Application of FT-IR Spectroscopy in Detection of Food Hydrocolloids in Confectionery Jellies and Food Supplements

JANA ČOPÍKOVÁ[1], ANDRIY SYNYTSYA[1], MARCELA ČERNÁ[1], JITKA KAASOVÁ[1] and MIROSLAVA NOVOTNÁ[2]

Institute of Chemical Technology – [1]Department of Carbohydrate Chemistry and Technology and [2]Central Laboratory, Prague, Czech Republic

Abstract

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FT-IR spectra of isolated high molecule fractions were measured and used for identification of food hydrocolloids in confectionery jellies and food supplements. The simple comparison of spectra of standards and samples proved that this technique is useful for the monitoring of food hydrocolloids in particular food products.

Keywords: FT-IR spectroscopy; polysaccharides; jelly; food supplements

The polysaccharides are widely used in food processing technologies as gelling agents, thickeners or replacers of fat and saccharose. Food product surveillance requires simple and rapid methods to identify all food components. This analytical problem is very significant in the case of polysaccharides, which frequently react as fat mimetics or have bulking properties. In the present study infrared spectroscopy was applied in the analysis of food supplements and various kinds of confectionery jellies, with the aim to recognize the type of polysaccharides or gelling agents.

At present FT-IR spectroscopy is very often applied in the analysis of plant cell wall polysaccharides. The different techniques of FT-IR spectroscopy allow the identification of particular polysaccharides present in the intricate network of the cell wall (CHIOVITTI 1997; COIMBRA *et al*. 1998, 1999; KAČURÁKOVÁ *et al*. 2000), or the monitoring of developmental and compositional changes in the cell wall (DOWREY & MARCOTT 1999). The effects of technological processing of fruit can also be observed by FT-IR spectroscopy (FEMENIA *et al*. 1998). The results published in a thesis (SYNYTSYA 2000) prove that FT-IR and FT Raman spectroscopic methods are useful in the structural characterization of natural and modified pectins as well as other plant cell wall polysaccharides. The content of feruloyl groups, the degree of methylation and amidation are estimated by these spectroscopic methods (SYNYTSYA 2000, SINITSYA *et al*. 2000).

The objective of the present study is to determine the type of polysaccharide in confectionery jelly or food supplements according to its FT-IR spectra.

MATERIAL AND METHODS

List of samples

No 1: high molecule fraction of starch confectionery jelly
No 2: high molecule fraction of pectin fruit jelly
No 3: high molecule fraction of gelatine-pectin fruit jelly
No 4: food supplement, mixture of carragenan and saccharose, suitable for stabilisation of cocoa milk UHT drinks
No 5: food supplement, guar gum, suitable for sausages
No 6: food supplement, mixture of guar gum, carragenan and saccharose, suitable for stabilization of neutral cocoa UHT drinks

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Instruments

Samples Nos. 1–3: Infrared spectra were measured using the FT-IR spectrometer Nicolet 740 (Nicolet Instruments Co., USA) with DTGS detector, beam splitter: KBr and OMNIC 3.1 software. Number of scans 256 at resolution 4 cm^{-1} was averaged. The spectra were recorded within the 4000–400 cm^{-1} range and the analytical spectral range was 2010–910 cm^{-1}. Standards of polysaccharides were measured by the method of KBr pellets and samples were measured as films on an ATR accessory, ZnSe, 45. Apodization: Happ-Genzel.

Samples Nos. 4–6: The FT-IR spectra of standard polysaccharides and samples were obtained using the Perkin-Elmer 2000 spectrometer equipped with the microscope AutoIMAGE with a MCT detector and software Spectrum for Windows 1.5. Number of scans 16 at resolution 4 cm^{-1} was averaged. The spectra were recorded within the 4000–700 cm^{-1} range and the analytical spectral range was 2010–910 cm^{-1} in the transmittance mode at attenuance 2. The samples as films were measured on a BaF_2 window.

Preparation of samples Nos. 1–3: Samples (2 g) of confectionery jelly were dissolved in 100 ml of distilled water and the high molecule fraction was precipitated with threefold volume of absolute ethanol at 5°C for 24 hrs. The precipitate was removed by centrifugation at 6000 RPM and washed with the mixture of ethanol and water (70:30 % v/v) up to negative reaction for carbohydrates. The amount of 0.2 g of precipitate was dissolved in 50 ml of distilled water and about 1.5 ml of solution was placed on an aluminium plate and water was evaporated at ambient temperature until a smooth film was obtained.

