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# Influence of hydration of food additive polysaccharides on FT-IR spectra distinction

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**Abstract**

Using the Fourier-transform infrared (FT-IR) spectra in the 1200–800 $cm^{-1}$ region and chemometrics, food additive polysaccharides such as pectin, starch, galactan and carrageenan can be distinguished. However, this vibrational spectroscopy technique is sensitive to the changes in conformation and to the constraints imposed by the hydrogen bonding with water, which could result in the destruction of all spectra qualities. In order to see if the water absorbed by carbohydrates can prevent the information necessary for their distinction in the 1200–800 $cm^{-1}$ region, six monosaccharides, three disaccharides, four carrageenans, four pectic polysaccharides, three galactans, two glucans and one commercial mixture of carrageenan–pectin were submitted to a 96% relative humidity environment and were also dissolved in saturated water solutions, and their spectra were compared with those obtained from the dry samples. The application of a principal component analysis (PCA) to the FT-IR spectra showed that the distinction of sugars and polysaccharides by FT-IR in the 1200–800 $cm^{-1}$ region can be achieved with no apparent loss of information in samples that can contain water. When the samples are in aqueous solution, the water influence is included in PC1 and the FT-IR spectral information of carbohydrates, previously given in PC1 and PC2 in dried samples, can be achieved in PC2 and PC3.


*Keywords:* FT-IR spectroscopy; Hydration; Sugars; Polysaccharides; Food additives

## 1. Introduction

Polysaccharides and their derivatives have always been of major interest in food industry because of their important role in the appearance, texture and taste of food products and due to their established properties in the promotion of longer shelf-life and as nutraceuticals.

Besides, the many methods concerning the identification or the determination of these compounds in foods, versatile and rapid analyses are desirable. Mid infrared spectroscopy appears as a very useful tool in the authentication of foods from raw materials to final products. Using the Fourier-transform infrared (FT-IR) spectra in the 1200–800 $cm^{-1}$ region in tandem with chemometrics, food additive polysaccharides such as pectin, starch, glucomannan and carrageenan can be distinguished (Černá, Barros, Nunes, Rocha, Delgadillo and Čopíková, 2003). However, this vibrational spectroscopy is sensitive to the changes in conformation and to the constraints imposed by the hydrogen bonding with water (Kačuráková & Mathlouthi, 1996). Polysaccharides are highly hygroscopic molecules (Whistler & BeMiller, 1997). Water sorption by polysaccharides has been described as a very important aspect of the physical behaviour of these polymers (Mazeau & Rinaudo, 2004). Infrared spectroscopy is so sensitive to hydrogen bonds that this property was the basis for its use for the observation of the conformational changes that occur when hyaluronan polysaccharide passed from the solid semi-crystalline state to the aqueous state (Haxaire, Maréchal, Milas & Rinaudo, 2003). An excess of water, nevertheless, would result in saturated bands that destroy all the qualities of the spectra.

If the analytical evaluation of the authenticity of the product by means of infrared spectroscopy should be rapid and reliable, the problem of scanning spectra of samples containing different water content can rise (Kačuráková and Mathlouthi, 1996; Kačuráková & Wilson, 2001). In order to see if the water absorbed by these compounds during their storage affects the spectra, six monosaccharides, three disaccharides, four

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carrageenans, four pectic polysaccharides, three galactans, two glucans and one commercial mixture of carrageenan–pectin submitted to a hydrated environment and in solution were studied in the FT-IR 1200–800 $cm^{-1}$ region and compared with those from the dry samples.

## 2. Materials and methods

### 2.1. Samples origin

*Standards*. Twenty three carbohydrate standards, mono-, di- and polysaccharide standard compounds, were used to build a FT-IR dataset based in their absorbances in the region 1200–800 $cm^{-1}$: L-arabinose (Sigma), D-fructose (Sigma), D-glucose (Sigma), D-mannose (Sigma), D-galactose (Sigma), D-galacturonic acid (Sigma), sucrose (Lachema), maltose (Sigma), lactose (Sigma), amylose (Sigma), amylopectin (Sigma), κ-carrageenan (Fluka), ι-carrageenan (Fluka), λ-carrageenan (Fluka), commercial carrageenan, mixture of commercial carrageenan and HM pectin, HM pectin 1 (Sigma), HM pectin 2 (Sigma), potassium pectinan (PectK3) [DE = 21.6%] (Sigma), potassium polygalacturonan (Sigma), arabic gum (Sigma), galactan (Koch-Light Laboratories), and arabinogalactan (Sigma).

