Determination of Polydextrose as a Fat Replacer in Butter

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Abstract

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Polydextrose is used in several countries as a low caloric sugar and fat substitute (bulking agent). It is prepared by condensation of glucose, D-glucitol, and citric acid (89:10:1). The resulting condensation product has no chemically defined structure but it represents a mixture of polymerisation products. The determination of polydextrose in butter is complicated owing to a large excess of fats and to the presence of other compounds, mainly proteins. FT-IR spectroscopy seems to be a satisfying method for the detection of polydextrose in samples derived from food products. The presence of polydextrose in butter was verified after the removal of fats by extraction with petroleum ether and deproteinisation with Sevag reagent, $CHCl_3$/*n*-butanol (v/v = 4:1) mixture, or trichlorocetic acid. The solid fraction of butter and butter containing a known amount of polydextrose were prepared and analysed by FT-IR spectroscopy. IR marker bands of polydextrose centred at 1150, 1076 and 1040 cm^{-1} were found only in the case of the sample of butter with polydextrose.

Keywords: polydextrose; litesse; fat replacer; butter; FT-IR

It has been recognised before that the ingestion of dietary fibres, especially or their major polysaccharide components, provide a variety of health benefits (Spiller 1994). This diverse group includes naturally occurring oligosaccharides, small polysaccharides, and semi-synthetic and synthetic carbohydrates. The resistant short-chain carbohydrates are compounds, which are not susceptible to hydrolysis by digestive enzymes but may be fermented by the microflora in the large intestine. The resistant short-chain carbohydrates include polydextrose (polydextrose), inulin, soybean galactooligosaccharides, and other carbohydrate oligomers.

Among the compounds mentioned, polydextrose is regarded as either a resistant polysaccharide or resistant short-chain carbohydrates and is recognised in a number of countries as dietary fibre. Physiological benefits of polydextrose include fermentation in the lower gastrointestinal tract, the production of volatile short-chain fatty acids, faecal bulking, transit time reduction, and an influence on glucose homeostasis (Craig *et al.* 1998). These effects are based on the improved bowel function (e.g. prevention of constipation), regeneration of colonic mucosa, improved environment for the growth of such useful intestinal bacteria as *Lactobacillus* and *Bifidobacterium* species, and thereby a decreased formation of harmful bacterial metabolites (Flood *et al.* 2004).

Polydextrose is a bulking agent used to provide body and texture in reduced-caloric foods. It is non-crystalline powder that can be used to stabilise foods

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by preventing sugar and polyol crystallisation. Polydextrose is a water soluble, randomly bonded bulk polymer with an average degree of polymerisation of about 10 glucose residues (Ribeiro *et al*. 2003).

It is available in several forms: polydextrose-A (acid form) and polydextrose-N (neutralised form), the latter being a practically neutralised product obtained by the addition of potassium hydroxide or carbonate to a solution of polydextrose-A (Burdock & Flamm 1999). It tastes bitter and sour and that is why it is modified by refinement to obtain commercial products Litesse. Litesse is a bulk material used as a sugar or fat replacer in the production of candies, jelly, and chocolate (Kopchik 1995). Additional forms, trade named Litesse® I–III, are more purified forms of polydextrose prepared primarily by ion exchange post-treatment. Partially, Litesse® III is a reduced form of polydextrose in which all anomeric (reducing glucose) end groups are converted to D-glucitol by catalytic hydrogenation to give a more colour-stable product.

A number of analytical methods, based mainly on liquid chromatography (LC) technique, have been developed for the determination of polydextrose in the food products (Noffsinger *et al*. 1990; Prosky 2001). These methods are precise and selective in contrast to the modified classical phenol-sulphuric acid photometry which had been used earlier for this purpose. LC methods involve aqueous extraction of polydextrose from the food matrix followed by the separation on a carbohydrate analysis column.

The LC methods work well in relatively simple food systems, however, interfering substances (soluble gums, hydrocolloids, bulking agents, etc.) can confound the chromatogram in some foods. Stumm and Baltes (1997) improved the test sample preparation step and demonstrated the removal of the possible interfering ingredients. This method used more rigorous enzyme hydrolysis with amyloglucosidase, isoamylase, and fructanase. This was the first collaborative study on polydextrose published.

