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Characterization of Irradiated Starches by Using FT-Raman and FTIR Spectroscopy

RAMAZAN KIZIL,† JOSEPH IRUDAYARAJ,*,† AND KOUSHIK SEETHARAMAN‡

Department of Agricultural and Biological Engineering, 227 Agricultural Engineering Building, and Department of Food Science, 107A Borland Lab, The Pennsylvania State University, University Park, Pennsylvania 16802

Fourier transform infrared (FTIR) and Fourier transform Raman (FT-Raman) methods were used for rapid characterization and classification of selected irradiated starch samples. Biochemical changes due to irradiation were detected using the two vibrational spectroscopic techniques, and canonical variate analysis (CVA) was applied to the spectral data for discriminating starch samples based on the extent of irradiation. The O−H (3000−3600 cm^{-1}) stretch, C−H (2800−3000 cm^{-1}) stretch, the skeletal mode vibration of the glycosidic linkage (900−950 cm^{-1}) in both Raman and infrared spectra, and the infrared band of water adsorbed in the amorphous parts of starches (1550−1750 cm^{-1}) were employed in classification analysis of irradiated starches. Spectral data related to water adsorbed in the noncrystalline regions of starches provided a better classification of irradiated starches with 5 partial least-squares (PLS) factors in the multivariate model.

KEYWORDS: Starch irradiation; FT-Raman spectroscopy; FTIR spectroscopy; detection of irradiated starches; discrimination analysis

INTRODUCTION

Starch, a semicrystalline polymer, is composed of two polysaccharides: amylose and amylopectin. Amylose, a mostly linear chain, typically consists of up to 3000 glucose molecules interconnected primarily by α-1,4 glycosidic linkages and is reported to contain a few branched networks (*1*). Amylopectin is a large branched polymer with linkages of α-1,4 that serve as the backbone and α-1,6 bridges that serve as branching points (*2*).

Chemical modification of starches resulting in structural changes including succinylation (*3*), acetylation (*4*), and maleination (*5*) can enhance their functional value and broaden their range of physicochemical properties. Detection of these structural changes in starch that are due to chemical modifications is an important industrial necessity in order to determine quality of modified starches (*6*). Determination of the degree of modification (*3*) and classification of chemically modified starches (*6*, *7*) using Raman or infrared spectroscopy have been explored.

Irradiation of food is used to extend the shelf life or to increase safety of food by reducing spoilage and pathogenic microorganisms (*8*). Irradiation can bring about structural modifications that could affect the functional and nutritional properties of foods. Being one of the most plentifully used ingredients, starch imparts structure, texture, consistency, and appeal to many food systems (*9*). Characterization of irradiated food samples was of great interest in the 1970s and 1980s. Conventionally, electron spin resonance (ESR) and thermoluminescence (TL) methods were employed for identification of irradiated food to detect free radicals (unpaired electrons) or energy trapped in crystalline or mineral (dust) regions of the food (*8*, *10*, *11*). Even though both of these techniques are widely used to determine radiation doses applied to food (*8*), they do not provide information on chemical modifications and formation of radiation-induced products. Sohkey and Hanna (*12*) have reviewed molecular changes in starches due to irradiation. Degradation of starch polymers resulting in decreased viscosity and increased water solubility, and increased acidity with increasing radiation doses are potential changes observed in irradiated starches. Detection of such modifications in starch was determined using time-consuming as well as destructive techniques such as luminescence and viscosity measurements.

Mass spectroscopy (MS), gas chromatography (GC), and high-performance liquid chromatography (HPLC) were generally used for the detection of radiation-induced byproducts (*13*−*15*). However, these techniques have limitations related to the difficulty of sampling and the high maintenance cost of the equipment. Vibrational spectroscopic techniques such as the Fourier transform infrared (FTIR) and Raman (FT-Raman) methods have also been employed as probes to investigate process-induced changes and to measure quality of food (*16*−*18*). Hrebicik et al. (*19*) investigated the small molecular changes in rice and oat using FTIR and reported an increase in the intensity of 1734 cm^{-1} band which was attributed to the effect of irradiation.

* To whom correspondence should be addressed. Phone: (814) 865 2807. Fax: (814) 863 1031. E-mail: josephi@psu.edu.
† Department of Agricultural and Biological Engineering.
‡ Department of Food Science.