Preparation of samples Nos. 4–6 and hydrocolloid standards: The polysaccharide standards and food supplements were dissolved in distilled water and 1 ml was pipetted into a cuvette equipped with an X-ray film Mylar (800-4-Chemplex, Chemplex Industries Inc., USA). The cuvettes were placed into an oven at 40 °C for 12 hours. The film was removed from the Mylar foil, transferred on a BaF_2 glass and recorded by the microscope of the FT-IR spectrometer.

RESULTS AND DISCUSSION

The study of hydrocolloids usually focuses on chemical composition, linkage between the monosaccharide units, and the size and shape of the molecule. A complete analysis of hydrocolloids or polysaccharides is unsuitable for their rapid identification in food or raw materials because the whole procedure is rather costly and time consuming. It seems to us that there are two possibilities how to solve the problem. One of them is the identification of saccharides or amino acids in a mixture resulting from the hydrolytic breakdown of a hydrocolloid by chromatography. The other alternative is the application of spectroscopic techniques, infrared spectroscopy and nuclear magnetic resonance spectroscopy (SYNYTSYA 2000).

In order to identify a specific gelling agent in confectionery jelly we used the infrared data of model compounds compared with the FT-IR spectra of the macromolecular part of the sample. The spectra of substances with high molecular mass isolated from confectionery jelly show general similarity to standards (Figs. 1–3). The samples No. 1 and No. 2 contained starch and pectin as a major macromolecular component, respectively. The IR band at 1152–1149 cm^{-1} is dominated by stretching of the glycosidic

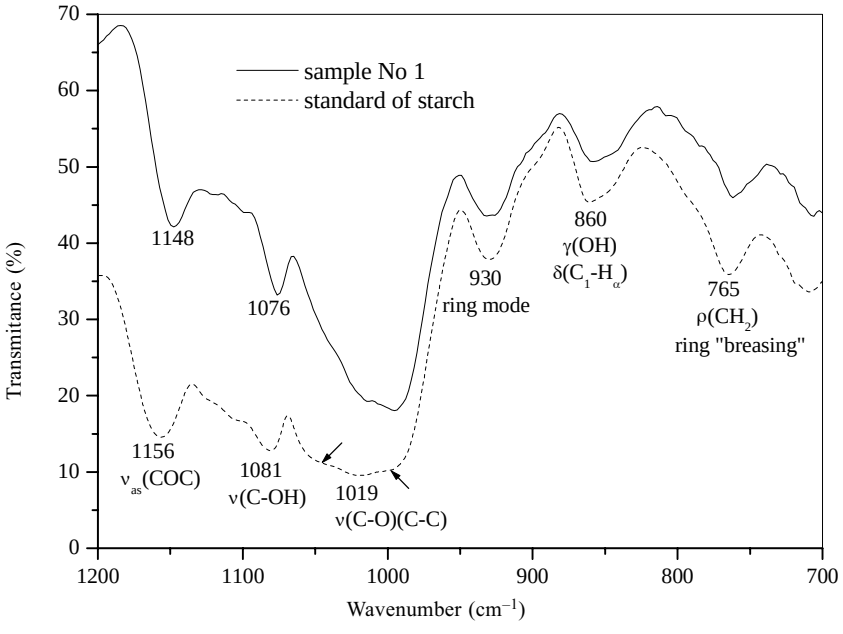

Fig. 1. FT-IR spectra of sample No 1 (starch confectionery jelly) and standard of starch

