAS software (Bran+Luebbe). For the germination percentage, the combination analysis of principal component analysis (PCA) and discriminant analysis (DA) was carried out with commercially available software that was slightly modified to be able to deal with many variables (5-7). First, PCA was applied to the second-derivative full spectral data to obtain the eigenvectors, and the PCA scores were calculated. Then, DA was carried out with these PCA scores.

RESULTS AND DISCUSSION

Major constituents. Table 1 shows the ranges of the major constituents and the quality criteria of the samples used in this study. Some constituents have narrow ranges of contents, namely moisture of the soybeans, oil of the defatted soybeans and total nitrogen of all three materials. Figure 2 shows the raw and the second-derivative NIR spectra of the soybeans (raw material), extracted residue (intermediate product) and defatted soybeans (final product). The absorption band at 1960 nm is due to water; those around 1700-1800 nm and 2300-2400 nm are due to fat. The absorbing region around 2180 nm is protein. After the oil was extracted, the absorption bands due to fat became weak or disappeared (Fig. 2), and both the extracted residue and the defatted soybeans have almost the same spectral pattern. Thus, the NIR spectra provide information about the constituents.

In the NIR method, the calibration equations for estimating the contents of the constituents and the quality criteria are first established by MLRA, from both the spectral data and the chemical data of the calibration set. Table 2 shows the results of the calibration process, including selected wavelengths, standard errors of estimation (SEE) and multiple correlation coefficients (R). Then, from the prediction set, which is independent from the calibration set, the performance of the calibration equations is confirmed.

Figure 3 shows the prediction test results for the analysis of moisture by NIR. As for moisture, in the case of the extracted residue and the defatted soybeans, correlation coefficient between the reference method and NIR method (r) and standard error of prediction (SEP) were good, and the regression line was in accord with the 1:1 line. NIR can be used for their analysis for process control. On the other hand, for soybeans, the regression line was skewed. According to the FOSFA Official Method for analyzing moisture in soybeans by NIR (8), the standard error of calibration (SEC) for moisture analysis should not be more than 0.2. Our SEP was not good. However, the oven drying method was not carried out on the ground samples but on the intact whole bean samples. The condition of the samples to be analyzed by the reference method was different from that by NIR. In the process of sample preparation for NIR analysis, there was a possibility of moisture loss during grinding of the samples because moisture and other volatile materials might evaporate. Further, the origins of the samples were diverse because of various cultivating areas and various cultivating seasons. This study was spread over two years and the samples were not analyzed all at once. Further, the data sets were merged for statistical analysis. The performance of the calibration equation depends on the width of the range of contents of the constituents. All these factors made the situation bad, but the inclination was caught by NIR. The methods of grinding the samples should be established for use in process control. On the other hand, the other two materials are easier to grind than whole soybeans. They were averaged in the plant process, and the results were improved.

Figure 4 shows the prediction test results for the analysis of oil by NIR. For soybeans, the SEP was 0.235. Hilliard and Daynard (9) and Rinne *et al.* (10) obtained residual standard deviations of 0.54 and 0.65, respectively.

TABLE 1

Range of Constituents and Quality Index[a]

	Moisture (%)	Oil (%)	Total N (%)	NSI (%)	Digest (%)	AV (mg-KOH/g)	Germ (%)
Soybeans	9.84–12.16	17.98–20.86	5.53–6.03	64.5–89.3	53.00–84.77	0.71–2.55	0.00–90.00
	(10.60–12.05)	(19.03–20.34)	(5.72–6.00)	(77.8–90.0)	(53.27–84.37)	(0.86–2.37)	(0.00–86.00)
Extracted	5.99–11.63	—	7.56–8.22	76.2–97.1	—	—	—
Residue	(6.86–11.58)	—	(7.67–8.15)	(80.0–92.2)	—	—	—
Defatted	7.47–11.45	0.37–0.97	7.85–8.32	16.8–36.9	76.26–93.88	—	—
Soybeans	(8.59–10.69)	(0.27–1.98)	(7.90–8.25)	(16.3–31.4)	(77.13–92.28)	—	—

[a]The upper figures in each column are for the calibration set, and the lower figures in parentheses are for the prediction set. AV = acid value; Digest = digestibility; Germ = germination percentage; NSI = nitrogen solubility index; Total N = total nitrogen.