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Although irradiation of starches at low and moderate doses introduced subtle modifications (*12*, *20*), it is likely that vibrational spectroscopic techniques, such as Raman and infrared spectroscopy, can be used to elucidate changes in the molecular structure and integrity of irradiated foods. To our knowledge, the use of vibrational spectroscopy to identify the biochemical changes in starches due to irradiation has not been attempted. Ciesla et al. (*21*) investigated the change in starch crystallinity and its relevance to starch degradation arising from irradiation using X-ray spectroscopy. Recently, De Kerf et al. (*22*) characterized high-dose irradiated (10, 50, and 100 kGy) starches which are used as excipients in pharmaceutical formulations. The results showed that disintegration of starches increases with an increase in irradiation dose. Disintegration properties of starches were evaluated using molecular weight distribution and solubility analyses. A rapid characterization will help in on-line quality assessments.

Several researchers have reported the effect of irradiation on the functional, chemical, and structural properties of starch. Kume et al. (*23*) and Greenwood and McKenzie (*24*) reported a decrease in viscosity and iodine affinity of starch following irradiation. Von Sontag (*25*) and Diehl (*26*) reported that the most prominent effect observed following irradiation of carbohydrates in an aqueous environment was the liberation of hydrogen atom from C−H. The hydroxyl radical formed upon radiolysis of water attacks the hydrogen of C−H bonds nonselectively and liberates the hydrogen atom. Several investigators (*26*−*28*) have reported the potential depolymerization of starch into glucose, maltose, and dextrins following exposure to high doses of ionizing radiation. It was hypothesized that glycosidic linkages, which hold glucose units of starch together, are broken by irradiation (*26*, *29*).

Formation of deoxy and carbonyl products upon irradiation is another important consideration of radiation chemistry of carbohydrates (*26*). Irradiation in the presence of atmospheric oxygen increases the amount of such radiolysis products. Winchester (*30*) developed a chemical method based on the analysis of malonaldehyde to detect irradiated starch samples. However, malonaldehyde formation was affected by humidity and acidity of starch samples, and the malonaldehyde content decreased over time.

In this study FT-Raman and FTIR spectroscopic techniques were used to characterize the changes in starch due to irradiation. Comprehensive characterization of infrared and Raman spectra of six selected starches (corn, high-protein-containing corn, high-oil-containing corn, wheat, potato, and waxy starches) was conducted. On the basis of that characterization, specific chemical groups and linkages corresponding to radiochemical changes were identified, and a chemometric method was developed to differentiate samples based on the extent of irradiation. The specific objectives of this research are to (i) characterize selected starches and their irradiated forms based on FTIR and FT-Raman spectra, and (ii) classify starch samples on the basis of the extent of irradiation.

MATERIALS AND METHODS

Four different starches (potato, waxy, wheat, and corn) were obtained from Sigma Chemical Co. (St Louis, MO). Starches from high-protein and high-oil corn were provided by Dr. Ralph Waniska at Texas A&M University. Aliquots of 2 g of starch samples were irradiated at 3, 5, or 10 kGy using a Gammacell 220 (MDS Nordion, Ottawa, ON) Co^{60} gamma irradiator with the dose rate of 2.1 kGy/hr at the Breazeale nuclear facility at Pennsylvania State University. The dose rate at the center of the chamber was measured using ferrous sulfate dosimetry as per MDS Nordion quality control specifications. Thirteen starch samples (three of high-protein corn starch and two each of the other starches) were irradiated at 10 kGy, and fourteen starch samples (three each of waxy and wheat starches and two each of other starches) were irradiated at both 5 kGy and 3 kGy. Twelve samples (two of each starch) were used as native samples for control. A total of fifty-three starch samples in six different types were used.

FTIR Measurements. FTIR spectra were recorded using a Nicolet model 870 spectrometer (Madison, WI) equipped with a deuterated tryiglycine sulfate (DTGS) detector. The sampling station was equipped with an overhead DRIFTS accessory. The sample holder was used for the background spectra without KBr, and 256 coadded scans were taken for each sample from 4000 to 400 cm^{-1} at a resolution of 16 cm^{-1}. Single-beam spectra of the samples were obtained, and corrected against the background spectrum of the sample holder, to present the spectra in absorbance units. Spectra were collected in duplicate and used for multivariate analysis.

