

Mean particle size determination of ground sugar using near infrared diffuse reflectance spectroscopy

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Abstract

Near infrared (NIR) diffuse reflectance spectroscopy is used for the measurement of size of sugar granules. Commercially available sugar samples were procured from the market and were ground using a home grinder to yield samples with varying particle size. The lot was subjected to differential sieving to create a set of hundred and ten samples. The mean particle size values of all the samples were determined using laser particle size analyzer and were used as reference values for calibration. NIR spectra of all the samples were recorded in diffuse reflectance mode. Partial least squares (PLS) chemometric method was applied for calibration. A separate set of twelve samples was created in a similar manner for prediction. Mean particle size values of all the samples in prediction set was also determined using laser technique and their near Infrared spectra were recorded. The mean particle size values of these samples were predicted using the derived calibration curve and were compared with laser reference values. A good correlation was obtained between NIR predicted values and laser reference values. The present work demonstrates that the near infrared diffuse reflectance spectroscopic technique can be successfully applied for determination of particle size of sugar.

Determinación del tamaño promedio de las partículas de azúcar molido utilizando espectroscopia del infrarrojo cercano con reflectancia difusa

La espectroscopia del infrarrojo cercano (NIR) con reflectancia difusa es utilizada para la medición del tamaño de gránulos de azúcar. Se obtuvieron muestras de azúcar comercial y se molieron usando un molinillo casero para producir muestras que contenían partículas de tamaños variados. Todas ellas fueron tamizadas diferencialmente y de esta manera se creó un grupo de 110 muestras. Se determinaron los valores del tamaño promedio de las partículas en todas las muestras utilizando un analizador láser de tamaño de partículas. Estos valores fueron usados luego como referencia para la calibración. Se registró el espectro del infrarrojo cercano (NIR) para todas las muestras en la modalidad de reflectancia difusa. Para la calibración se aplicó el método quimiométrico de cuadrados mínimos parcial (PLS). Se creó de manera similar, un grupo separado de 12 muestras, para predicción. Los valores del tamaño promedio de las partículas en todas las muestras del grupo de predicción, también fueron calculados usando el método láser y el espectro del infrarrojo cercano fue registrado. Se predijo el valor promedio del tamaño de las partículas de dichas muestras usando la curva de derivación y fueron comparadas con valores de referencia láser. Se obtuvo una buena correlación con los valores NIR pronosticados y los valores de referencia láser. El presente trabajo demuestra que la técnica espectroscópica del infrarrojo cercano con reflectancia difusa, puede ser aplicada con éxito para la determinación del tamaño de partícula del azúcar.

Bestimmung der mittleren Partikelgröße gemahlener Zuckers unter Verwendung von Nahinfrarot-Spektroskopie

Die diffuse Reflexionsspektroskopie im Nahinfrarot (NIR) Bereich wird zur Messung der Zuckerkorngröße verwendet. Handelsübliche Zuckerproben wurden auf dem Markt gekauft und mit einer Haushaltsmühle gemahlen, so dass Proben unterschiedlicher Partikelgröße entstanden. Diese wurden verschiedenen Siebverfahren unterzogen, so dass ein Satz von 110 Proben entstand. Die mittleren Größenwerte aller Proben wurden mittels eines Laser-Teilchengrößenanalysators bestimmt und als Referenzwerte für die Kalibrierung genommen. Die NIR-Spektren aller Proben wurden im diffusen Reflexionsmodus vermerkt. Für die Kalibrierung wurde die chemometrische Methode der partiellen kleinsten Quadrate (PLS) gewählt. Zu Prognosezwecken wurde auf ähnliche Weise ein separater Satz von zwölf Proben erstellt. Die mittleren Partikelgrößenwerte aller Proben im Prognosesatz wurden ebenfalls mittels Lasertechnologie ermittelt und es wurden ihre Nahinfrarotspektren vermerkt. Die mittleren Partikelgrößenwerte dieser Proben wurden mithilfe der abgeleiteten Kalibrationskurve prognostiziert und mit den Laser-Referenzwerten verglichen. Es wurde eine gute Korrelation zwischen den NIR-Prognosewerten und den Laser-Referenzwerten erreicht. Die vorliegende Arbeit demonstriert, dass sich die diffuse Reflexionsspektroskopie im Nahinfrarot (NIR) Bereich erfolgreich zur Bestimmung der Partikelgröße von Zucker einsetzen lässt.

