

Near-infrared optical spectroscopy of sugar-based mixtures – A snapshot to identify issues of influence

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Abstract Optical spectroscopy is one method used to identify products and ingredients in food industries. This article presents a review of the literature concerning carbohydrates spectra (especially sugar) and compares it to the results that can be obtained with standard hyper spectral imaging (laboratory equipment). The possibility to identify sugar in mixtures is also investigated. The near infrared region is the most accurate to qualitatively detect the presence of sugar. A differentiation between different types of sugar seems not to be possible with the equipment, because of too small differences and the overlap of absorption bands.

1 Introduction

Nowadays the use of spectral signatures is more and more usual in food industries. It is already known how to detect other nutrient families such as proteins [1] or fat [2]. Challenge is the wide application of this technology with a standard measurement equipment. Influences, such as the various reflection of organic products, the needs for a comparable calibration, and the different types of sensors are only some of factors, that need to be taken into account. In the literature, the spectral signatures of products or their ingredients are mostly shown as a function of

their mean and the knowledge about the dispersion of values in measurements becomes more important.

As a snapshot, we did within the laboratory of Fraunhofer IOSB a study, focusing on sugars and carbohydrates. This was undertaken, in order to gather the results already published in the literature and to compare them with those obtained with our own measurements. The aim was to evaluate the possibility of standard optical spectroscopy to detect and characterize especially carbohydrates and sugars. This finding may be a significant advantage for the food-processing industry.

2 Current status of research

Materials and matter interact with the electromagnetic field, atoms can respectively absorb and emit once again photons with the energy $h * \nu$ where h is the Planck's constant and ν is the frequency of the electromagnetic radiation. With the hyper spectroscopy method, cameras take a 2D picture of the sample for each wavelength of the device spectrum that is the "third dimension" of the shot. [3] All the images of this "hyper spectral cube" are then segmented to separate the different parts of the image and analyzed with the software developed at the Fraunhofer Institute IOSB. The reflection spectra obtained in UV, visible or IR areas with a material are specific to this material and constitute its "spectral signature".

The far-infrared area is not here studied, because it can only be evidenced by Fourier transform infrared spectroscopy. In the infrared region, the incident radiation makes the atoms in the molecules rotate and vibrate leading to a rotation-vibration absorption spectra. In the mid-infrared (MIR) region, the stretching and deformation modes give the fundamental absorption bands. In the near-infrared (NIR) range, harmonics, overtones and combinations of fundamental stretching bands are visible. [4,5] In the visible and the ultraviolet areas, the electronic transitions appear and require much energy from the photons of the incident beam.

Optical spectroscopies bring relevant information about the structure of molecules. NIR spectroscopy is basically chosen instead of visible or ultraviolet spectroscopies, because it gives better results and is very simple of use. This method is rapid, relatively precise, cheap, and non-

destructive. [5, 6] Several studies have already been done on carbohydrates to find the specific absorption peaks of sugars. According to Robert and Cadet, [4] these specific wavelengths are related to the C-H, O-H, C-O and C-C bonds. The region 1100nm-1800nm is linked to the first and second harmonics of the O-H and C-H stretching frequencies, whereas the 1800-2500nm area corresponds to the combination bands of the O-H and C-H stretch. [4, 5] The most accurate wavelengths for monosaccharides are 1457nm (first harmonic O-H stretching), 2062nm (combination of O-H stretching and deformation), 2263nm (O-H and C-C stretching) and 2440nm (C-H and C-C stretching) and for oligo and polysaccharides, they are shifted to 1432nm, 1931nm, 2310nm and 2477nm, as confirmed by the graphs of Henry [7–9].

In the agri-food sector, NIR spectra contain a lot of information about internal and external properties of fruits, such as sugar content, total acidity, pH, soluble solid contents, dry matter, firmness and bruises. [5] NIR spectroscopy is often used to check if fruits or vegetables are green or rotten, to detect surface defects and is also employed to check the sugar concentrations for instance in apples [10, 11], oranges [12, 13], mango [14], kiwifruits [15], sugar beet [16], jujube [17], onion [18], potato tubers [19] but also in fruit juices [20], wine [21] or cakes [22].

Besides, UV spectroscopy requires much more energy so that spectral effects are only detected on gamma-irradiated sugar in water solutions with a peak in the region 260nm-280nm, especially at 267nm for sucrose according to Yordanov, Gancheva and Georgieva and the intensity of the peak is proportional to the gamma-rays absorbed dose. This is due to free radicals created in sugar during irradiation [23–25].

3 Equipment and Methods

For these measurements the spectroscopic equipment of Fraunhofer IOSB was used. A spectral workbench (spectral characterisation with image analysis from UV to NIR, 240 - 2500nm) and a database (including a software for first analysis) were available. This database allowed the study of different parameters of the registered spectra, such as the pixel intensity of the camera, the average value of the sample reflection intensity, the derivative intensity or a filtered intensity versus wavelength. For this study the NIR domain (750nm - 2500nm) has been the

main focus, because of the specific energy reflection within this area. We have also checked that the UV and visible areas did not bring any relevant information. Advantage of the database with its integrated software is the possibility to compare the raw spectra with those out of the database. This way, unknown materials can be investigated and the similarity with the already retained data can be calculated with algorithms with several methods.