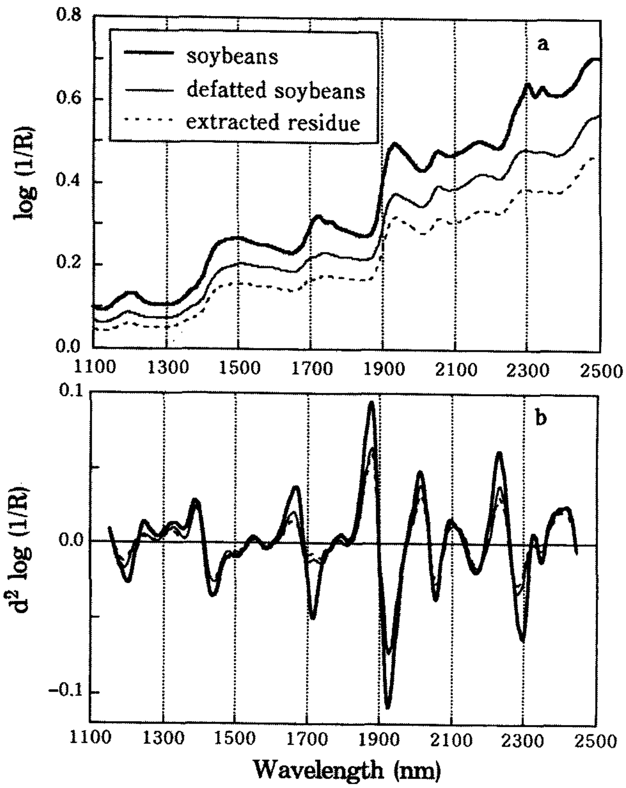


FIG. 2. Raw (a) and second-derivative (b) near-infrared spectra of whole soybeans, extracted residue and defatted soybean. Samples were ground.

According to the FOSFA Official Method (8), the SEC should not be more than 0.3. Compared with those values, our results indicate that NIR was satisfactory for use in oil analysis. For defatted soybeans, the SEP was satisfactory for use in process control. Further, if the outlier was removed, the SEP was improved from 0.135 to 0.101, and the regression line also became closer to the 1:1 line. By the way, we also analyzed the oil content of the extracted residue by NIR, and almost the same level of SEP was obtained as for the defatted soybeans.

Figure 5 shows the prediction test results for the analysis of total nitrogen by NIR. Good results were obtained. In all cases, the ranges of the contents were narrow. However, SEP was good, especially for the defatted soybeans; the regression line was in accord with the 1:1 line. Hilliard and Daynard (11) or Rinne *et al.* (12) obtained residual standard deviations of protein nitrogen of 0.83 and 0.84, respectively. According to the FOSFA Official Method (8), the SEC should not be more than 0.4. Compared with those values, our result was sufficient for use in protein analysis if a conversion coefficient of 6.25 was used for calculating protein contents from total nitrogen contents. The SEP was sufficient for NIR to be used for process control of protein.

The wavelengths chosen in the calibration equations (Table 2) were assigned to the molecular structure of each component (1), i.e., 1978, 1936 or 1960 nm to water; 1712, 1744, 1718 or 1738 nm to triglycerides; 2190, 2180 or 2202 nm to peptide linkage. As for the major constituents, it was confirmed that the NIR method has the capability for measuring these constituents for process control in the plant.

Deterioration indices or quality criteria. Figure 6 shows the prediction test results for NSI by the NIR method. For extracted residue and defatted soybeans, SEP obtained was not so good, and the regression lines were skewed. However, the inclination in the changes of the contents could be caught by NIR. On the other hand, for whole soybeans, the regression line almost agreed with the 1:1 line. Selected wavelengths included in the calibration equations (Table 2) were near the protein absorption bands, where the denaturation of protein might be affected because NSI seems to be related to protein quality or enzyme activity.