Introduction

The particle size of sugar is an important factor affecting the powdered sugar functionality in various sugar-based industries. It is important to know the particle size of powdered sugar to optimize different processing operations in these industries. Baking is one of

the examples where particle size of raw materials has a direct impact on the quality of products. The grittiness of chocolate is also affected by the size of sugar crystals to a great extent. Optimum size sugar particles have to be used for proper dissolution in beverages and ice-creams¹. In most of the pharmaceutical industries particle size determination of sugar sample is needed for its judicious selection since it

affects the processes of tablet coating and also making of oral suspensions²⁻⁴. Since quality control of its products is of paramount interest to the industry, particle size determination of sugar to be used is highly crucial and it is convenient to monitor the size before combining with other ingredients. The grading of sugar in sugar refineries, which is needed for fixing the price is also done on the basis of its crystal size. In a previous report, Mohamed *et al.*⁵ have studied size distribution of sugar as a measure of its quality.

Size analysis of powdered samples is conventionally done using microscopy⁶, sieving⁶, variable angle light scattering^{7,8} (mainly forward angle laser light scattering or FALLS) techniques. In the case of sugar crystals particle size is usually measured by sieve analysis. Although the method of sieving is universally recognized, the main drawbacks are that it is time consuming and imparts only the two dimensional information about the particle size⁹. Finer particles remain adhered to the sieve mesh leading to imprecision in measurement¹⁰. The added disadvantage with powdered sugar samples is formation of aggregates due to moisture in air. The technique is, therefore, subjective and prone to errors. Elsewhere the sugar particles have been sized using variable angle light scattering techniques, primarily FALLS^{8,11}. The main problem with light scattering techniques has been that they are based on volume distribution and so only take into account the larger particles in the sample. These methods are sample destructive and become ineffective where large bulks of samples have to be analyzed.

The landmark papers of Norris and Williams had reported that NIR spectra primarily the log 1/R values are greatly affected by the particle size of the sample¹²⁻¹⁴. Since then, the sensitivity of NIR reflectance has been frequently exploited for particle size determination by various researchers^{8,15-17}. Franke *et al.* determined particle size of lactose using chemometric methods based on NIR spectra¹⁸. Potential of near infrared reflectance spectroscopy for online particle size analysis of powders and ground materials have been recently reviewed by Pasikatan and coworkers¹⁹. Due to speed, simplicity, accuracy and low operating costs of the NIR technique it has now been adopted as a viable alternative for particle size determination to the traditional methods like sieving, light scattering by suspensions, microscopic analysis or gas adsorption on solid surfaces.

This paper demonstrates the use of near infrared spectroscopy in diffuse reflectance mode for the measurement of crystal size of sugar. The calibration has been performed using partial least squares multivariate regression method on a set of hundred and ten samples whose reference values have been measured by laser particle size analysis. Laser method was chosen for obtaining the reference values since it has better precision than sieve analysis. The main objective was to develop a rapid and accurate technique for determination of particle size of sugar that can be further developed into an online technique.

Experimental

Samples preparation

Sugar samples were procured from different sources in the market. All the samples were mixed and the bulk sample was ground in a domestic grinder for varying intervals of time to obtain different sample lots. All crushed sample lots thus obtained were combined and subjected to differential sieving with sieves of mesh sizes in the range 28 µm to 78 µm.

Laser particle size analysis

For obtaining the reference values mean particle size of all the samples was determined using GALAI CIS -1 laser particle size analyzer. The instrument is based on the principle of time of transition. The laser beam scans the particles at a constant speed and a photocell records time during which the beam is obstructed by the particles. The speed of beam and time of transition are used to calculate the size of particles. Each sample (~ 1 mg) was suspended in a practically insoluble and transparent dispersing medium (absolute alcohol 99.9%) in a quartz cuvette, capacity ~ 3ml, equipped with a magnetic stirrer situated at the bottom of the cuvette. The particle size was recorded as volume moment mean diameter expressed as volume means diameter

$$D = \frac{\sum D^4 N(D)}{\sum D^3 N(D)} \quad (1)$$

where N(D) is the number of particles with diameter D.