FT-Raman measurements. FT-Raman spectra were obtained using a Nicolet 870 spectrometer with the Raman module 32B (Madison, WI) and Nd:YAG laser operating at 1064 nm with a maximum power of 2 W. The system was equipped with an InGaAs (Indium−Gallium Arsenide) detector, XT-KBr beam-splitter with 180° reflective optics, and a fully motorized sample position adjustment feature. A laser output power of 0.77 W was used, which was low enough to prevent possible laser-induced sample damage yet provided a high signal-to-noise ratio. Data were collected at 16 cm^{-1} resolution with 256 scans. Spectra were obtained in the Raman shift range between 400 and 4000 cm^{-1}. The system was operated with the OMNIC 5.1 software and experiments were done in duplicate.

Chemometrics (Discriminant Analysis). Discriminant analysis of irradiated samples was conducted using the Win-DAS (Wiley, Chichester, U.K.) software package. Before processing the spectral data, area normalization and baseline correction of the spectra were done to eliminate certain unwanted instrumental and cosmetic effects on the data set (*31*). Multivariate methods such as principal component analysis (PCA) and partial least squares (PLS) methods were used to compress the data to a manageable size. A total of fifty-three samples in four groups (twelve native, fourteen irradiated at 3 kGy, fourteen irradiated at 5 kGy, and twelve irradiated at 10 kGy) were analyzed and their respective spectra were used for multivariate analysis. PCA or PLS was first used to compress the data to obtain the scores or factors (reduced form of raw spectral data). These factors or scores were then used in canonical variate analysis (CVA) to classify starches within the 95% tolerance level based on extent of irradiation level.

RESULTS AND DISCUSSION

Band Assignments for Infrared and Raman Spectra of Non-Irradiated Starches. The infrared (**Figure 1**) and Raman (**Figure 2**) spectra of starches exhibited almost identical bands, because these bands originate mainly from the vibrational modes of amylose and amylopectin. The most significant differences between the Raman and infrared spectra of different nonirradiated starches were observed in the O−H stretching regions of water molecule (3000−3600 cm^{-1}), possibly due to differences in water content. The FTIR and FT-Raman band assignments are listed in **Table 1**.

Investigation of both FT-Raman and FTIR spectra of starches in four main regions helps in successive interpretation and characterization of the key bands. These regions were as follows: below 800 cm^{-1}, 800−1500 cm^{-1} (the fingerprint region), the region between 2800 and 3000 cm^{-1} (C−H stretch region), and finally the region between 3000 and 3600 cm^{-1} (O−H stretch region).

Both Raman and infrared spectra of starches exhibited complex vibrational modes at low wavenumbers (below 800 cm^{-1}) due to the skeletal mode vibrations of the glucose pyranose ring (*32*, *33*). In this study, major bands at 627 and 581 cm^{-1} and minor bands between 560 and 400 cm^{-1} in the infrared spectra (**Figure 1**) of starches were attributed to the

