Rapid determination of vitamin C by NIR, MIR and FT-Raman techniques

Hong Yang and Joseph Irudayaraj

Abstract

Rapid spectroscopic determination of vitamin C in food and pharmaceutical products using infrared and Raman techniques was proposed. In this study, near-infrared (NIR), Fourier transform near-infrared (FT-NIR), Fourier transform infrared-attenuated total reflectance (FTIR-ATR), diffuse reflectance (DRIFTS), Fourier transform infrared-photoacoustic (FTIR-PAS) and FT-Raman spectroscopy were used in conjunction with partial least squares (PLS) regression to quantify vitamin C in powdered mixtures and solutions. Results indicate that the methods adopted have high prediction correlation. R^2 values were 0.999 for FTIR-ATR, 0.976 for DRIFTS, 0.966 for FTIR-PAS, 0.988 for NIR, 0.992 for FT-NIR and 0.95 for FT-Raman, with an overall prediction error of 0.2–3.0%. The time required to complete an experiment ranged from 5 s (NIR) to 3 min (FT-Raman). The FTIR and FT-Raman techniques can be complementary tools for qualitative and quantitative characterization of the samples. Infrared and Raman techniques can be used to quantify vitamin C in foods and pharmaceutical products.

Introduction

Vitamin C (ascorbic acid), one of the water-soluble vitamins, can be found widely in raw fruits, vegetables and other food products, such as juices and sports drinks. As the awareness of the health benefits of vitamin C as an essential nutrient and antioxidant is increasing, so are its products and by-products. Even vitamin-C-fortified foods, such as breakfast cereals, are becoming more and more popular and in demand. Normally, the concentration of vitamin C varies in different products. Manufacturing processes, such as heating, can cause loss of vitamin C in the products. Therefore, there is a need to quantify vitamin C present in foods and pharmaceutical products for quality control purposes.

Arya et al (1998, 2000) have summarized the techniques used to determine vitamin C in a variety of samples; these include colorimetry, titrimetry, UV spectrophotometry and chemiluminescence, as well as kinetic, electrochemical, fluorometric, chromatographic and other spectroscopic methods. However, each method has its limitations. For example, the titrimetric method is rapid but requires a large quantity of sample and is unsuitable for the analysis of coloured samples (Özgür & Sungur 1995). HPLC, one of the chromatographic methods, is very accurate but is time consuming. There is a need for a fast, selective, non-destructive and accurate method to routinely determine the vitamin C concentration in food and pharmaceutical products.

Infrared and Raman techniques have been used to non-destructively quantify and characterize biological samples. These techniques can rapidly provide a considerable amount of information about an individual sample. In the past, the near-infrared (NIR) region between 1100 and 2500 nm (9091–4000 cm^{-1}) has been used successfully to determine multiple components, such as fat, protein and moisture, in foods and agricultural products (Williams & Norris 1987). In the NIR region, characteristic bands of each component typically overlap with each other and generally hinder the identification of individual components. NIR spectroscopy was used to determine vitamin C in pharmaceutical products at concentrations of 16.67, 22.88 and 40% using step-wise multiple linear regression (SMLR) and partial least squares (PLS) regression (Blanco et al 1993); the prediction errors were 1–2%.

Department of Human Environment and Family Sciences, North Carolina A&T State University, 161 Carver Hall, Greensboro, NC 27411, USA

Hong Yang

Department of Agricultural & Biological Engineering, The Pennsylvania State University, 227 Agricultural Engineering Building, University Park, PA 16802, USA

Joseph Irudayaraj

Correspondence: H. Yang, Department of Human Environment and Family Sciences, North Carolina A&T State University, 161 Carver Hall, Greensboro, NC 27411, USA. E-mail: hyang@ncat.edu

Mid-infrared (MIR) spectroscopy has been used for qualitative and quantitative characterization of food materials. Normally, spectral analysis in the MIR region is carried out using Fourier transform infrared (FTIR) spectroscopy. Compared with NIR, FTIR spectroscopy is preferred for qualitative analysis because of its high signal-to-noise ratio, sensitivity, resolution and narrower bands. However, when moisture is present in the sample, a very strong absorbance in the MIR region occurs which overlaps with the other key bands. Moisture bands in the 3700–3100 cm^{-1} region (O—H stretch) and at 1640 cm^{-1} (O—H bend) overlap with protein bands at 3300 cm^{-1} (amide A), 1650 cm^{-1} (amide I), and 1450 cm^{-1} (amide II). In recent years, quantitative analysis in the MIR region has become more popular due to the availability of low-cost FTIR spectrometers and appropriate accessories, such as the diffuse reflectance (DRIFTS), attenuated total reflectance (ATR) and photoacoustic spectroscopy (PAS).