AOAC methods for the determination of total dietary fibre in foods include an ethanol precipitation step in which polydextrose and similar carbohydrates are discarded and therefore are not quantified. A novel method (Craig *et al*. 2000, 2001) includes water extraction, centrifugal ultrafiltration, multienzyme hydrolysis, and HPAEC-PAD analysis. The value obtained is added to that obtained for the dietary fibre contents in foods using the AOAC methods.

Polydextrose was studied as a fat replacer in dairy products (Ronchetti 1994; Prindiville *et al*. 2000), in skim milk-based preparations containing probiotic bacteria (Ananta *et al*. 2005), a fat replacer in dough (Sudha *et al*. 2007) and bars (Trudell *et al*. 1996). Polydextrose can be applied in the formulation of cocoa products (Edwards 1997; Rausch 1998; Goldman 2006) and other food products (Giese 1996).

FT-IR spectroscopy is very often applied in the analyses of polysaccharides in foods (Čopíková *et al*. 2001; Černá *et al*. 2003; Prado *et al*. 2005). This method can be useful in the analysis of polydextrose in food products after an appropriate sample preparation. The objective of the present study is FT-IR detection of polydextrose in butter after the previous removal of fats and proteins.

MATERIAL AND METHODS

Sample preparation. The samples used are listed in Table 1. Polydextrose (Sample No. 1) was granted by the company Danisco-Chemopharma (Vrchlabí, Czech Republic). Sample No. 2 was obtained from retail (80.10% fat, 0.92% protein).

Table 1. Sample information

Sample No.	Specification
1	Polydextrose-Litesse® Ultra Powder (Danisco-Chemopharma, Vrchlabí, Czech Republic)
2	Butter from retail (80.10% fat, 0.92% protein)
3	Sample No. 2 after fat removal by petroleum ether extraction
4	Sample No. 3 deproteinised with Sevag reagent
5	Sample No. 3 deproteinised with TCA
6	Sample No. 2 with the addition of polydextrose

Samples No. 3–6 (10 g) were prepared from butter (Sample No. 2) by petroleum ether extraction to remove fat. The defatted solid fraction was deproteinised with Sevag reagent ($CHCl_3$/*n*-butanol (v/v = 4:1) mixture)) (Chuanguang *et al.* 2002), providing samples No. 4 and 6, or with 25% aqueous trichloroacetic acid (TCA) (Sample No. 5). After removing the Sevag reagent, resp. TCA, by distillation under vacuum, ethanol was added to the water phase (v/v = 4:1) and the mixture was kept at 4°C overnight in a refrigerator to precipitate carbohydrate compounds. After filtering with a Buchner funnel under vacuum and washing with ethanol, the sediments were dried and stored under P_2O_5 and then analysed by FT-IR. The model Sample No. 6 was prepared by mixing butter (Sample No. 2) with polydextrose (Sample No. 1) in the amount 1% at 50°C, and then processed in the same way as Sample No. 4.

FT-IR spectroscopy. FT-IR absorption spectra of the samples were measured with FT-IR spectrophotometer BRUKER IFS 66v/S (Bruker, USA) combined with HYPERION microscope, magnification was 15×. Second derivative (SD, 9 ppt smoothed) and Fourier self-deconvolution (FSD, band width 77.2, enhance 2.0) of the spectrum of polydextrose (Sample No. 1) were made using Omnic 6.1a (Thermo Nicolet, USA) software. The spectra were recorded within the spectral range of 4000–400 cm^{-1}, scan number was 128, resolution 4 cm^{-1}. The spectra obtained were processed and appropriate graphs were constructed using Origin 6.0 software (Microcal Origin, USA).