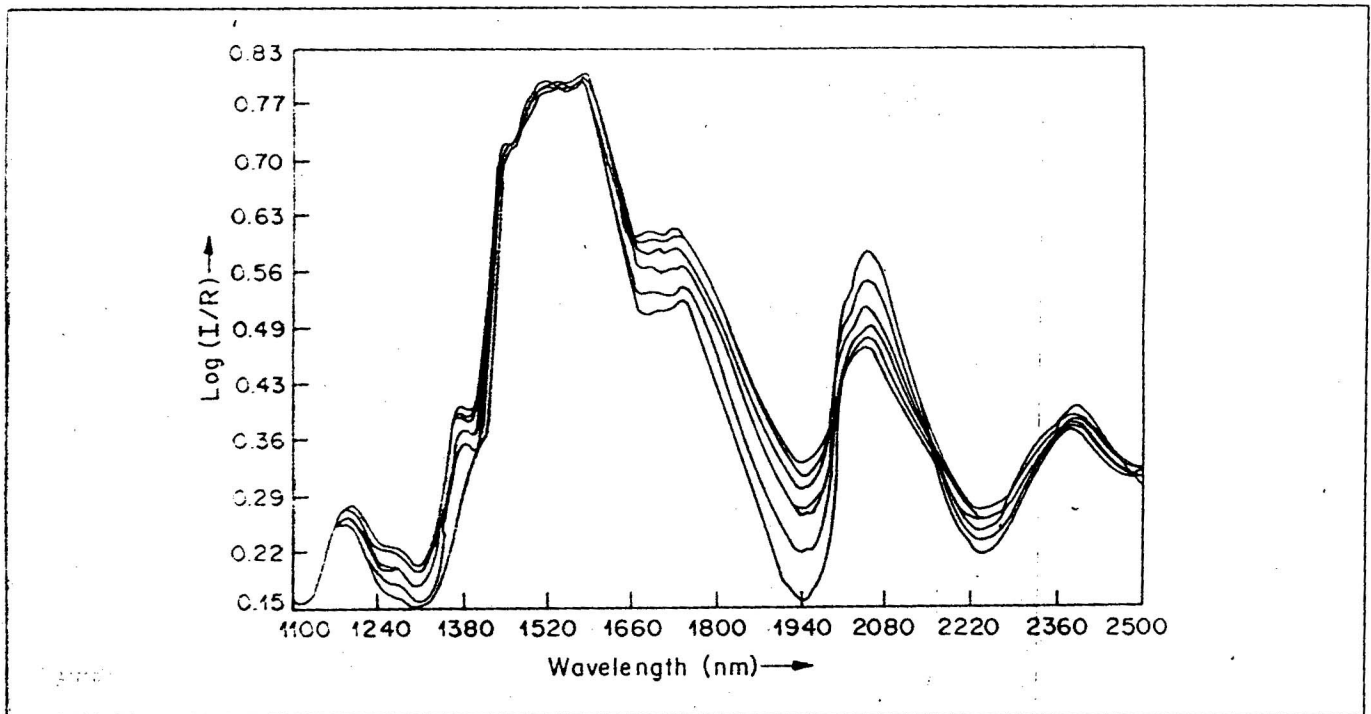
Spectroscopy

Spectra of all the samples were collected in NIR region, 1100 nm to 2500nm on ELICO SL 153 spectrophotometer in diffuse reflectance mode. Prior to being scanned all the samples were dried for ~ 3 hours in an oven at ~ 70°C. The spectra were recorded with a bandwidth of 20 nm. The absorption values were measured as log 1/R where R is the relative intensity of light reflected from the sample compared with light reflected from reference standard (ceramic block).

Results and discussion

The sugar particles being evaluated in this study range from 28 µm to 78 µm. Figure 1 shows the overlaid NIR spectra in the range 1100 – 2500 nm, for few sugar samples under study differing in their particle size distributions. The spectral characteristic of the radiation does not change on scattering as the scattered radiation is incoherent. Since no spectral shift takes place due to scattering there is no modification of the spectra. All the spectra exhibited non-uniform baselines. This has often been attributed to non-homogeneity of the samples which leads to multiple scattering according to previous observations^{20,21}. Otsuka¹⁷ has recently highlighted the effect of particle size on diffuse reflectance spectra and attributed it to variation in pathlength and sample porosity depending on particle size of the sample. In present case, although the response to varying particle size of sugar samples is visible at two wavelength regions near 1680 nm and near 2070 nm but it is not possible to correlate any band shift or change in intensity to increasing or decreasing particle size (figure 1). The change in the backscattered intensity of the spectra is because of the difference in particle size of the samples. The observation is in agreement with earlier reported responses of change in particle size on reflectance spectra, which have been observed to be multiplicative in nature^{8,19}. The spectra contain broad bands and shoulders, which are composites of numerous individual bands that cannot be visibly resolved. The spectra are dominated by absorption band centered at ~1520 nm which has a shoulder at ~ 1670 nm. This broad envelop starting from 1250 nm and extending upto 1940 nm mainly contains contributions from first overtone bands of O-H in crystalline sucrose (~1440 nm), and C-H stretch first overtones (1690 – 1755 nm)