TABLE 2

Results of Calibration Process by Multiple Linear Regression Analysis[a]

	Wavelengths selected	SEE	R
Soybeans			
Moisture^2	1158 1602 1978 2142 2330 2342	0.379	0.749
Oil^2	1712 1744 1884	0.323	0.768
Total N^2	1710 1890 2190 2266	0.070	0.600
NSI^2	1606 2010 2066 2094 2434	2.833	0.799
Digest^2	2318 2358	5.508	0.659
AV^2	1506 1606 2070 2250	0.303	0.734
Germ^0	2356 2364	18.497	0.588
Extracted residue			
Moisture^0	1936 2244	0.514	0.945
Total N^0	1892 2048 2088 2180 2212	0.077	0.818
NSI^1	1179 2099 2487	2.947	0.706
Defatted soybeans			
Moisture^2	1152 1684 1900 1960	0.376	0.946
Oil^2	1718 1738 2326	0.084	0.788
Total N^2	1282 1426 1990 2042 2202	0.048	0.908
NSI^2	1162 2138 2366	3.458	0.529
Digest^0	1192 1200 1252	2.497	0.745

[a]Superscript 0 = analysis for raw spectra, superscript 1 = analysis for first-derivative, superscript 2 = analysis for second-derivative spectra. SEE, standard error of estimation, R, multiple correlation coefficient. See Table 1 for other abbreviations.

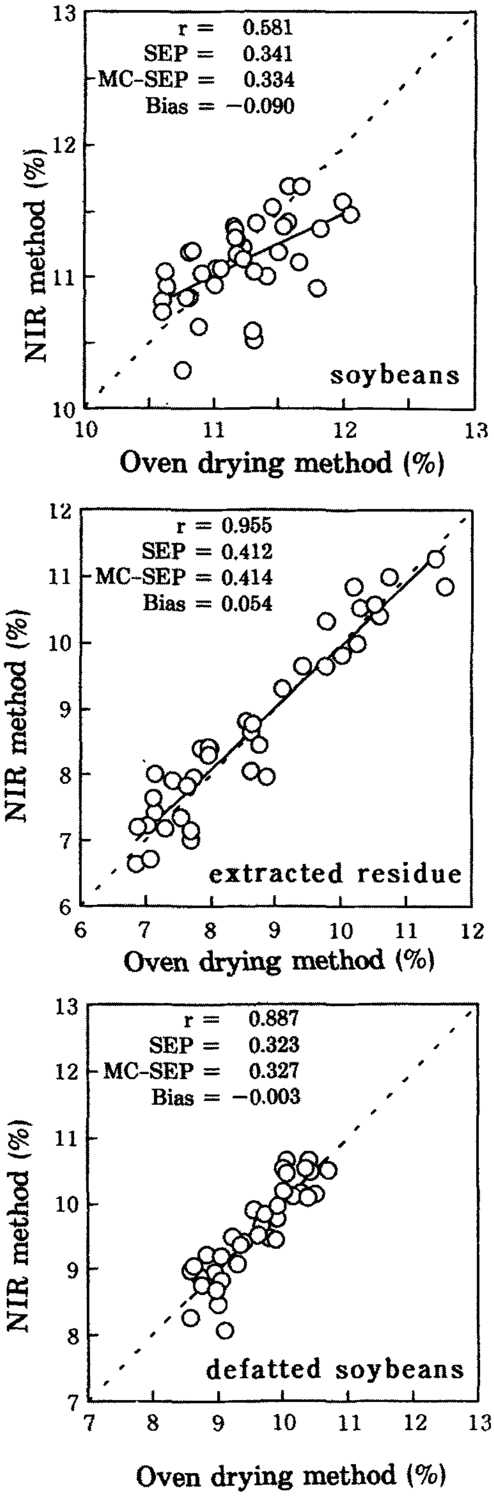


FIG. 3. Results of prediction test for moisture. X-axis of abscissa represents values obtained by the reference method, and Y-axis of ordinate represents values obtained by near-infrared spectroscopy (NIR). Dotted line is a 1:1 line and solid line is a regression line, r: correlation coefficient between the reference method and NIR method, SEP: standard error of prediction, MC-SEP: mean-centered SEP.