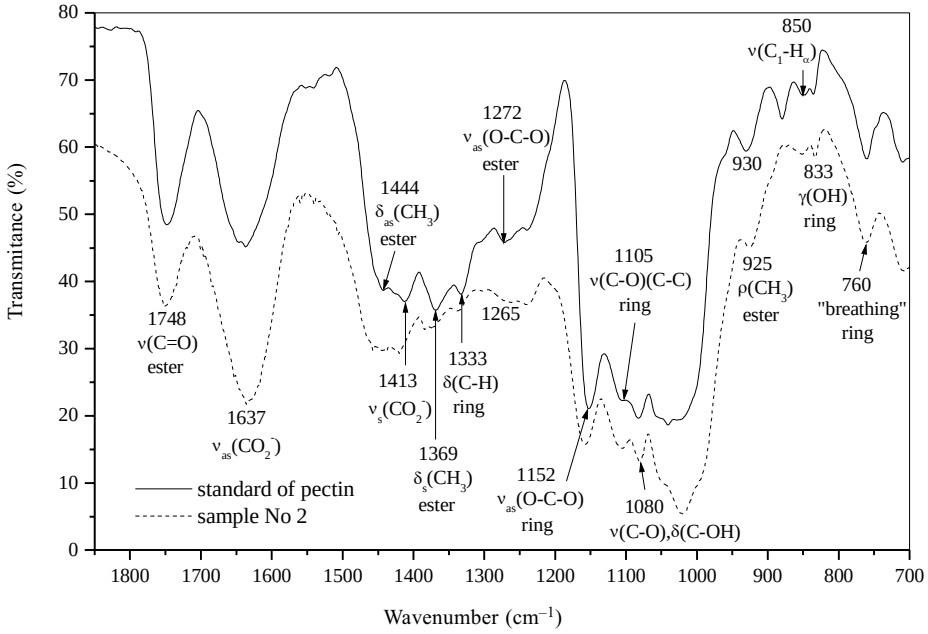

Fig. 2. FT-IR spectra sample No 2 and of pectin (fruit pectin jelly)

linkage C-O-C (KAMNEV *et al*. 1998; KAČURÁKOVÁ *et al*. 2000; WILSON *et al*. 2000). The highly coupled and conformational specific region between 1100 and 700 cm^{-1} belongs to non-localised, highly coupled vibrations of polysaccharide backbones (ENGELSEN & NORGAARD 1996). In the case of starch standard and sample No. 1, the spectra have several significant bands of starch in the region of 1200–700 cm^{-1} (Fig. 1).

In the case of pectin standard and sample No. 2, the spectra had two intense pectin bands at 1748 cm^{-1} and 1637 cm^{-1} assigned to stretching C=O vibration of esters and bending of water δ(H$_2$O) overlapped with the asymmetric stretching vibration of carboxylate anion ν$_{as}$(COO$^-$), respectively (Fig. 2). Both spectra of pectin and sample No. 2 have additional bands at 1444, 1413 (1420), 1369 (1374), 1272 (1266) and 930 (925) cm^{-1}, which may be ascribed) to ester and carboxylate groups (FILIPPOV 1978; ENGELSEN & NØRGAARD 1996; WELLNER *et al*. 1998). The band at 1333 (1338) cm^{-1} was assigned to C-H bending vibration of pyranoic ring. This band is very resistant to any changes of C-6 carboxyls (FILIPPOV 1978). In the region of 1200–950 cm^{-1} of both spectra, several intense

