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Infrared spectroscopy and outer product analysis for quantification of fat, nitrogen, and moisture of cocoa powder

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ABSTRACT

The combination of the near infrared (NIR) and Fourier-transform infrared (FTIR) absorbance spectra (1100–2500 nm and 4000–600 cm^{-1}) of 100 cocoa powder samples was used to build calibration models for the determination of the content of fat, nitrogen, and moisture. The samples that comprised the dataset had an average composition of 13.51% of fat, 3.77% nitrogen, and 3.98% moisture. The fat content ranged from 2.42 to 22.00%, the nitrogen from 0.88 to 4.48%, and moisture from 1.60 to 7.80%. For NIR, the relative root mean square error of cross-validation (RMSECV) was 7.0% ($R^2 = 0.96$) for fat, 1.7% ($R^2 = 0.98$) for nitrogen, and 5.2% ($R^2 = 0.94$) for moisture. For FTIR, the relative RMSECV was 10.4% ($R^2 = 0.94$) for fat and 3.9% ($R^2 = 0.95$) for nitrogen. However, for moisture, it was not possible to build a calibration model with suitable predictability. The combination of the NIR and FTIR domains (data fusion) by outer product analysis PLS1 allowed to predict these parameters and to characterise frequencies in one domain based on the information of the other domain. This work allows to conclude that the second derivative of NIR is the recommended procedure to quantify fat, nitrogen, and moisture content in cocoa powders by infrared spectroscopy.

1. Introduction

Cocoa powder is formed from the cocoa mass where presses are used to remove some of the fat, leaving a solid material called cocoa press cake. These cakes are then crushed to form cocoa powder. The processing can be altered to produce cocoa powders of different composition and with different fat levels. The content of main components in cocoa powder, given by the International Cocoa Organization, is summarized in Table 1 [1,2]. Cocoa bean products such as chocolate tablets, chocolate confectioneries, chocolate cookies, cocoa powder, instant chocolate drinks, etc., are very popular commodities.

Infrared spectroscopy offers a number of important advantages over traditional chemical methods. It is a physical, non-destructive and non-invasive method, requiring minimal or no sample preparation and its precision can be high. It is a

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Table 1 – Main components in cocoa powder [1,2]

Component	Content (%, w/w)
Carbohydrates	41
Cocoa butter	11
Ash	5.5
Total nitrogen	4.3
Moisture	3.0
Theobromine	2.8
Water soluble ash	2.2
Shell (calculated to unalkalised nib)	1.4
Ash insoluble in 1:1 (w/w) HCl	0.08

multi-analytical technique, that is, several determinations can be made simultaneously. The method offers the possibility of measuring physical and chemical properties. Once calibrated, the NIR and mid-infrared (MIR) spectrometers are simple to operate. The main disadvantages are the dependence on time-consuming and laborious calibration procedures and the complexity in the choice of data treatment.

NIR spectroscopy has been shown a rapid non-destructive, non-invasive method for the characterisation of chocolate [3] and cocoa powder [4]. The preliminary studies were performed on the set of 20 samples of cocoa powder with different, predetermined compositional values. Experiments showed satisfactory accuracy for fat, protein, and carbohydrate prediction in cocoa powder [5]. Analysis of powdered cocoa products showed that moisture, fat, and sucrose could be analyzed in such products by NIR spectroscopy because good correlation coefficients and low standard errors of prediction were achieved [6]. Fourier-transform near infrared (FT-NIR) spectroscopy [7] was used to establish calibration models with the aim of determining sucrose, lactose, fat, and moisture in chocolate. The validation results proved that all these parameters, with exception of moisture, can be predicted with sufficient accuracy. NIR spectroscopy technique has also been developed for the prediction of procyanidins in cocoa beans. In addition, very robust calibration models were obtained for the prediction of the total procyanidin oligomers [8].

The MIR spectroscopy has been commonly applied to the structural identification or qualitative determination of the "fingerprint" of organic compounds, as some groups of atoms display characteristic vibrational absorption. Moreover, MIR spectroscopy is amenable for quantitative analysis applications, as the intensities of the bands in the spectrum are proportional to the concentration of their respective functional groups, although the NIR is the preferred method as it is more robust with respect to the MIR/FTIR approaches. Foodstuff is a subject that may strongly profit from FTIR spectroscopic technique because foods have compounds with characteristic absorption bands in this region of the electromagnetic spectrum, namely, lipids, proteins, carbohydrates, and water. FTIR spectroscopy has been proposed for analysis of potential lard adulteration in chocolate and chocolate products [9], as a tool for the rapid detection of other vegetable fats mixed in cocoa butter [10], and for routine analysis of chocolate milk fat, sucrose, lactose, and total solids using an automated heated flow cell [11].

The aim of this work is twofold: (i) to use the reflectance NIR and attenuated single total reflectance FTIR spectroscopy in order to build calibration models for the analysis of fat, nitrogen, and moisture in cocoa powder samples; (ii) to combine both spectroscopic domains, by means of outer product analysis (data fusion), in tandem with partial least squares (PLS1) regression [12–16] for a better characterisation of the samples as a function of the parameters under study. Outer product analysis (OPA) is a method which makes it possible to emphasise co-evolutions of spectral regions in signals acquired in two different domains (heterospectral) or even for the same domain (homospectral) [17–25].

2. Experimental

2.1. Cocoa powder samples

The sample set comprised 100 samples of cocoa powder of different brands obtained mainly in Czech Republic and in different other countries. Samples of cocoa powder and sucrose mixture, cocoa fibre, and cocoa powder containing dried milk and wheat starch were also included.

2.2. Fat determination

A conventional Soxhlet extraction with petroleum ether was used for determination of the fat content [26]. The difference between two parallel determinations was less than 0.20% (w/w).

2.3. Nitrogen determination

Nitrogen content determination according to Kjeldahl was used [27]. The determination was performed on a Kjeltec System (Kjeltec, Sweden). The results were expressed as percentage of nitrogen. The difference between two parallel determinations was less than 0.10% (w/w).

2.4. Moisture determination

Samples were dried to constant weight in platinum dish in an aerated oven at 100 °C. Loss in weight was reported as H_2O [28]. The difference between two parallel determinations was less than 0.20% (w/w).

2.5. NIR spectroscopy

Near infrared spectra were acquired on a NIR Systems 6500 (Perstop Analytical Company, USA) with software NIR3 version 3.10 Infrasoft International (ISI). Wavelengths are specified by grating monochromator with the range of 400–2500 nm. Tungsten filament lamp was used as a source of radiation. Spectra were recorded at the reflectance mode from 1100 to 2500 nm at the resolution of 2 nm. Three replicated spectra (36 co-added scans), in the small ring cup, were collected for every sample. A ceramic standard was used as a photometric standard. The scanning speed to obtain one replicate was 62 s. No spectral changes were detected during the replicate measurements. The background spectrum was obtained by an internal reference.