Figure 1. NIR reflectance spectra for few sugar samples with different mean particle sizes in the region (1100nm – 2500 nm)



although O-H 1st overtone peaks (1460 – 1600 nm) appear to predominate. O-H stretch 1st overtone peaks are known to appear as series of peaks between 1460 and 1600 nm. Two other bands in the spectra at ~ 2080 nm and 2360 nm may be attributed to combinations of O-H stretch with C-H bending vibrations and C-H stretch with C-H bending vibrations respectively²².

GRAMS 32 software was used for data processing and developing calibration model using partial least squares method. All spectra were mean-centered before analysis. Necessary smoothing was done by box-car smoothing method. Calibration was performed using the complete wavelength range, 1100 nm to 2500 nm. This seemed appropriate since according to earlier reports particle size is an integral part of NIR absorbance at all wavelengths¹⁴. A multivariate calibration method was selected due to the offered advantage of possibly including multiple spectral intensities simultaneously.

The calibration model was initially developed using the laser value from all the one hundred and ten samples. The samples used for calibration were also used as test sample to assess the validity of the technique by the cross-validation method, which is done by leaving out one sample at a time. The optimum numbers of PLS factors used in the model was five. In order to improve the precision accuracy of calibration model, five outliers were found and discarded and final calibration was obtained on 105 samples. The outliers may be attributed to error in the reference or spectral analysis or due to sample contamination. The values of the root mean square difference

(RMSD), which is an indication of the average error in the analysis, for each component, was calculated as

$$RMSD = \left[\frac{1}{N} \sum_{i=1}^N (A_i - B_i)^2 \right]^{0.5} \quad (2)$$

The square of the correlation coefficient (R_2), which is an indication of the quality of fit, was determined as

$$R^2 = \frac{\sum_{i=1}^N (A_i - C)^2}{\sum_{i=1}^N (B_i - C)^2} \quad (3)$$

Where A_i is the actual concentration of the analyte in the sample i , B_i represents the estimated concentration of the analyte in the sample i , C is the mean of the actual concentrations in the prediction set and N is the total number of the samples used in the prediction set. Table 1 gives the statistics of the developed calibration model. A good correlation was obtained as indicated by R_2 and RMSD values in calibration set. The actual vs predicted values of particle size is shown in Figure 2. It may be noticed in Figure 2 that all the data points lie close to the fit, shows the effectiveness of calibration.

A separate set of twelve samples was created in a similar manner as the calibration set for prediction. NIR spectra of these samples were recorded in diffuse reflectance mode. Same set of twelve samples was used for laser technique, in order to compare the results and

Table 1. NIR calibration statistics

	Range	No. of Samples	Factors	R^2	RMSD	No. of Outliers
Calibration set	1100-2500 nm	110	5	0.8812	2.156	5
		105	5	0.9961	1.454	-
Prediction set	1100-2500 nm	12		0.9935	1.835	-

Figure 2. Results of PLS calibration using sieve values. NIR predicted particle size values versus laser values in micron for sugar samples