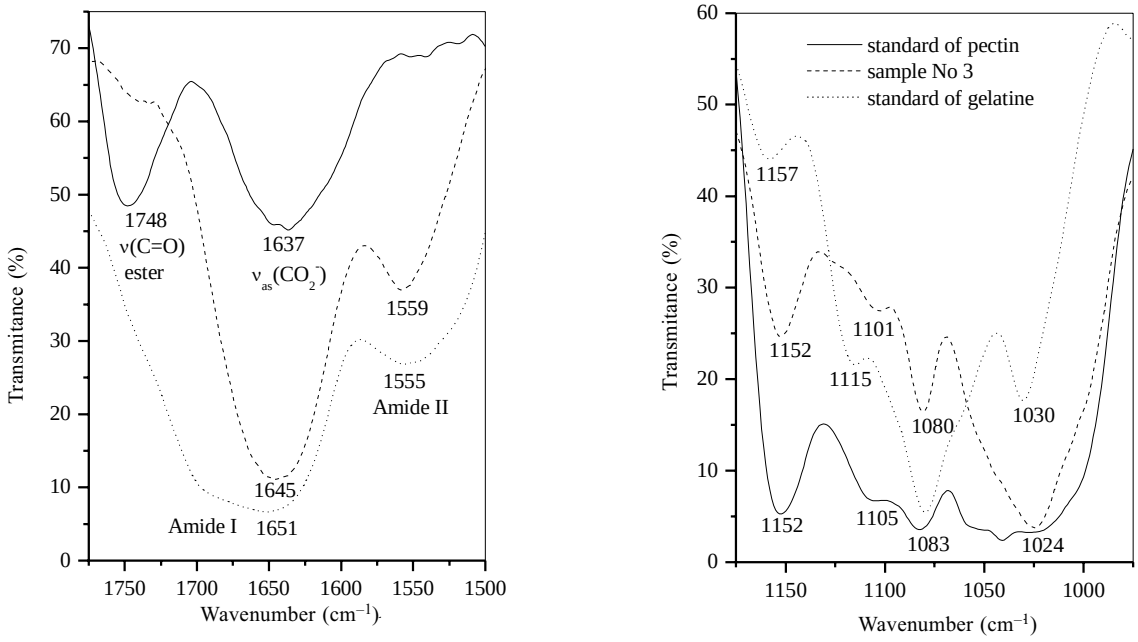

Fig. 3. FT-IR spectra of sample No 3 (fruit gelatin-pectin jelly) and standards of pectin and gelatin

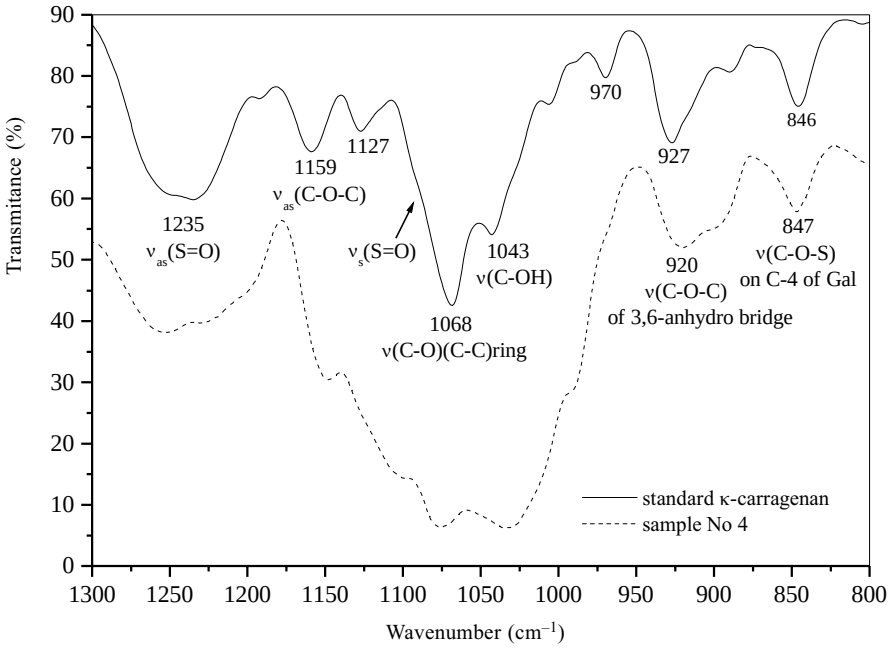

Fig. 4. FT-IR spectra of sample No 4 and standard of κ-carragenan

bands at 1152 (1158), 1105 and 1083 (1080) cm^{-1} contributed to vibrations of glycosidic bonds and pyranoid rings (Fig. 2). In addition, two weak bands at 850 and 833 cm^{-1} also confirm that pectin is the major component of sample No. 2.

Sample No. 3 contained confectionery jelly prepared from a mixture of gelatine and pectin. The isolated portion of high molecule substances has significant bands of pectin (1742, 1152, and 1105 cm^{-1}) and two intense bands at 1641 and 1557 cm^{-1} assigned to amide bonds of gelatine (amide I and amide II modes, respectively). The intense band at 1080 cm^{-1} is present in both pectin and gelatine, thus it cannot be used for the identification of these gelling agents in a mixture. The fact that all pectin bands, especially that of ester C=O stretching vibration at 1742 cm^{-1}, are relatively weak confirm that pectin, in contrast to gelatine, could be present in sample No. 3. only in small amount.