RESULTS AND DISCUSSION

FT-IR absorption, Fourier self-deconvolution (FSD) and the second derivative (SD) spectra of polydextrose (sample No. 1) are shown in Figure 1. FSD and SD algorithms were used to obtain the positions of the overlapped bands. The band assignments are summarised in Table 1 according to the reports relating FT-IR spectra of various glucans (Mathlouthi & Koenig 1986; Šandula *et al.* 1999; Shingel 2002). It is evident that the anomer sensitive characteristic bands of polydextrose are attributive for α- and β-linked glucose residues. These are, first of all, C1-H deformation bands at 893 and 848 cm^{-1} indicating α- and β-glucans, respectively. The band at 991 cm^{-1} is completely overlapped by an intense stretching vibration band of CC and CO bonds in pyranoid ring centred at 1037 cm^{-1}. The former band was detected only by SD. It was assigned to C6-OH bending of primary alcoholic groups of glucose residues (Shingel 2002). The band at 1145 cm^{-1} arising from stretching vibrations of COC glycosidic linkage is indicative of glycosidic bonds in polydextrose. The intense absorbance in the region of 1200–900 cm^{-1} is characteristic for sugars and can be used for the detection of polydextrose in food samples.

As a fat replacer, polydextrose can be used in the preparation of butter products in food industry. FT-IR spectroscopy can be a useful tool for the detection of polydextrose, which has quite specific IR spectroscopic features and can be easily

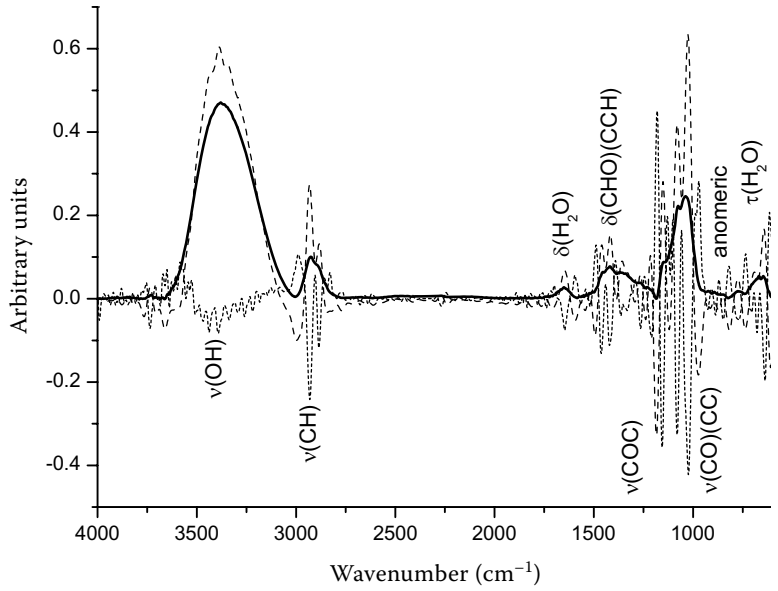

Figure 1. FT-IR absorption (—), Fourier self-deconvolution (FSD, – –) and the second derivative (SD, ---) spectra of polydextrose (Sample No. 1)

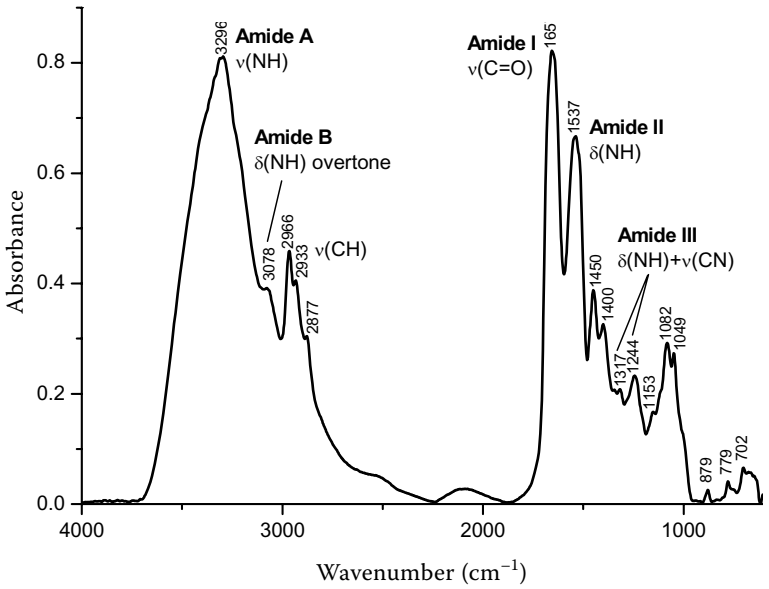

Figure 2. FT-IR spectrum of butter after fat removal (Sample No. 3)