DRIFTS is mostly used for analysis of powders. Sample preparation usually involves mixing or diluting (in the ratio 1:19) the powder sample in a non-absorbing matrix, such as potassium bromide (KBr), to minimize spectral artifacts (Blitz 1998). Mixing a powdered sample with KBr for quantitative analysis avoids effects of non-linearity and saturation in the DRIFTS spectrum. However, direct analysis of powdered samples using DRIFTS, without mixing with KBr, was successfully accomplished in conjunction with chemometrics (Reeves & Zapf 1998; Yang & Irudayaraj 1999). The work presented here explores DRIFTS analysis without sample preparation.

FTIR-ATR suitable for liquid analysis was successfully applied to characterize oils and fats (Yang & Irudayaraj 2000) and to determine sugars in commercial beverages (Sivakesava & Irudayaraj 2000). FTIR-ATR spectroscopy has also been used to determine water-soluble vitamins B_1, B_2, B_6 and niacin (Wojciechowski et al 1998). Fourier transform near-infrared (FT-NIR) spectroscopy has been used for quantitative analysis of vitamin C in a mixture of vitamin C and rutin, using SMLR, PLS and principal component analysis (PCA) to obtain a correlation coefficient of 0.99 (Du et al 2000). However, an evaluation of the spectroscopic methods and a comparative study of vitamin C determination was neither attempted nor conducted. A more recent non-destructive procedure using FTIR photoacoustic (FTIR-PAS) spectroscopy was also used in vitamin C analysis. Details of FTIR-PAS for powder analysis have been published by Yang & Irudayaraj (1999).

The application of Fourier transform Raman (FT-Raman) spectroscopy in food (Ozaki et al 1992) and pharmaceuticals (Cutmore & Skett 1993) is gaining acceptance, because of its excellent frequency precision, good signal-to-noise ratio and minimal data acquisition time (Schrader 1996). Like MIR spectra, FT-Raman spectra can provide chemical fingerprints of functional groups in the sample. However, moisture does not interfere with FT-Raman measurement because the Raman spectrum of water contains three low intense peaks (Findlay & Bugay 1998). There are, however, differences between Raman and infrared techniques due to different phenomena. For example, the polar O—H group has a strong absorbance in the infrared spectra but a weak Raman scattering in the Raman spectra. On the other hand the non-polar C—C group has a strong Raman scattering band in Raman spectra but weak absorption bands in the infrared. Only one study has been reported (Hancewicz & Petty 1995) on the FT-Raman determination of vitamins (vitamin A).

The purpose of this study is to compare and evaluate the feasibility of the non-invasive NIR, MIR and Raman spectroscopy for determination of vitamin C in powdered and liquid systems.

Materials and Methods

Materials

Determination of vitamin C in powdered mixtures and in liquid was performed. Vitamin C powder (99.99%; Alfa Aesar, Ward Hill, MA) and pregelatinized starch (Instant TENDER-JEL C; A. E. Staley Manufacturer Co., Decatur, IL) were used to prepare powdered binary mixtures. Note that starch, generally considered as the base material, was chosen as a substrate in our experiments. The concentration of vitamin C in the binary mixture varied from 0 to 35% in steps of 3%. The study of liquid systems consists of aqueous solutions of vitamin C prepared by dissolving vitamin C in distilled water in the concentration range 0–21% (in steps of 3%). The sample was then used for spectroscopic measurement; all experiments were replicated four times.

NIR measurement

A DA 7000 Visible/NIR dispersive spectrometer (Perten Instruments Inc., Springfield, IL) with silicon and InGaAs diode arrays was used for the determination of vitamin C in binary powder mixtures in NIR. A fibre optic probe was attached to the spectrometer for data collection as described by Oskin (2000). White PVC tubing two inches in diameter was used to maintain a two-inch distance between the sample and the probe. The powder sample (~ 3.5 g) was placed in a 50-mL aluminium weighing dish (VWR) for NIR measurement. For each spectrum, an average of 30 scans over the 400–1700 nm wavelength range at 10-nm intervals was recorded. A white Spectralon plate (Labsphere Inc., North Sutton, NH) was used as a reference. Each test was set up to automatically obtain three measurements.