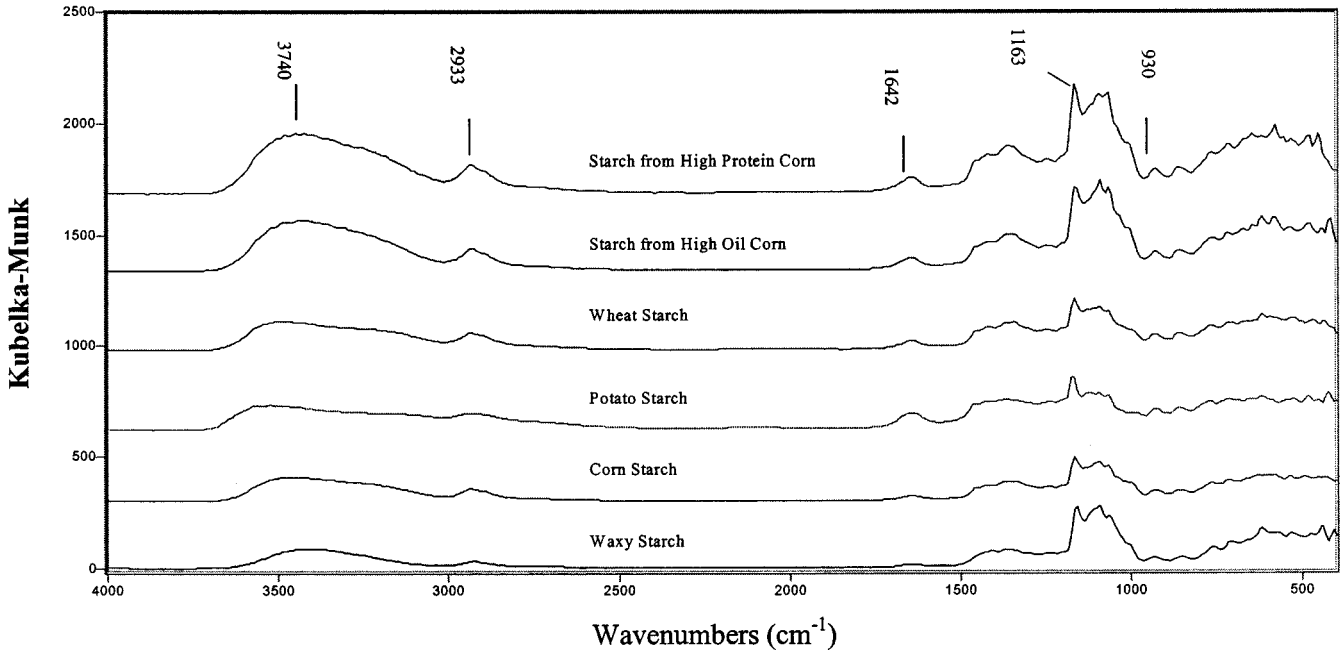

Figure 1. FTIR spectra of native (nonirradiated) starches.

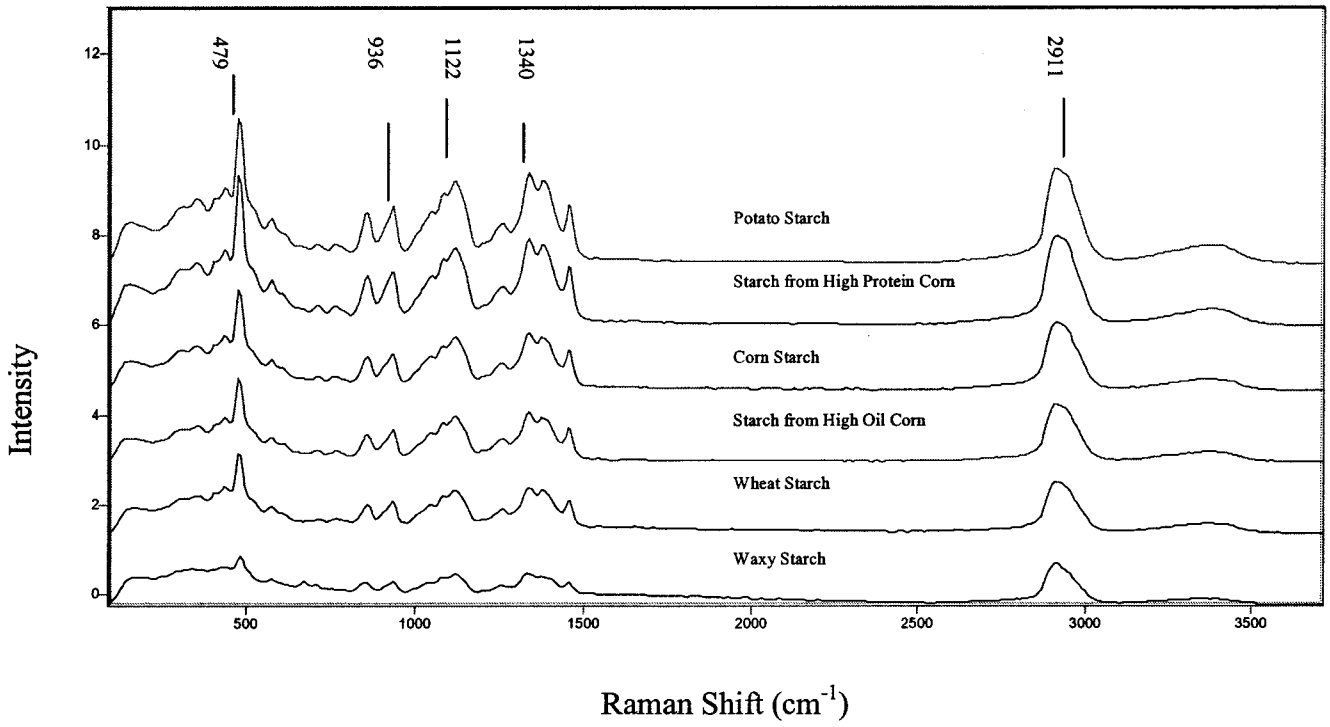

Figure 2. FT-Raman spectra of native (nonirradiated) starches.

skeletal modes of the pyranose ring. Raman bands at 673, 576, 478, and 440 cm^{-1} (**Figure 2**) were also attributed to the skeletal vibrations of the pyranose ring in the glucose unit of starches. Among the Raman bands, a strong band at 478 cm^{-1} (**Figure 2**) depicting the degree of polymerization in polysaccharides (*34*) was one of the dominating and important skeletal vibration modes of the pyranose ring.