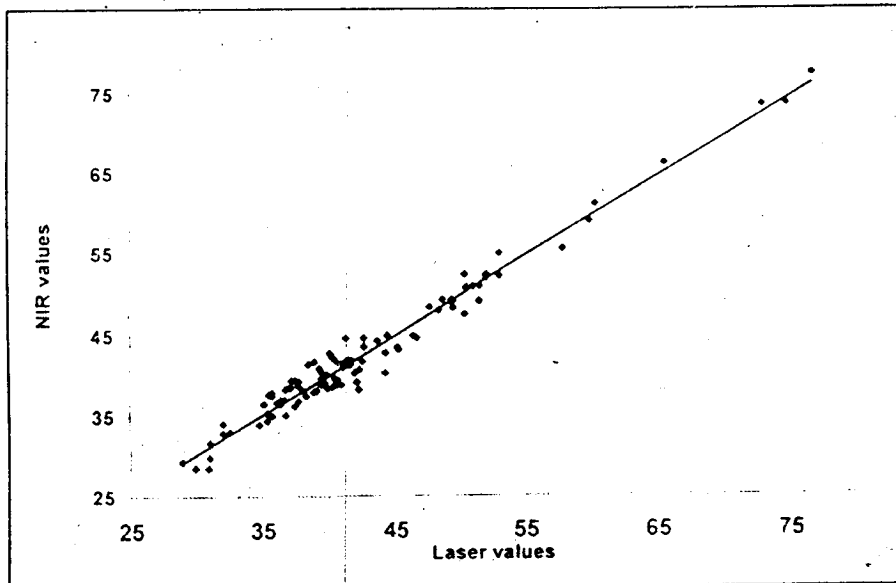


Table 2. Laser Vs NIR values of mean particle size of powdered and sieved sugar samples in prediction set

Laser values (mm)	NIR values (mm)	Bias
38.46	41.38	-2.92
31.03	29.84	1.19
29.93	28.56	1.37
35.38	34.34	1.04
76.75	77.15	-0.40
36.78	35.05	1.73
57.77	55.36	2.41
30.93	28.53	2.40
50.34	52.25	-1.91
74.75	73.30	1.45
37.46	39.44	-1.98
35.74	37.51	-1.77
R2 = 0.9935		
RMSD = 1.835		

to find out the reliability of NIR spectroscopic method. The comparison of NIR predicted values with laser values for mean particle size is given in Table 2. It may be observed from the table that agreement between laser technique and NIR spectroscopic method is quite good, which is evident from R_2 and RMSD values. Even though the maximum deviation of 7 % between the actual laser values and NIR values is observed the correlation coefficient is much high. It is because the fact that the actual laser values and predicted NIR values are random and for calculating the correlation coefficient the actual and predicted values are deviated from the mean of the laser values (equation 3). Hence it is clear from data presented above that NIR method on sieved samples is robust and has provided good results.

Conclusion

NIR spectroscopy is a suitable technique for determination of particle size of sugar. The technique is highly advantageous over the con-

ventional technique of sieving which is usually adopted by the sugar industries for process control. Comparison between laser particle size analysis and NIR technique for sugar samples has shown good agreement in particle size range, 28 μm to 78 μm . Good correlation between the reference, laser values and predicted NIR values is obtained using partial least Squares algorithm. Although derivation of calibration equation is a tedious procedure but once a calibration equation is generated rapid determination of particle size of unknown samples is possible.

NIR technique also offers definite advantages over laser technique, which focuses only on determination of median or mean particle size. In addition the laser technique is sensitive to aggregation and therefore it is important to assure that all the particles are well dispersed in the medium. However the present NIR diffuse reflectance spectroscopic method is accurate and analysis is possible on solid

samples. The technique has the ability to provide direct measurement of particle size of solid sugar samples.

References

- 1.M. Robins (2000). Particle Size Analysis in Food. *Encyclopedia of Analytical Chemistry*, Vol 5, Ed. by R. A. Meyers, John Wiley & Sons, Ltd., C.A. USA.
2. A. J. O'Neil, R. D. Jee and A. C. Moffat (1999). Measurement of the cumulative particle size distribution of microcrystalline cellulose using near infrared spectroscopy. *The Analyst*, 124: 33-36.
- 3.C. Washington (1992). *Particle size Analysis in Pharmaceuticals and Other Industries*, Ellis Horwood, New York.
4. M. Blanco, J. Coello, H. Iturriza, S. Maspocho and C. De la Pezuela (1998). Near- infrared spectroscopy in the pharmaceutical industry : a critical review. *The Analyst*, 123: 135R-150R.
5. M. A. Mohamed, K.A. Hammady and S.H. Abou-el-hawa, (1976). *International Sugar Journal*, 78, 355.
6. T. Allen (1997). *Particle Size Measurement*, Chapman & Hall, London.
7. M. Kerker (1969). *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, London.
8. A.J. O'Neil, R.D. Jee and A.C. Moffat (1998). The application of multiple linear regression to the measurement of median particle size of drugs and pharmaceutical excipients by near-infrared spectroscopy. *The Analyst*, 123: 2297-2302.
9. M. Otsuka and Y. Matsuda (1996). Comparative evaluation of mean particle size of bulk drug powder in pharmaceutical preparation by fourier transformed powder diffuse reflectance infrared spectroscopy and dissolution kinetics. *Journal of Pharm. Sci.*, 85: 112-116.
10. A.G. Hareland (1994). Evaluation of flour particle size distribution by laser diffraction, sieve analysis and near-infrared reflectance spectroscopy. *J Cereal Sci.*, 21: 183-190.
11. L. S. Aucott, P. H. Garthwaite and S. T. Buckland (1968). Transformations to reduce the effect of particle size in near-infrared spectra. *The Analyst*, 113: 1849-1854.
12. K.H. Norris (1978). *Proceedings of 6th International Cereal and Bread*