The calibration of the devices was made by a 'white plastic reference', which was measured before each experiment. It gave the reference intensity in the calculation of the reflection index. A reflection intensity was then measured after the absorption in the material. If I_0 is the incident reference intensity, I_n the dark current, obtained without any light and I_{sample} the intensity reflected by the sample, the normalized reflection index R is:

$$R = \frac{(I_{\text{sample}} - I_n)}{(I_0 - I_n)} \quad (3.1)$$

The absorption coefficient is then:

$$\alpha = \log\left(\frac{1}{R}\right) \quad (3.2)$$

On the spectra, absorption matches convex parts of the reflection curve.

Sugar in mixtures was investigated in the 1050 – 2450nm range. To get rid of the influence of the color, only white materials were used. Commercial powdered sugar was mixed with only one other extra material: commercial flour and gypsum respectively. The different proportions were 0% extra material-100% sugar, 20% extra material-80% sugar, 40% extra material-60% sugar, 60% extra material-40% sugar, 80% extra material-20% sugar, 100% extra material-0% sugar. The influence of sugar in the spectra of more complex mixtures was then examined in commercial candies with edible gelatin and biscuits.

4 Results and Findings

Analysis of results shows that it is possible to detect the presence of carbohydrates in mixtures using NIR spectroscopy. Problems with color

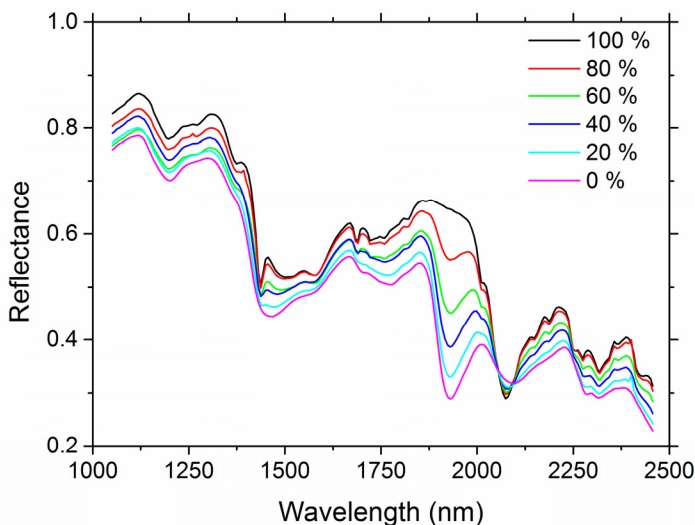


Figure 3.1: Reflectance spectra of sugar - flour mixtures: The percentages given are sugar mass percentages for a constant mass of the sugar-flour mixture.

appear in the visible area and too much energy is required in the ultraviolet one. The results reveal that the relevant wavelengths for sugars depend on the type of bonds, the atoms involved and the geometry (conformation, steric space). The wavelengths can therefore vary in small range from one sugar to another and it is preferable to speak of specific bands. There are mainly two types of influence in measurements with optical spectroscopy, on the one hand from the products and on the other hand from the measurement itself.

Figure 3.1 represents the reflectance spectra for several samples containing a decreasing quantity of sugar and an increasing quantity of flour for a constant total mass. Each one was scanned and the mean value of the reflected light intensity was calculated for each wavelength of the spectra. The graphs reveal that the rise in sugar concentration is linked to an increase in the reflection ratio. More precisely, the spectra obtained indicate that there is a continuous evolution between the

sugar concentrations in the samples and the areas of the concave parts of the curves. The more sugar there is, the more absorption occurs and the bands are really pronounced. The absorption bands characteristic of sugar are located approx. at 1200nm, 1437nm, 2074nm and 2320nm. This result is very close to that of Robert and Cadet [4] and it is really noticeable on the 100% sugar - 0% flour curve. Another trend is that there is a decrease in reflectance when the wavelengths go higher [4, 8].

Besides, the band located at 1930nm that increases with the flour content is related to water absorption. Then, it can not be taken into account to detect sugar in mixtures. In fact, water absorbs a lot in specific regions, hydrogen bonding creating clusters of water molecules. This phenomenon can hide the carbohydrates bands [26]. Previous studies showed that water molecules without OH group bonded absorbs at 1160nm, those with one OH group with H-bonded absorb at 1200nm, those with two OH with H-bonded absorb at 1250nm and the combination band of water is located in the 1800-2100nm range [27]. In addition, the intensity of water peaks depends also on the external conditions of the surrounding air and on the hygrometry rate.