The region between 800 and 1500 cm^{-1} provided highly overlapping and complex spectra making the exact band assignment difficult (*32*). The infrared and Raman spectra of polysaccharides (amylose, amylopectin, cellulose, and starch) in this region mainly originate from the vibrational state of its monomer glucose unit (*35*−*37*). For this reason, information obtained from glucose spectra have been used in the assignment of wavenumbers to the corresponding vibrational mode of starches. Because the vibrations of glucose molecules dominate the spectral region below 1500 cm^{-1} in both Raman and infrared spectra, starches exhibit very similar spectral characteristics in this region. The vibrations originating from the C−O−C of α-1,4 glycosidic linkages could be observed as a strong Raman band in the vicinity of 920−960 cm^{-1} (*32*). As glucose does not represent any Raman band in the region between 914 and 998 cm^{-1}, the band obtained at 940 cm^{-1} in the amylose Raman spectra was attributed to the α-1,4 glycosidic linkage (*32*, *37*, *38*). In our study, the infrared absorption band at the 930 cm^{-1} (**Figure 1**) and Raman band at 936 cm^{-1} (**Figure 2**) were attributed to the glycosidic linkages in starches. In both the FT-Raman and FTIR spectra of native starches, very subtle

Table 1. Band Assignments[a] for Raman and Infrared Spectra of Starch

Raman (cm^{-1})	Raman band assignment	Infrared (cm^{-1})	Infrared band assignment
440	skeletal modes of pyranose ring (*32–34*)	537	skeletal modes of pyranose ring[*33*]
478		581	
576		627	
673		711	
710		764	C–C stretching (*37, 38*)
763	C–C stretching (*37, 38*)	860	C(1)–H, CH_2 deformation (*37, 38*)
860	C(1)–H, CH_2 deformation (*37, 38*)	930	skeletal mode vibrations of α–1,4 glycosidic linkage, (C–O–C) (*33, 37, 39*)
936	skeletal mode vibrations of α-1,4 glycosidic linkage, (C–O–C) [(*32, 33 ,37, 39*)	1067	C(1)–H bending (*37, 38*)
1087	C–O–H bending (*38*)	1094	C–O–H bending (*38*)
1122	C–O stretching, C–O–H bending (*38, 39*)	1163	C–O, C–C stretching (*38*)
1260–1280	CH_2OH (side chain) related mode (*38, 39*)	1242	CH_2OH (side chain) related mode (*38*)
1339	C–O–H bending, CH_2 twisting (*38*)	1344	C–O–H bending, CH_2 twisting (*38*)
1382	CH_2 scissoring, C–H and C–O–H deformation (*38, 39*)	1415	CH_2 bending, C–O–O stretch (*38*)
1460	CH_2 bending (*37, 38*)	1642	water adsorbed in the amorphous regions of starch (*39, 41*)
2800–3000	C–H stretching (*39*, *40*)	2800–3000	CH_2 deformation (*39*)
3100–3600	O–H stretching (*39*, *40*)	3000–3600	O–H stretching (*39*)

[a] Corresponding references for band assignments are given in parentheses ( ).

changes in the peak location and intensity of the glycosidic linkage band occurred. The reason for change in the location can be attributed to the presence of α-1,6 linkage of the amylopectin that shifts the band to higher wavenumbers.

The Raman band at 1260 cm^{-1} (**Figure 2**) was attributed to CH_2OH related deformation that is characteristic of the V-form amylose (*38, 39*). The band at 1122 cm^{-1} was attributed to contribution of two main vibrational modes, C−O stretching and C−O−H deformation, and the band at 1087 cm^{-1} could be attributed to the C−O−H bending mode (*38*). Raman band at 1460 cm^{-1} was attributed to the CH_2 deformation and the 1382 cm^{-1} band in the Raman spectra was probably due to the bending modes of C−H (*37, 38*). The FTIR absorption band at 1242 cm^{-1} was attributed to the CH_2OH related mode as well as the C−O−H deformation mode (*38*). The peak at 1163 cm^{-1} was due to the coupling modes of C−O and C−C stretching, and the band at 1094 cm^{-1} could be could be attributed to the C−O−H bending modes (*38*). The vibrational bands (bending and deformation) related to the carbon and hydrogen atoms could be observed in the region 1500−1300 cm^{-1} (*40).* The infrared band at the 1344 cm^{-1} could be originated from CH_2 bending modes (*38*).