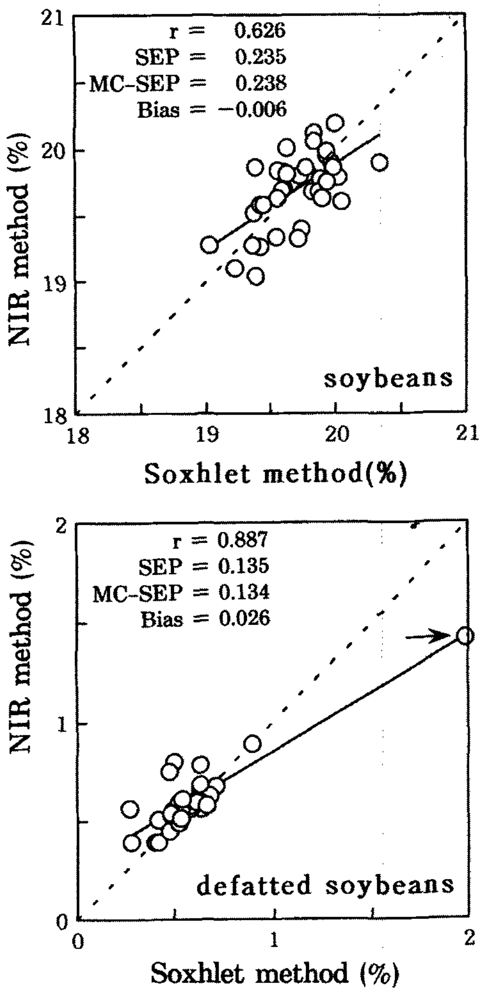


FIG. 4. Results of prediction test for oil. The arrow indicates an outlier. See Figure 3 for abbreviations and details.

Figure 7 shows the prediction test results for digestibility. In both cases, NIR seemed to catch the inclination in the changes of digestibility. Further, for defatted soybeans, if the outlier was removed, SEP was drastically improved from 2.124 to 1.737, and the regression line agreed with the 1:1 line.

Figure 8 shows the prediction test results for AV. The AV range was narrow, but NIR seemed to catch the inclination in the changes. It is useful that NIR has the feasibility to evaluate AV in the raw material stage, and SEP was sufficiently low for NIR to be used for the purpose of process control.

Figure 9 shows the prediction test results for germination percentage. NIR seemed to catch the inclination in the changes of this variable. The germination percentage was also analyzed by DA. First, from the second-derivative full spectral data, PCA was carried out to compress the data. Then, from the eigenvectors obtained, the PCA scores were calculated. DA was carried out on these new variables (from the first to the seventh PCA scores). Table 3 shows the results. More than 80% of the samples were classified successfully in the prediction test. This result shows the possibility of using PCA and DA in NIR analysis instead of MLRA.

