Abstract

Cocoa is a product of high value, not only because of its sensory characteristics, but also because it has a high content of antioxidants and stimulating alkaloids with health effects. Due to the high demand, the cocoa powder industry has the challenge of ensuring the quality of large volumes of production in a fast and accurate way, avoiding the presence of contaminants or adulterants in the raw material, offering products where the healthy properties are preserved. The near infrared spectroscopy (NIR) is a rapid and non-destructive technology useful in the analysis of food products. The present doctoral thesis focuses on evaluating the potential use of NIR as a quality control tool in order to solve problems that arise in the cocoa industry powdered. The problems to solve include the detection of unwanted materials or adulterants in the cocoa powder, and the rapid and accurate monitorization of the flavanols and methylxanthines content in the cocoa powder during the alkalization process. The first chapter evaluates the viability of the NIR, in combination with chemometric analysis, in the detection of presence of unwanted materials or adulterants such as cocoa shell or carob flour. For this, different samples of natural cocoa powder and with different levels of alkalization (light, medium and strong) were mixed with different proportions of cocoa shell (with natural cocoa) or carob flour (with natural and alkalized cocoa).

The results obtained indicate that the NIR combined with statistical models such as the partial least squares discriminant analysis (PLS-DA) and the partial least squares regression (PLS), is a fast and efficient method to identify qualitative and quantitative unwanted materials or adulterants such as shell and carob in cocoa powder, regardless of the degree of alkalization or level of roasting of carob flour. By PLS-DA analysis, for the study of the adulteration with cocoa shell, 95.2% of the samples were correctly classified into two groups: samples with a shell content of less than 5% (considered the acceptance limit in cocoa powder by the Codex Alimentarius) and shell contents between 5 and 40%. In the study of the adulteration of cocoa powder with carob flour, the 100% of the samples were correctly classified into three groups: cocoa, carob flour and mixtures. In both studies, was possible to calculate the percentage of adulterant and non-wanted material present in the samples by means of the construction of PLS regression models. In relation to cocoa shell, the best PLS prediction model was obtained with 1 LV, with an R^2 of 0.975 and 0.967, respectively, and an average square error of 1.91 and 2.43%, respectively. For the study of adulteration with carob flour, the PLS model was obtained with 1 latent variable (LV), with an R^2 of 0.980 and 0.974, and a root mean square error (RMSE) of 2.9 and 3.2% for the calibration and external validation sets, respectively.

In the second chapter, the compositional analysis of cocoa powder was oriented to the control of the changes produced in the content of flavanols and methylxanthines due to the process of

alkalization to which the cocoa powder is subjected. The content of catechin, epicatechin, caffeine and theobromine were determined by high performance liquid chromatography (HPLC), correlating the contents obtained for each of these compounds with the NIR determinations. Good models were obtained for the prediction of compounds by regression PLS with values above 3 for the ratio of performance to deviation (RDP), which shows that the obtained models can be used for the quick and reliable prediction of flavanol content and methylxanthines in natural cocoas and with different alkalization levels.