FT-NIR measurement

The Nexus 870 FTIR spectrometer (Nicolet Instrument Corp., Madison, WI) with a deuterated tri-glycine sulfate (DTGS) detector and an interferometer was used. White light was selected as the light source for FT-NIR measurement. The whole system was purged of moisture and CO_2, by filtered dry air from FTIR purge gas generator (Model 75-52; Whatman, Inc., Haverhill, MA). The resolution was kept at 16 cm^{-1} with a scan number of 256, and the spectral

region considered was in the range 8000–4000 cm^{-1}. A spectrum of Spectralon, placed on the surface of a Petri dish, was used as a reference. For actual measurements, the powdered sample was placed in a transparent Petri dish (VWR) at the top of a Nicolet Near-IR UpDRIFT accessory.

FTIR-ATR measurement

The Nexus 870 FTIR spectrometer with a DTGS detector was used for FTIR-ATR vitamin C measurement in the MIR region. A ZnSe ATR sampling accessory from Spectra-Tech (Shelton, CT) was used for ATR measurements. ATR spectra were collected at the rate of 256 scans/sample with 16 cm^{-1} resolution. Before scanning each sample, a background spectrum of distilled water was stored in the computer. Aqueous solution of vitamin C was poured onto the ATR ZnSe crystal for measurement.

DRIFTS measurement

The Nexus 870 FTIR spectrometer (Nicolet Instrument Corp., Madison, WI) with the diffuse reflectance accessory (Spectra-Tech, Shelton, CT) was used for DRIFTS measurements. The background spectrum was recorded with KBr powder and stored in the computer. The powder was placed directly in the sample cup used for actual measurement. The spectra were collected using 256 scans/sample at a resolution of 16 cm^{-1}.

FTIR-PAS measurement

An FTS 6000 research-grade FTIR spectrometer (Bio-Rad Laboratories, Cambridge, MA) with a helium-purged photoacoustic (PA) detector (MTEC Photoacoustics Inc., Ames, IA) was used to collect the PA spectra. Carbon black was used as the background. Half of the stainless-steel cup (10 mm diameter, 3 mm depth) of the PA accessory was filled with the sample using a suitable sample funnel. The PA detector was purged with helium for 5 min and then sealed. Spectra of samples were obtained at a resolution of 16 cm^{-1} and scan numbers of 256.

FT-Raman measurement

The FT Raman spectrometer (Nicolet Instrument Corp., Madison, WI) equipped with an InGaAs detector and HeNe laser operating at 1064 nm excitation with a maximum power of 0.7 W was used. The powder was simply loaded in a glass vial (17 × 60 mm) and FT-Raman measurements taken; spectra were collected using 256 scans/sample at 16 cm^{-1} resolution.

Data analysis

The PLS analysis can provide useful information relevant to the chemical composition from the complex infrared spectra (Bjørsvik & Martens 1992). PLS was applied to decompose the calibration spectra into a series of variables, to simultaneously account for the variance in the spectral data, and to correlate with the analyte concentration. Of the spectra obtained, 75% was used for calibration and 25% was used for validation. The PLS regression using the PLSplus/IQ from GRAMS/32 (Galactic Industries Co., Salem, NY) was used to determine the concentration of vitamin C in the sample. The selection of the spectral region is the first step in obtaining the calibration model. This process will help to eliminate regions dominated by the noise and non-useful information that might reduce the predictability of the model. An optimal calibration model based on the highest R-square and the lowest standard error of calibration was chosen as the best-fit model. Before computing the calibration model, highly correlating regions in the spectra need to be identified for proper variable selection and to reduce the number of variables. Multiplicative scatter correction (MSC) was used to assist in this PLS analysis. Optimal number of factors for the calibration model was selected based on the minimal value of the predicted residual sum of squares (PRESS) and the highest correlation coefficient (R^2) between actual and predicted values. The resulting models were evaluated in terms of the number of factors, standard error of estimate (SEE), standard error of cross-validation (SECV) and correlation coefficient (R^2). The SEE can provide information on the degree of fit of the regression and is calculated as the square root of the residual variance divided by the number of degrees of freedom. The SECV is an estimate of the expected magnitude of error.

Results and Discussion

FTIR-ATR

Figure 1A shows the FTIR-ATR spectra (2000–800 cm^{-1}) of solutions containing concentrations of vitamin C. The major peaks and their assignments assessed from the general spectroscopic absorption (Silverstein et al 1991) are given in Table 1. The peaks corresponding to the functional groups of vitamin C are listed in Table 1. All of the C—H, C=O, C=C, C—O—C and O—H groups were displayed in the MIR region as shown in Figure 1A. In general, spectral intensity increased as the concentration of vitamin C increased. The O—H bending due to a small shoulder at 1650 cm^{-1} gradually disappeared as the concentration of vitamin C increased. The intensity or absorbance of C=C (1682 cm^{-1}) also increased with increase in concentration of vitamin C and eventually overlapped with the weak shoulder at 1650 cm^{-1}.