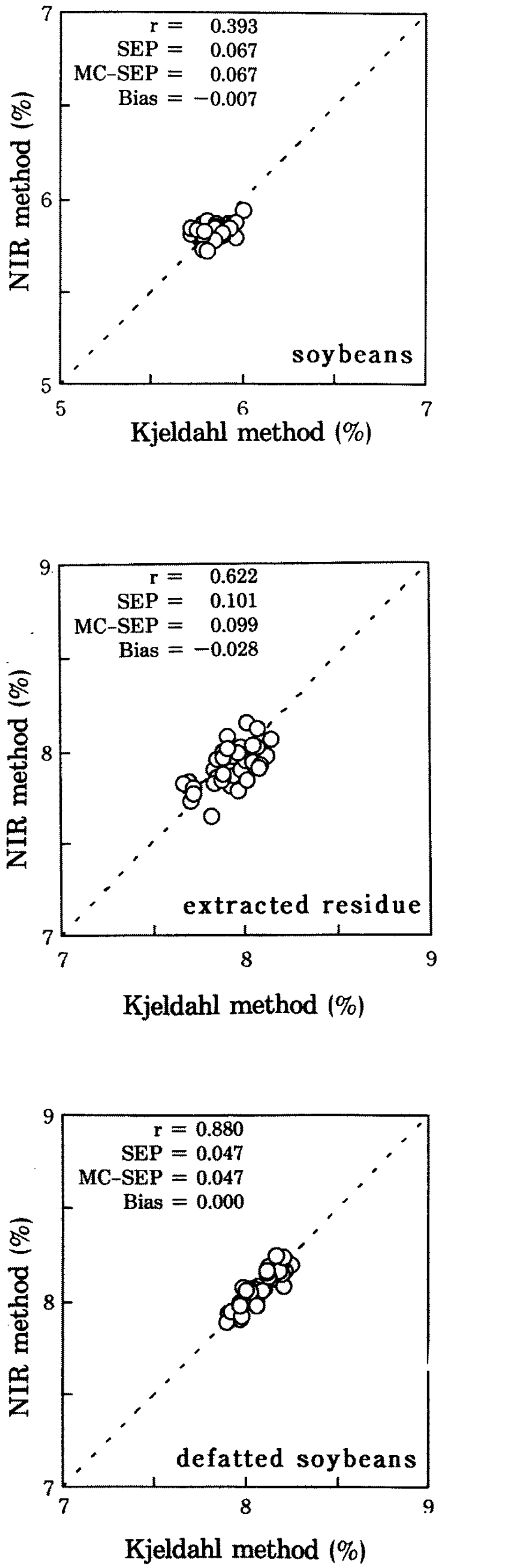


FIG. 5. Results of prediction test for total nitrogen. See Figure 3 for abbreviations and details.

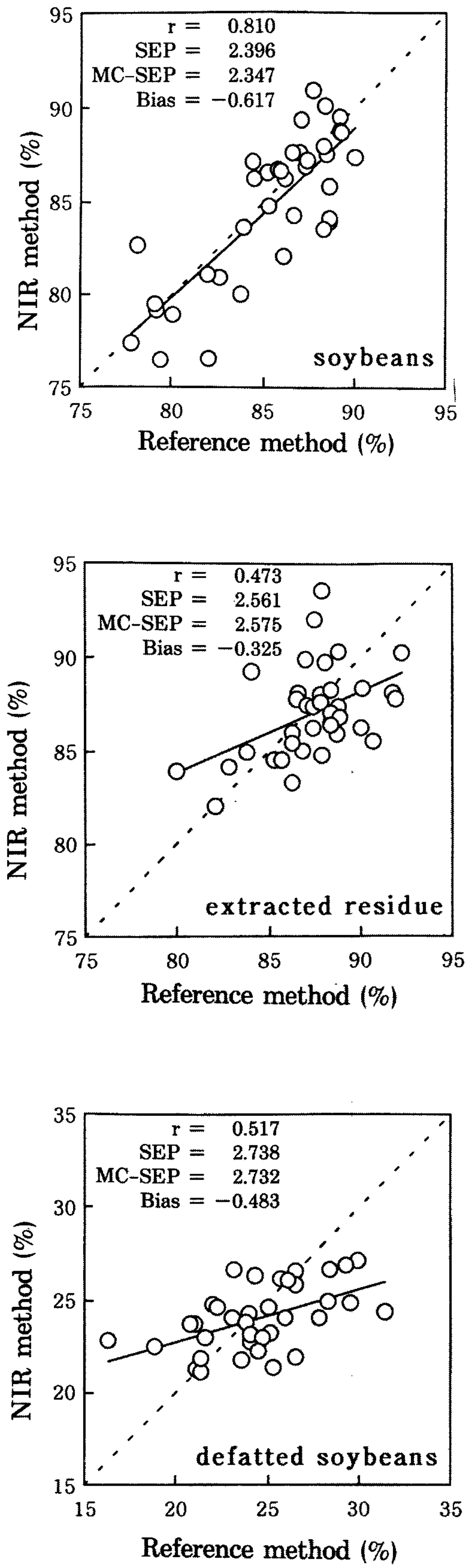
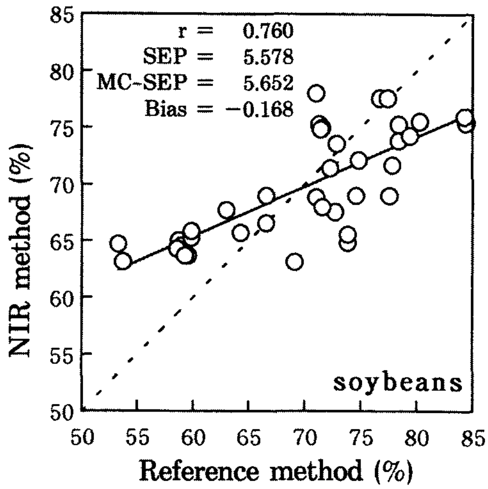


FIG. 6. Results of prediction test for nitrogen solubility index. See Figure 3 for abbreviations and details.