The food supplement sample No. 4. was a mixture of algae polysaccharide carragenan and saccharose. Carra-

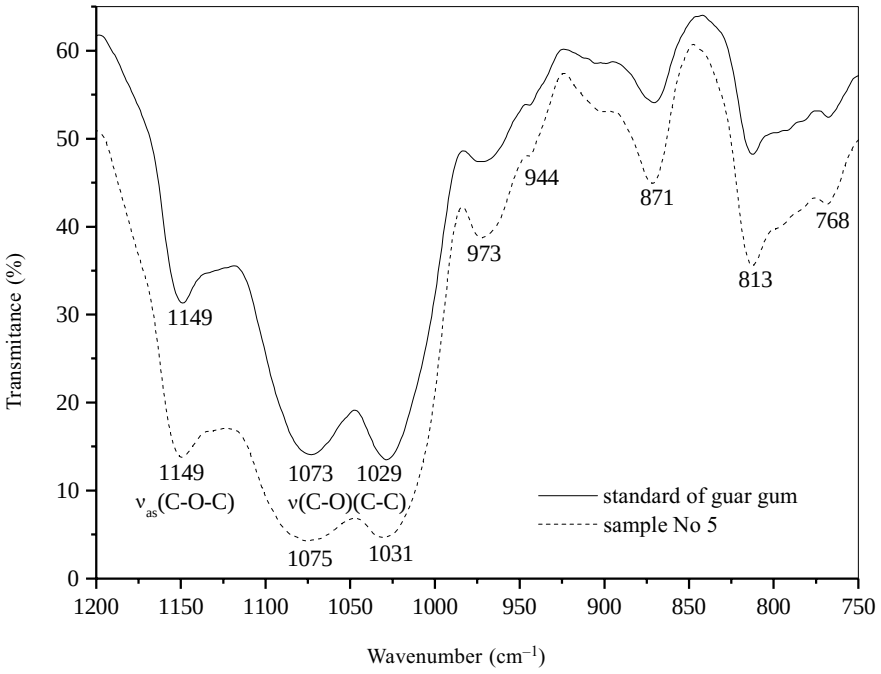

Fig. 5. FT-IR spectra of sample No 5 and standard of guar gum

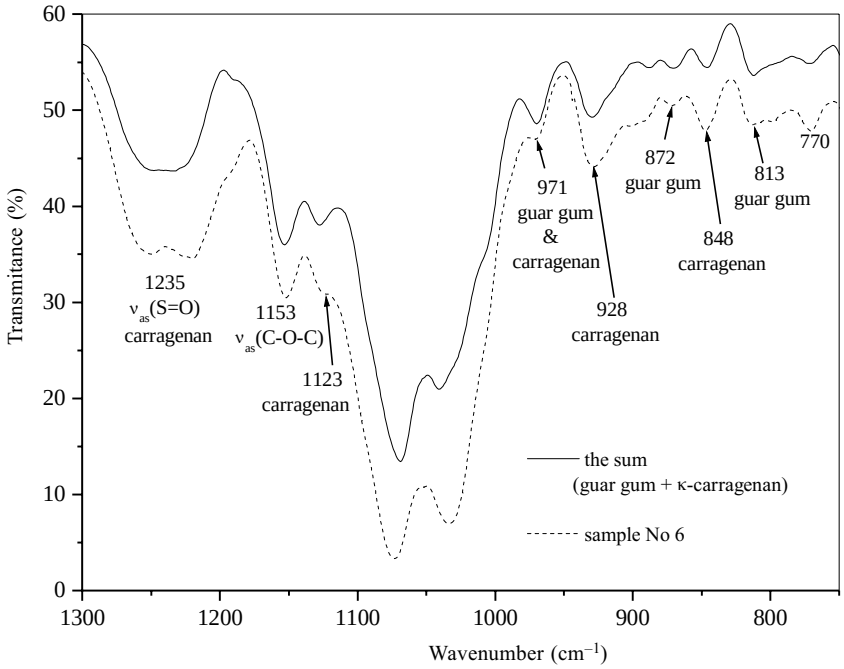

Fig. 6. FT-IR spectra of sample No 6 (mixture of two polysaccharides) and of the sum of κ-carragenan and guar gum

genan molecules are linear chains of D-galactopyranosyl units with most sugar units having one or two sulphate groups esterified to carbon atoms C-2 or C-6 (WHISTLER & BEMILLER 1997). The infrared spectra of both the standard and the sample have an intense broad band at 1235 cm^{-1} contributed to asymmetric stretching vibration of S=O bonds (SILVERSTEIN *et al*. 1991) of carragenans (Fig. 4). The corresponding symmetric stretching mode of S=O is present in the spectra as a small shoulder near 1090 cm^{-1} (WILSON *et al*. 1988). In addition, both these spectra have two bands at 927 and 846 cm^{-1}, which were assigned to the coupling of the C-O stretching vibrations of the 3,6-anhydro bridge and to the coupling of C-O and O-S vibrations of D-galactose-4-sulphate, respectively (SEKKAL & LEGRAND 1993). The presence of these bands confirmed the κ-type of carragenan (CHOPIN & WHALEN 1993).