Water adsorbed in the amorphous region of starches could be identified as a broad infrared band with a peak at 1637 cm^{-1} (*39, 41*). Because water has a weak Raman cross-section, the water band observed in the infrared spectra could be hardly noticed in the Raman spectra. As the crystallinity of starch increases, this band becomes weaker in the infrared spectra, and for most crystalline cellulose, the band at 1637 cm^{-1} was barely observed (*39*). This finding supports the hypothesis that the 1637 cm^{-1} band is a result of the vibrations of water molecules adsorbed in the noncrystalline region of starch. The band observed at 1642 cm^{-1} (**Figure 1**) was attributed to the water adsorbed in the amorphous region of starch granules. As this band is related to the crystallinity of starch, variations in the crystallinity of different starches have the potential to affect this band. It is observed in this study that potato starch offered sharper bands around 1642 cm^{-1} than those of other starches probably because of differences in the crystal polymorph of the starches. Potato starch has a B-type polymorph, whereas other starches used in this study have A-type crystals (*42*).

Characterization of C−H and O−H stretch could be readily accomplished by spectral analysis. Both FT-Raman and FTIR spectra of starches showed C−H stretching modes in the 2800−3000 cm^{-1} region. Intensity changes in this range could be attributed to the variations in the amount of amylose and amylopectin present in starches. For example, corn starch has 28% amylose, whereas potato starch has 20% amylose content (*43*). The O−H stretching mode of starches was observed in the region of 3100−3500 cm^{-1} in the Raman spectra (**Figure 2**) and between 3000 and 3600 cm^{-1} in the FTIR spectra (**Figure 1**).

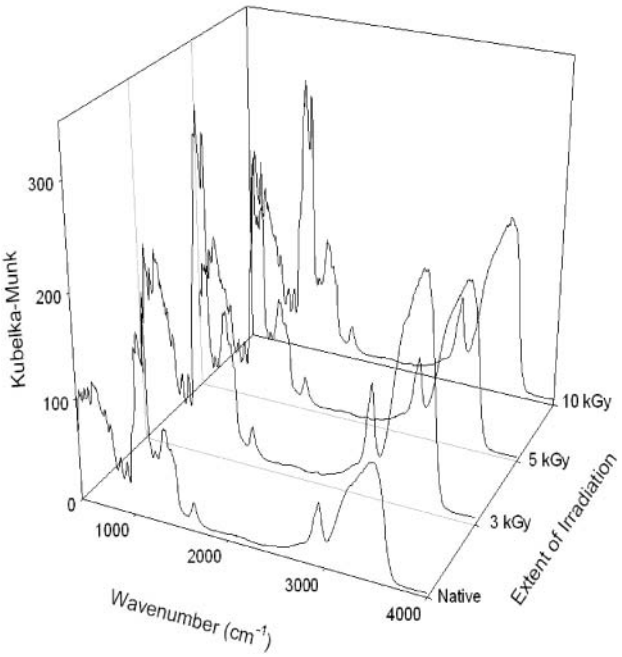

Figure 3. FTIR spectra of corn starches irradiated at different radiation doses.

Classification of Irradiated Starches. Figures 3 and **4** show the spectra of native (nonirradiated) and irradiated (3, 5, and 10 kGy irradiation doses) forms of corn starches obtained from FTIR and FT-Raman spectrometers, respectively. The multivariate statistical technique CVA was applied to classify starches based on the extent of irradiation. Four different spectral regions (the adsorbed water, glycosidic linkage, the C−H stretch, and the O−H stretch bands) were selected as inputs for the CVA analysis to discriminate the irradiated starches and nonirradiated starches based on the variations in their spectral data.

