

Determination of cocoa purine content by near infrared spectroscopy



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Caffeine and theobromine are involved in cocoa flavour development. Measurement of their contents is still used to determine the cocoa content of chocolate. It also seems to be accepted that the contents of these two compounds are linked to genetic and geographical origin.

This study, which was conducted on cocoa varieties of different geographical origins, showed that near infrared spectroscopy can be a rapid and non-destructive alternative for determining these compounds.

Experimental procedure

The study was carried out on 189 cocoa samples over 3 production years (1999 to 2002). The cocoas came from Ivory Coast, Venezuela and Trinidad, and were varieties of the Forastero, Criollo and Trinitario types. Sampling in this way ensured good representativeness of the spectral and chemical variability of fermented dried cocoas.

Methode

✓ Wet chemical methods

After reflux extraction in water, caffeine and theobromine contents were determined by HPLC (detection: 280 nm).

✓ Near infrared spectroscopy

NIRS acquisitions were obtained on a Foss-Perstorp 6500 analyser using a spin cell. Spectral data were collected and processed with NIRS 2 version 4.11 software (InfraSoft International). 3 g of cocoa taken from 100 g of shelled, ground and sieved beans (0.5 mm) were analysed by diffuse reflection from 400 nm to 2,500 nm in 2 nm steps.

Results

✓ Reference analyses

Caffeine contents were between 0.08% and 0.74%, with an average content of 0.28%. The standard deviation for caffeine contents was 0.16. Theobromine contents were between 0.58% and 1.48%, with an average content of 0.94%. The standard deviation was 0.20.

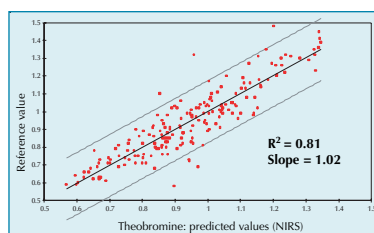
✓ Calibration

Partial Least Square models (PLS) were used to establish quantitative relations between NIR spectral bands and caffeine and theobromine content. The models developed (table1) fitted the data well, with coefficients of determination of 0.96 for caffeine contents and 0.86 for theobromine contents. The coefficients of determination for regressions (figures 1 and 2) between the reference values and the predicted values were 0.93 for caffeine and 0.81 for theobromine. The standard errors of prediction (SEP) were 0.04 for caffeine and 0.09 for theobromine.

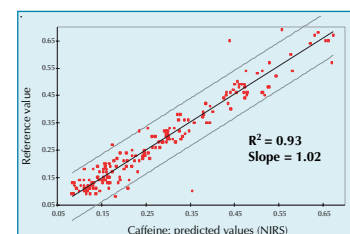
Table 1. Calibration statistics for caffeine and theobromine.

Constituent	N	M	SD	SEC	R ²	SECV	Number of PLS terms
Caffeine	179	0.28	0.15	0.03	0.96	0.04	11
Theobromine	182	0.94	0.19	0.07	0.86	0.08	8

N: number of samples adopted by the model (t test)
 M: mean
 R²: coefficient of determination
 SD: standard deviation of the calibration population
 SEC: standard error of calibration
 SECV: standard error of cross validation



Figures 1 and 2. Correlation between wet chemistry and NIRS predicted values for caffeine and theobromine.



✓ Purine contents and origins

The graph of the ratio of theobromine contents to caffeine contents as a function of caffeine contents (figure 3) made it possible to separate Ivorian Forastero cocoas from the Trinitario cocoas from Trinidad and the Criollo cocoas from Venezuela. The Trinitario cocoas from Venezuela were grouped with the cocoas from Trinidad.

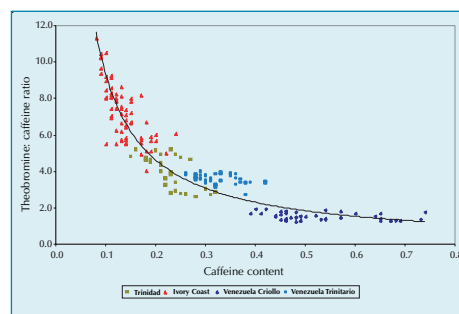


Figure 3. Representation of samples according to their purine content (Theo/Caf = t(Caf)).

The average ratio values were 7.3 for Ivory Coast, 4.0 for Trinidad, and 3.6 and 1.5 respectively for the Trinitario and Criollo cocoas from Venezuela. The average ratio found for the Ivorian cocoas, and more generally for cocoas from West Africa, was over 7 and around 3-4 for the Trinitario type cocoas. The average caffeine contents decreased from the Criollo cocoas (0.5%) to the Forastero cocoas (0.1%); the average content of the Trinitario cocoas was 0.2%. The theobromine contents of the Trinitario cocoas from Venezuela were higher on average (1.2%) than those found for the Trinitario cocoas from Trinidad (0.9%), which explained the difference seen in figure 3 for these two origins.

Conclusion

Given the performance of the equations developed from representative sampling of spectral variability, NIRS can be considered as a routine purine analysis method.

Whilst this study did not lead to any definitive conclusions on discriminating between genotypes according to their purine compositions, it did confirm earlier observations. With a tool enabling rapid determination of purine composition it will be possible to make progress in that field.



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