Congress, 245.

13. P.C. Williams (1975). Application of near-infrared reflectance spectroscopy to analysis of cereal grains and oilseeds. *Cereal Chem.*, 52: 561-576.

14. K.H. Norris and P.C. Williams (1984). Optimization of mathematical treatment of raw near-infrared signal in the measurement of protein in hard red spring wheat. I. Influence of particle size. *Cereal Chem.*, 61: 158-165.

15. J.L. Ilari, H. Martens, and T. Isaksson (1988). Determination of Particle Size in Powders by Scatter Correction in Diffuse Near Infrared Reflectance. *Appl. Spectrosc.*, 42(5): 722-728.

16. J. Rantanen, J. Yliruusi (1998). Determination of particle size in fluidized bed granulator with a near infrared set. *Pharm. Pharmacol. Commn.*, 4: 73-75.

17. M. Otsuka (2004). Comparative particle size determination of phenacetin bulk powder by using Kubelka-Munk theory and principle component regression analysis based on near-infrared spectroscopy. *Powder Technology*, 141: 244-250.

18. P. Frake, C.N. Luscombe, D.R. Rudd, I. Gill and J. Waterhouse, A. Jayasooria (1998). Near-infrared mass median particle size determination of lactose monohydrate, evaluating several chemometric approaches. *The Analyst*, 123: 2043-2046.

19. M.C. Pasakiatan, J.L. Steele, C.K. Spillman, and E. Haque (2001). Near infrared reflectance spectroscopy for online particle size analysis of powders and ground materials. *Journal of Near Infrared Spectroscopy*, 9: 153-164.

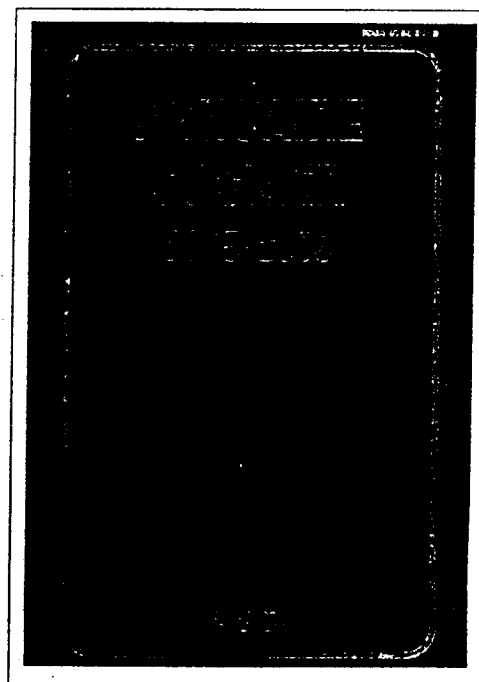
20. P. A. Hailey, P. Doherty, P. Tapsell, T. Oliver and P.K. Aldridge (1996). Automated system for the online monitoring of powder blending processing using near-infrared spectroscopy part I. System development and control. *J. Pharma Biomed. Anal.*, 14: 551-559.

21. C.R. Bull (1991). Compensation for particle size effects in near-infrared reflectance. *The Analyst*, 116: 781-786.

22. L.G. Weyer and S.C. Lo. Spectra-structure correlation in the near infrared. *Handbook of Vibrational Spectroscopy*, Eds. J.M. Chalmers and B.R. Griffiths. John Wiley & Sons, New York.

Book review

Annuaire Sucrier 2005-2006 (Paris, France: Antenne Générale de Publication, 290 pp, hardback. Euros 100)



This finely produced directory provides a:

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