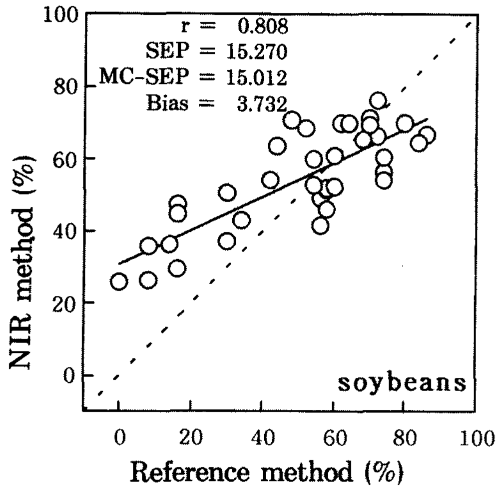


FIG. 9. Results of prediction test for germination percentage. See Figure 3 for abbreviations and details.

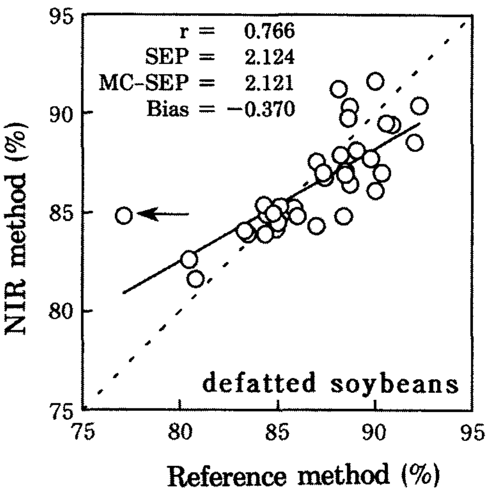


FIG. 7. Results of prediction test for digestibility. The arrow indicates an outlier. See Figure 3 for abbreviations and details.

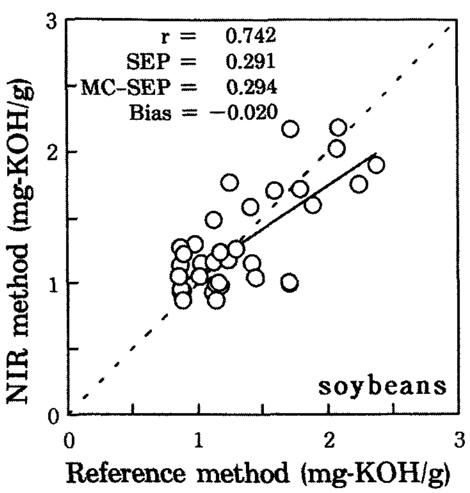


FIG. 8. Results of prediction test for acid value. See Figure 3 for abbreviations and details.

TABLE 3

Results of Discriminant Analysis for Germination Percentage

Group		Total count	Number of cases classified G1[a]	Number of cases classified G2	Percent correct
Calibration	G1	18	12	6	66.67
	G2	38	5	33	86.84
Prediction	G1	13	11	2	84.62
	G2	24	2	22	91.67

[a]G1 means less than 50%, and G2 means more than 50% germination percentage.

The feasibility of the NIR method for process control in the oil milling plant was examined. The feasibility of NIR in the analysis of the major constituents was already widely recognized and has been adopted. On the other hand, for the deterioration indices, although it is still necessary to improve accuracy, we concluded that the NIR method has the capability to measure quality criteria for the purpose of process control in place of time-consuming chemical analyses that are conventionally used. For example, it takes several hours to obtain most measurements by the reference methods. For germination percentage, a few days are needed, and in the case of digestibility, two weeks.

In the oil milling plant, various materials need to be analyzed rapidly and easily. Further, rapid analysis of quality of not only the raw materials but also of the intermediate or final products is needed. The NIR method has the ability to analyze various types of samples. Sometimes, a less-precise rough index is sufficient, and rapidity is more important for process control in the plant. Use of the NIR method makes it possible to adjust the conditions of the processing in time, maintain constant quality of the products and to reduce cost.

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