distinguished from other non-sugar components of the food products. The determination of polydextrose in butter, however, is complicated owing to the large excess of fats and to the presence of other hydrocolloids, mainly proteins. Therefore, it was important to remove fats and proteins from the sample before the spectroscopic analysis. The extraction with petroleum ether was used for the fat removal from the butter samples. Subsequently, the samples were deproteinised in two ways: (a) extraction with Sevag reagent or (b) precipitation with TCA. The effectiveness of these methods was estimated by FT-IR spectroscopy.

FT-IR spectrum of sample No. 3 (defatted butter) is shown in Figure 2. The absence of fats is evident (no ester and methylene vibration bands), but several bands at 3296 cm^{-1} (amide A, NH stretching), 3078 cm^{-1} (amide B, NH bending overtone), 1657 cm^{-1} (amide I, C = O stretching), 1537 cm^{-1} (amide II, NH bending), and 1244–1317 cm^{-1} (amide III, CN stretching) indicate the presence of proteins as major components of the sample. Three bands at 2966, 2933, and 2877 cm^{-1} were assigned to CH stretching vibrations of aliphatic amino acids in proteins. No evident band of polydextrose or other carbohydrates was found in the spectrum.

FT-IR spectra of the defatted butter samples after the protein removal using Sevag (Sample No. 4) and TCA (Sample No. 5) reagents are shown in Figure 3. The sample No. 4, but not the sample No. 5, showed two intense bands of proteins at 1657 and 1537 cm^{-1}. An intense band of C=O

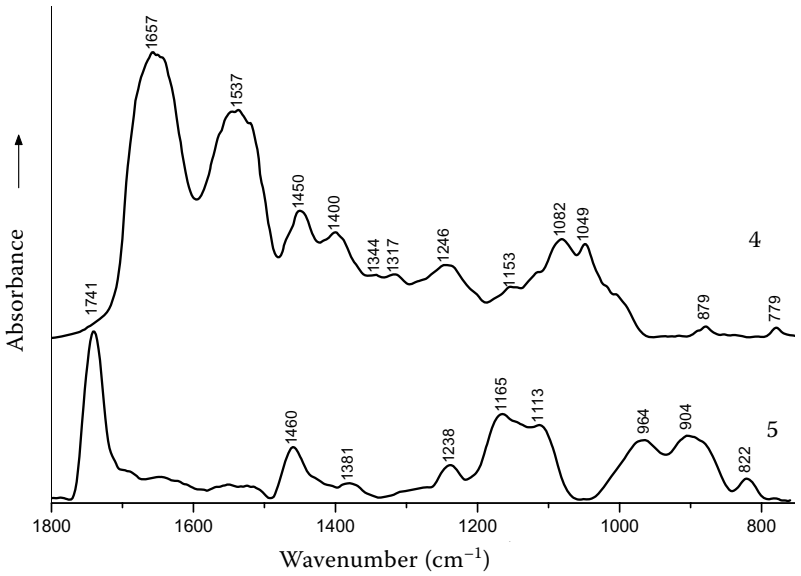

Figure 3. FT-IR spectrum of the defatted butter after protein removal using Sevag (Sample No. 4) and TCA (Sample No. 5) reagents

Table 2. IR bands of polydextrose (Sample No. 1)

Wavenumber (cm^{-1})			Assignments	Wavenumber (cm^{-1})			Assignments
Spectrum	SD	FSD		Spectrum	SD	FSD	
3380		3388	ν(OH)	1037	1039		ν(CO), (CC), β Glc
2925	2931	2933	ν(CH), $\nu_{as}(CH_2)$		1019	1026	ν(CO), (CC), α Glc
	2885	2883	ν(CH), $\nu_{s}(CH_2)$		991		δ(C6-OH)
1650	1647	1647	$\delta(H_2O)$		947	933	α-(1,4) Glc
1458	1463	1460	$\delta(CH_2)$	923	925		α-(1,4) Glc
1419	1421	1417	δ(CHO), (CCH)	893	887	895	δ(C1-H), β Glc
1369	1363	1357	δ(CHO), (CCH), β Glc	848	842	848	δ(C1-H), α Glc
1338	1332	1335	δ(CHO), (CCH)	781	777	775	β Glc
1263	1265	1265	δ(CHO), (CCH)		754		δ(C1-H), α Glc
1232	1230		δ(CHO), (CCH)			690	
	1201	1215	ν(COC), (CC)	669	679		β Glc
1145	1157	1151	ν(COC), (CC), α Glc	646	638	644	
	1116		ν(CO), (CC), β Glc		598		α-(1,4) Glc
1074	1080	1080	ν(CO), (CC)	578	588	582	α-(1,4) Glc
	1051		ν(CO), (CC)	555	549		β Glc