The results of chemical analysis of the samples were as described by Černá et al. (2003).

### 2.2. Hydratation of samples

All standards and lyophilised polysaccharides were kept over phosphorus pentoxide and their infrared spectra were collected. This collection had been equilibrated at 25 °C and relative humidity of air 96% in a desiccator for 72 h. The samples were labelled as 'hydrated' and their infrared spectra were acquired. Then, to each sample, a few drops of water were added and the saturated solution or gel was created. These samples were labelled as 'solution' and their infrared spectra were collected. The water content of saccharides in dry and hydrated states is presented in Table 1.

### 2.3. FT-IR spectroscopy and chemometric analysis

The FT-IR spectra of the three collections of samples were obtained using a Golden Gate single reflection diamond ATR system in a Bruker IFS-55 spectrometer. The spectra were recorded at the absorbance mode from 4000 to 400 $cm^{-1}$ (mid infrared region) at the resolution of 8 $cm^{-1}$. Five replicate spectra (128 co-added scans) were collected for each sample. The measured spectra were transferred via a JCAMP.DX format into the data analysis software package for PCA and each spectrum, within the 1200–800 $cm^{-1}$ region, was SNV (standard normal deviates) corrected. The PCA analysis could allow the characterisation of the sample relationships (scores plans or axis) and, at the same time, the recover of their sub-spectral profiles (loadings).

Table 1
Water content of the samples used in dry and hydrated states

| | Water content (%) | |
|---|---|---|
| | Dry state | Hydrated state |
| Arabinose | 0.12 | 10.6 |
| Fructose | 0.25 | 39.5 |
| Glucose | 0.15 | 23.5 |
| Mannose | 0.18 | 47.6 |
| Galactose | 0.16 | 64.5 |
| Galacturonic acid | 0.15 | 11.8 |
| Sucrose | 0.012 | 13.4 |
| Maltose | 0.13 | 8.5 |
| Lactose | 0.015 | 6.0 |
| Amylose | 0.12 | 20.1 |
| Amylopectin | 0.11 | 13.8 |
| κ-Carrageenan | 0.39 | 77.1 |
| λ-Carrageenan | 0.31 | 32.7 |
| Pectin HM 1 | 0.51 | 23.2 |
| Pectin HM 2 | 0.53 | 48.3 |
| Galactan | 0.32 | 30.0 |
| Arabic gum | 0.55 | 50.6 |
| Galactan | 0.39 | 80.6 |
| Arabinogalactan | 0.13 | 20.7 |

### 2.4. Water content analysis

The water content in dry and hydrated samples was determined by the Karl–Fischer method (ThermoOrion AF8) using the reagent Hydranal-Composite 5 from Sigma-Aldrich. The Karl–Fischer apparatus was first calibrated with deionized water. The sample (1 g) was weighed accurately and transferred into automated titrating chamber. The titration was carried out according to the procedure of Isengard and Präger (2003). Experiments were made with three sample replicates and coefficients of variation of less than 2% were obtained for all samples.

The moisture content in solutions was determined by refractometry.

## 3. Results and discussion

### 3.1. Hydrated samples

Fig. 1 shows the PCA scores scatter plot and PCA loadings plot of the FT-IR spectra of dry and hydrated mono-, di-, and polysaccharides in the 1200–800 $cm^{-1}$ region. The distribution of the samples in the PC1 × PC2 axes (Fig. 1a) was done according to their composition in glucose (PC1 negative), galactose (PC1 positive), galacturonic acid (PC2 negative) and sucrose (PC2 positive), independently of the monomeric or polymeric nature of the samples, as previously observed by Černá et al. (2003). Also, it can be observed that the presence of water in amounts that ranged from 6 to 40% (Table 1) did not change significantly this separation trend. The exception was mannose (containing 48% of water) that was shifted from PC1 negative to PC1 positive.

Although the hydration of the samples gave broader bands, attributed to molecular disorientation and disappearance of the crystalline structures, as was observed for model