For quantitative analysis, the intensities in the spectral region 1800–1000 cm^{-1} were chosen because of the predominant peaks that correlated highly with the concentrations of vitamin C from PLS analysis. The minimal PRESS value will assist in determining the optimum number of factors in the calibration model. A minimal PRESS value of 0.0002 was obtained corresponding to 11 factors in the PLS calibration model (Table 2) evaluated by cal-
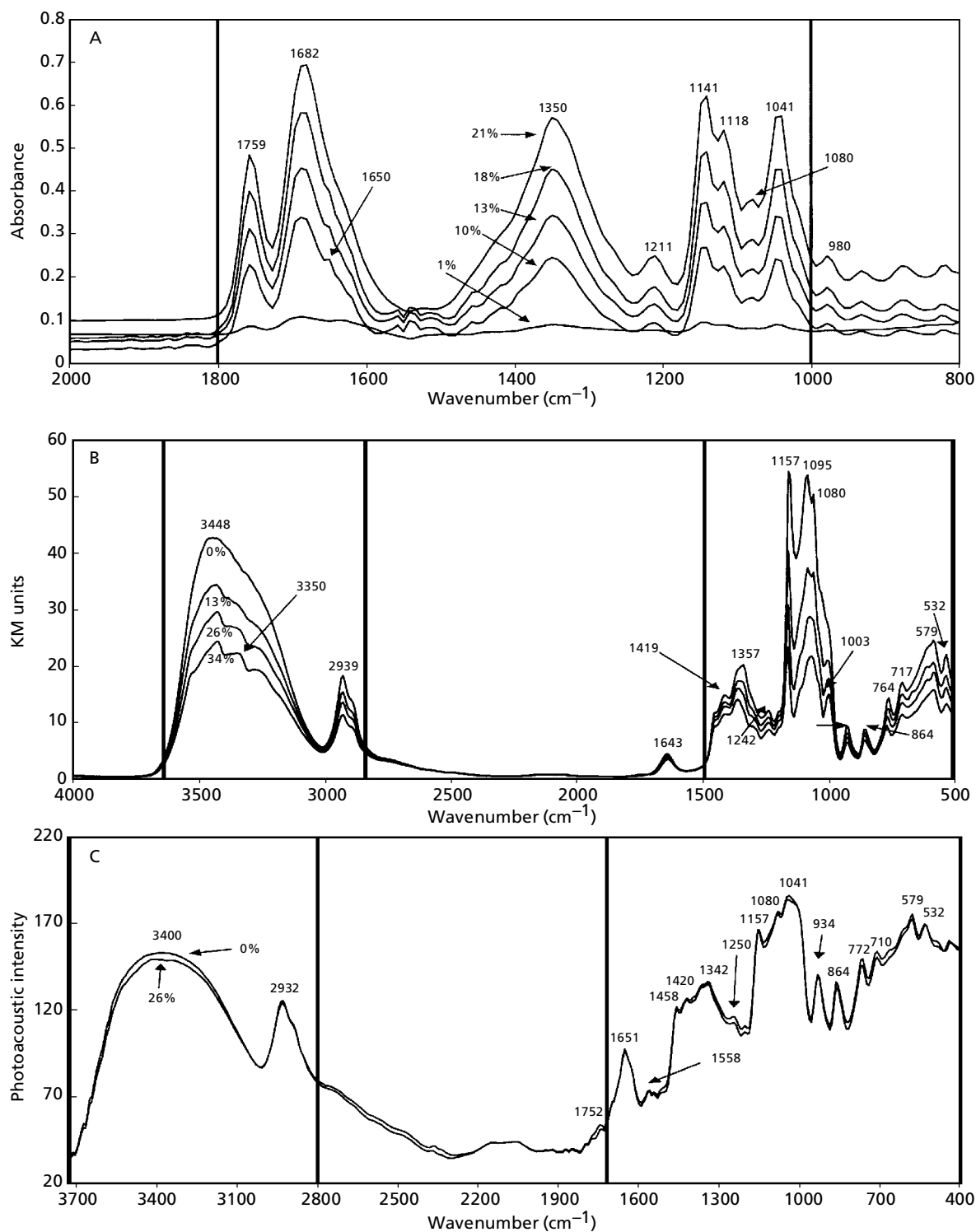
Figure 1   Plots of FTIR-ATR spectra (A), DRIFTS spectra (B) and FTIR-PAS spectra (C) of vitamin C in binary mixtures.

culating the SECV and R^2 values for the calibration and the SEE and R^2 values for the validation data set. Results of the calibration and validation sets for vitamin C in solution are listed in Table 2. An R^2 value of 0.999 and 0.998, and an SECV of 0.27% and SEE of 0.28% were obtained for calibration and validation data sets, respectively. Results show that FTIR-ATR successfully predicted the concentration of vitamin C in solution and has the potential for vitamin C determination in complex systems such as fruit juices and other aqueous systems.