stretching vibration at 1741 cm^{-1} was found in the spectrum of the sample No. 5. This band was assigned to ester groups of fat that was still present in the sample. Therefore, TCA seems to be more efficient for the deproteinisation of butter than Sevag reagent, the latter, however, improved the fat removing procedure. Moreover, the conditions of deproteinisation are less aggresive to carbohydrate compounds.

FT-IR spectra of polydextrose (Sample No. 1) and polydextrose containing butter (Sample No. 6) after the removal of fats and proteins are shown in Figure 4. The sugar region (1200–900 cm^{-1}) of the spectrum of the sample No. 6 showed highly overlapped intense features at ca. 1146, 1074 and 1037 cm^{-1} assigned to polydextrose. Several other polydextrose bands are also present outside this region. On the other hand, the intense amide I

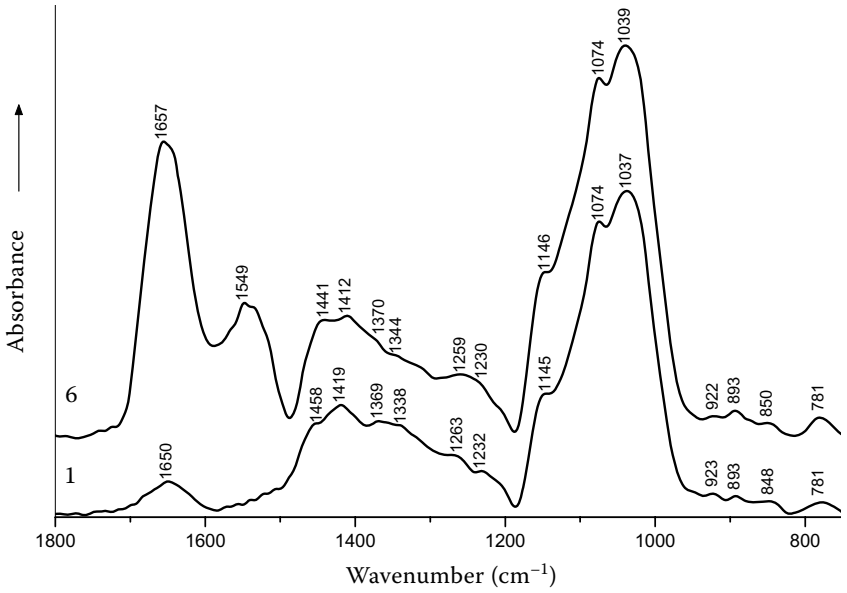

Figure 4. FT-IR spectra of polydextrose (Sample No. 1) and polydextrose containing butter (Sample No. 6)

(1657 cm^{-1}) and amide II (1549 cm^{-1}) bands indicate the presence of proteins in the sample No. 6, nevertheless, this fact does not affect the proof of the polydextrose presence or absence in the model mixture of butter. The bands characteristic for polydextrose were not present in the spectra of the defatted and deproteinised butter samples Nos. 4 and 5 (Figure 3).

CONCLUSION

The procedure described allowed the proof of the polydextrose presence in butter on the basis of FT-IR spectroscopy. For the model mixture of butter and polydextrose (1%), a combination of fat and protein removal was used to obtain a component acceptable for FT-IR spectroscopic analysis. IR marker bands of polydextrose centred at 1147 (resp. 1149), 1074 and 1037 (resp. 1039) per cm were found only for the processed model mixture that contained polydextrose.

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