The food supplement sample No 5. was declared as pure guar gum, i.e. galactomannan from a leguminous plant, *Cyanopsis teragonolobus*. The simple comparison of the standard and the sample spectra shows a very similar profile (Fig. 5). The spectrum has two bands, at 1149 cm^{-1} contributed to glycosidic bonds and several bands at 1075, 1029, 973 and 944 cm^{-1} contributed to sugars region. The two bands at 871 and 813 cm^{-1} are also characteristic of guar gum.

The food supplement No. 6 contained two polysaccharides, i.e. a mixture of guar gum and carragenan. The spectrum of sample No. 6 was nearly identical to the spectrum of the arithmetic sum of the spectra of pure standards (Fig. 6). The spectrum contains the band at 1151 cm^{-1} contributed to glycosidic bonds of both polysaccharides, 1235 cm^{-1} contributed to asymmetric stretching vibration of S=O bonds in carragenan, and two weak bands at 872 and 813 cm^{-1}, which are present in the guar gum spectrum. The bands of sample No. 6 at 1123, 928 and 848cm^{-1} strongly indicates the presence of α-carragenan, whereas the characteristic band at 971 cm^{-1} is present in both studied polysaccharides and cannot be used in the analysis of carragenan – guar gum mixtures.

CONCLUSIONS

The results show that FT-IR spectra of food hydrocolloids (starch, pectin, carragenan, guar gum and gelatine) isolated from fruit jellies and food supplements contain information that enables the identification of respective food hydrocolloids in food samples. The procedure based on mid-infrared absorption spectroscopy is comfortable, compared with chromatography. There is no need of the hydrolysis of isolated hydrocolloids and the subsequent identification of resulting products by chromatography. Nevertheless, quantitative evaluation still remains to be worked out.

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Souhrn

ČOPÍKOVÁ J., SINITSYA A., ČERNÁ M., KAASOVÁ J., NOVOTNÁ M. (2001): **Využiti FT-IR spektroskopie k detekci potravinářských hydrokoloidů v cukrovinkářském želé a potravinových doplňcích.** Czech J. Food Sci., **19**: 51–56.

V této práci byla naměřena FT-IR spektra frakce vysokomolekulárních látek isolovaných ze tří vzorků cukrovinkářského želé (vzorky 1–3) a potravinářských doplňků (vzorky 4–6) a porovnána se spektry standardů (škrob, pektin, želatina, karragenan a guarová guma). Analýza FT-IR spektrálních dat potvrdila, že vzorky 1 a 2 obsahovaly škrob a pektin jako želírující látku a vzorek 3 obsahoval směs želatiny a pektin, přičemž převažovala želatina. Přítomnost spektrálních pásů 1235, 927 a 876 cm^{-1} potvrdila, že vzorek 4 obsahoval κ-karragenan. Profil spekter vzorku 5 a standardu guarové gumy měl stejný průběh, což bylo důkazem, že vzorek obsahoval guarovou gumu. Spektrum vzorku 6, který byl směsí dvou polysacharidů a sacharosy, bylo téměř identické s aritmetickým součtem spekter čistých standardů, guarové gumy a karragenanu. Získané výsledky potvrdily užitečnost FT-IR spektroskopie při identifikaci potravinářských hydrokoloidů ve vybraných potravinářských vzorcích.

Klíčová slova: FT-IR spektroskopie; polysacharidy; želé; potravinový doplněk

Corresponding author:

Ing. JANA ČOPÍKOVÁ, Vysoká škola chemicko-technologická, Ústav technologie a chemie sacharidů, Technická 3, 161 05 Praha 6, Česká republika, tel.: + 420 2 24 35 31 14, fax: + 420 2 311 99 90, e-mail: jana.copikova@vscht.cz