Figures 3.2 and 3.3 confirm the localization of the carbohydrates peaks. They show similarly to the previous figure the evolution of the reflection ratio for several concentrations in sugar and gypsum and in flour and gypsum respectively.

Convexe parts are visible on the curves in figures 3.2 and 3.3 because of the presence of carbohydrates and water. In the sugar and gypsum mixtures, the bands 1200nm, 1437nm, 2074nm and 2320nm are still fine enough in the samples containing sugar, whereas there is just the influence of water on the curve 0% sugar - 100% gypsum due to the inorganic nature of gypsum. In our experiment, the influence of water appears mainly around 1915nm and the higher its absorption is, the less dissociable the other spectral effects are. In the flour and gypsum mixtures, the sugar bands 1200nm, 1437nm, 2074nm and 2320nm are softened in flour, which contains many other components. Water absorption bands are really visible in gypsum, more than in flour that is dry.

Nevertheless, it is not possible to distinguish various sorts of sugars, for instance make a difference between the saccharose of the powdered sugar and the numerous carbohydrates present in flour. The carbohydrates curves remain global because the precision about the wavelengths is not sharp enough, due to the infrared camera resolution (6nm)

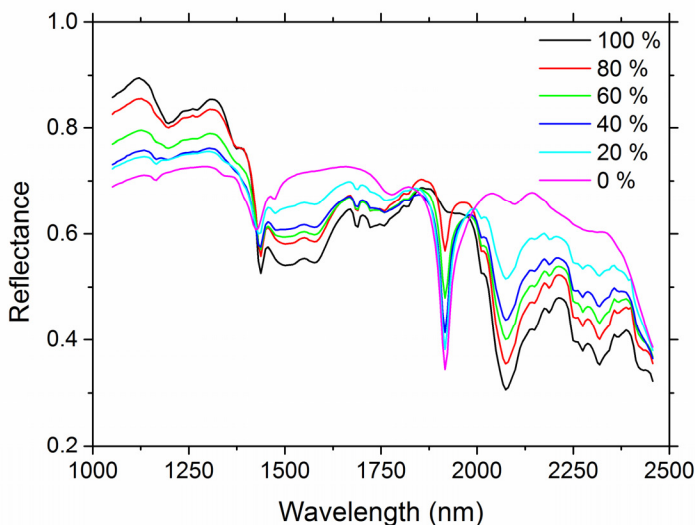


Figure 3.2: Reflectance spectra of sugar - gypsum mixtures: The percentages given are sugar mass percentages for a constant mass of the sugar-gypsum mixture.

and because near-infrared spectroscopy contains much information that is often overlapped in mixtures and complex heterogeneous materials. Moreover, some differences can appear according to the crystalline, liquid or dry form of the sugars [26]. Some variables can also affect the measurements, such as the lightning and light-scattering but also the white balance and the precision of the apparatus itself. Data processing and analysis is therefore required and a second-derivative calculation can give better results and refine the small differences between the spectra [12,15].

5 Summary

Optical spectroscopy allows to detect the presence of carbohydrates like sugar. But the device used cannot distinguish between the vari-

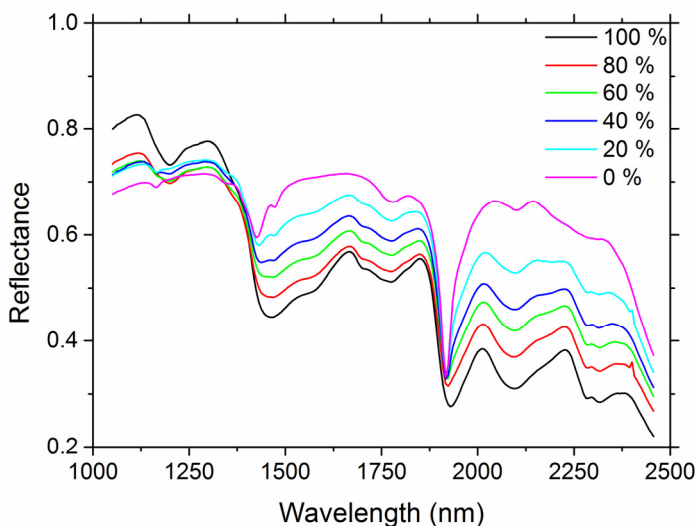


Figure 3.3: Reflectance spectra of flour - gypsum mixtures: The percentages given are flour mass percentages for a constant mass of the flour-gypsum mixture.

ous molecules of sugar, because of too little difference between specific carbohydrates peaks. NIR spectroscopy gives good results about the characteristic absorption bands of sugars, which are 1200nm, 1437nm, 2074nm and 2320nm. The dispersion of experimental values and the resolution of the machine remain an additional challenge. Important is the consideration of absorption due to water around 1915nm. The level of moisture influences directly the dynamics of spectral signatures. The identification of specific signatures of sugars can be very useful for rapid detection in the industrial sector.

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