Table 2. Classification of Starches Using CVA

bands used in CVA analysis	type of spectroscopy	number of PLS factors required to discriminate native starch from irradiated ones	number of PLS factors required to discriminate starches in terms of their radiation doses
water adsorbed in amorphous region (1550–1750 cm^{-1})	Infrared	5	8
C–H	Infrared	10	14
region (2800–3000 cm^{-1})	Raman	12	NA
O–H	Infrared	12	NA
region (3000–3600 cm^{-1})	Raman	14	NA
glycosidic linkage	Infrared	12	16
region (900–950 cm^{-1})	Raman	14	NA

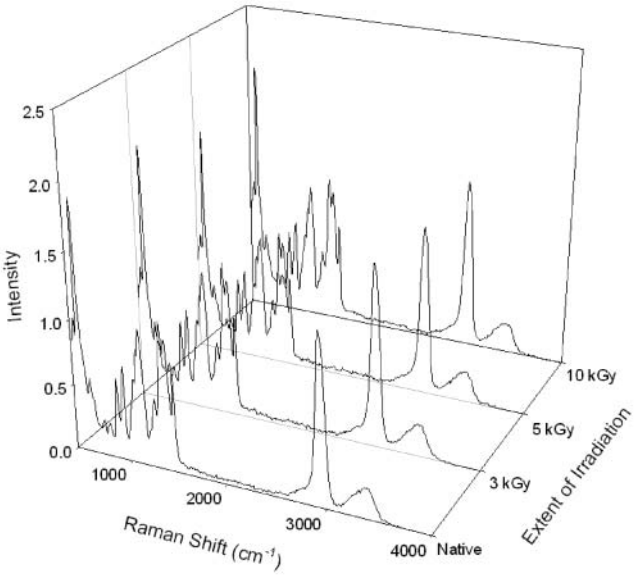

Figure 4. FT-Raman spectra of corn starches irradiated at different radiation doses.

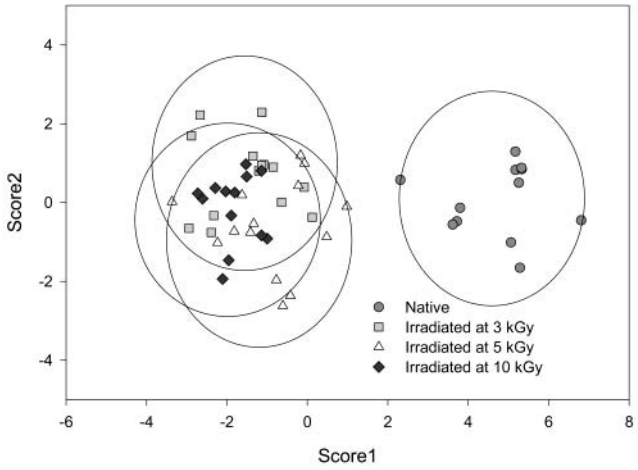

Figure 5. Discrimination of irradiated starches from native starches using CVA with 5 PLS factors. FTIR amorphous band spectral data in the 1550–1750 cm^{-1} region were employed.

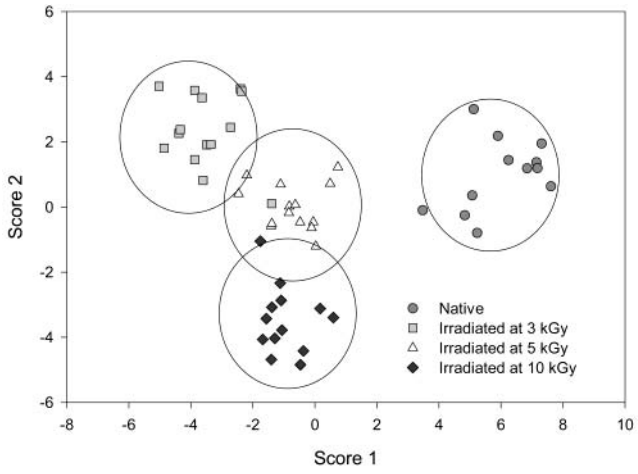

Figure 6. Discrimination of starches in terms of radiation doses using CVA with 10 PLS factors. FTIR amorphous band spectral data in the 1550–1750 cm^{-1} region were employed.

The infrared band observed between 1550 and 1750 cm^{-1} (**Figure 3**) with a peak at 1642 cm^{-1}, due to water adsorption in the amorphous region, was selected for classification analysis using CVA. Because investigations of the vibrational band due to water adsorbed on the amorphous regions of starch may correspond with the change in crystallinity upon irradiation, monitoring the changes in this band could be used for the detection and classification of irradiated starches.

Using the wavenumber range 1550−1750 cm^{-1}, five PLS factors (as same as PC scores) were necessary in the CVA model for a complete discrimination of irradiated starches from the nonirradiated starches (**Table 2**). **Figure 5** shows the CV score plot obtained with 95% tolerance regions for each group predefined. A better separation of irradiated starches could be obtained by using a higher number of factors in the CVA model. Ten PLS factors were required to create clusters of starches based on the extent of the irradiation (**Figure 6**). It is noteworthy to mention that potato starch and waxy corn starch samples were always placed on the borders of clusters, probably because waxy corn starch is composed primarily of amylopectin and potato starch has a B-type crystal polymorph, whereas others have an A-type polymorph (*44*). Excluding potato and waxy starch spectra may offer better clustering of irradiated starches. The findings obtained in the CVA analysis of the adsorbed water band suggested that crystallinity of starches could be affected by irradiation.

The spectra obtained from the C−H stretch (2800−3000 cm^{-1}) region could also be used to detect irradiated starches, as the hydroxyl radicals formed by water radiolysis rapidly attack the hydrogen of any C−H bonds liberating the hydrogen atom from the bond (*26*). This effect is most apparent for aqueous solutions of carbohydrates, because more hydroxyl radicals can be formed under aqueous conditions. Using the FTIR C−H stretch data, a CVA model using ten PLS factors was able to completely separate nonirradiated starches from irradiated ones (**Figure 7**). Fourteen PLS factors were needed to obtain a fairly good clustering of starches based on irradiation doses (**Table 2**). Raman spectral data in the same region with twelve PLS factors provided a reasonable CVA model for complete segregation of nonirradiated starches (**Table 2**). The

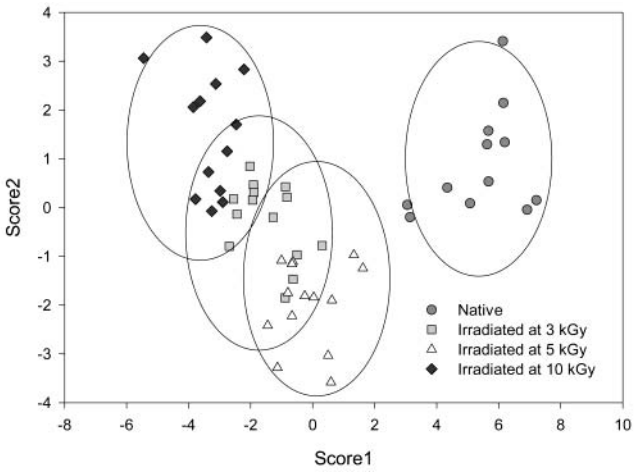

Figure 7. Discrimination of irradiated starches from native starches using CVA with 10 PLS factors. FTIR C–H stretching band spectral data in the 2800–3000 cm^{-1} region were employed.

need for high PLS factors in the discrimination models using the C−H stretch data suggests that hydrogen abstraction from C−H bonds is not severe for starch granules. This statement is in agreement with the past research on carbohydrate irradiation that irradiation of starches under nonaqueous conditions results in subtle changes in the structure (*25*, *26*).

Because ionizing energy breaks down the structure of water, forming hydroxyl and hydrogen radicals, the bound water and the moisture content of starch samples would be affected by irradiation. CVA models using the 3000−3600 cm^{-1} region (O−H stretch) showed that discrimination of irradiated starches from their nonirradiated forms could be obtained only if more PLS factors were used (**Table 2**), suggesting that radiolysis of bound moisture does not produce an excessive amount of free radicals. If the amount of free radicals (solvated electrons, hydroxyl radical, and hydrogen atom) formed by the radiolysis of water is not sufficient, radiation-induced reaction in food macrostructure will not be significant.

Glycosidic linkage is described as the connection of the first carbon atom of a glucose unit with the fourth carbon atom of the other glucose molecule via an oxygen atom (C_1-O-C_4). Stretching vibrations of (C_1-O) and (C_4-O) of the glycosidic linkage could be detected by vibrational spectroscopic methods. The region 900−950 cm^{-1} is where glycosidic-linkage-related vibrational modes are observed in both spectroscopic techniques. CVA models with very high factors (more than 12) exhibited a reasonable clustering of native starch from others using either FTIR or Raman data in 900−950 cm^{-1} region (**Table 2**). Irradiation of monosaccharides in an aqueous environment results in destruction of pyranose ring and formation of some radicals (*45*). However, no report on the destruction of pyranose ring of starch or any other polysaccharides has been stated. The bands at low wavenumbers are associated with skeletal mode of pyranose ring vibration. Our spectral detection on these bands showed no significant variations in either band shift or intensity. Most research on the irradiation of starch suggests that some glycosidic linkages are broken after irradiation (*12*, *25*, *26*). As a result, depolymerization of starch by ionizing radiation can be exploited in the detection of irradiated granular starches using FTIR or FT-Raman spectroscopy.

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