Table 1 Chemical assignment of bands in MIR region for the FTIR-ATR, DRIFTS and FTIR-PAS spectra.

Wavenumber (cm^{-1})			Vibration of mode	Intensity
FTIR-ATR	DRIFTS	FTIR-PAS		
	3448	3400	O—H stretch	s, br
	3360		Overtone of C=O stretch	sh
	2939	2923	C—H stretch	m
1759		1752	C=O stretch	s, m
1682			C=C stretch	s
1650	1643	1651	O—H bend and C=O stretch	sh, m
		1558	C=O stretch and C—C ring stretch	w
	1458	1458	C—H bend	sh
	1419	1420	C—O—H bend	sh
1350	1357	1342	C—O—H bend	s, m
	1242	1250	C—O—H bend	w
1211			C—C(=O)—O stretch	w
1141	1157	1157	C—O—C stretch	m
1118			C—O—C stretch	sh
	1095		C—O—C stretch	s
1080	1080	1080	C—O—C stretch and C—O—H bend	sh
1041		1041	C—O—C stretch and C—O—H bend	s, m
	1003		C—O—C stretch and C—O—H bend	sh
980			C—H and O—H bend	w
	925	934	C—H bend and C—C ring bend	m
	864	864	C—H bend	m
	717	710	C—H bend	sh
	579	579	C—H bend	m
	532	532	C—H bend	m

s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Table 2 Calibration and validation model evaluation of the NIR, MIR and FT-Raman methods.

	Calibration				Validation	
	Factor no.	PRESS	SECV	R^2	SEE	R^2
FTIR-ATR	11	0.0002	0.23%	0.999	0.28%	0.998
DRIFTS	9	0.0148	1.82%	0.976	1.93%	0.975
FTIR-PAS	9	0.0183	1.95%	0.966	1.45%	0.985
NIR	5	0.0280	1.35%	0.988	1.23%	0.973
FT-NIR	3	0.0062	0.96%	0.992	1.64%	0.980
FT-Raman	5	0.0219	2.47%	0.950	2.68%	0.941

DRIFTS

The DRIFTS spectra of vitamin C in powder are presented in Figure 1B. The major peaks in the MIR region were labelled and their modes of vibration listed in Table 1. Unlike FTIR-ATR, DRIFTS spectra clearly show an increase in the intensity of the major peaks as the concentration of vitamin C decreases. The absorbance peak at 3350 cm^{-1} gradually diminished as the concentration of vitamin C in the mixture decreased. The absorbance due to C=O stretching decreased with vitamin C, because of the strong absorbance of O—H stretching nearby. The strong absorbance of O—H stretching gradually overlaps with the weak absorbance of C=O stretching at the lower vitamin C concentration. The changes in peaks occurred mostly between 1100 and 950 cm^{-1} when the concentrations of vitamin C varied (Figure 1B). At decreasing concentration of vitamin C, the shoulder at 1080 cm^{-1} gradually appears, while the shoulder at 1003 cm^{-1} gradually disappears. Although peaks at both 1080 and 1003 cm^{-1} were assigned to C—O—C stretching and C—O—H bending, the starch might have a greater effect on the shoulder at 1080 cm^{-1} while vitamin C might have a pronounced effect on the shoulder at 1003 cm^{-1}. The disappearance of the band at 1080 cm^{-1} (one of the common bands in the infrared spectrum of starch (Rubens et al 2000)) due to an increase of vitamin C in the mixture demonstrates this trend (Figure 1B).

Spectral regions 3656–2831 cm^{-1} and 1489–501 cm^{-1}, that contained dominant peaks, had a high correlation with the concentration of vitamin C, and were selected to construct the PLS calibration model. A minimal PRESS value of 0.0148 was obtained corresponding to 9 PLS factors (Table 2). An R^2 of 0.976 and 0.975, and SECV of 1.82% and SEE of 1.93% were obtained for the calibration and validation (Table 2) data sets, respectively.
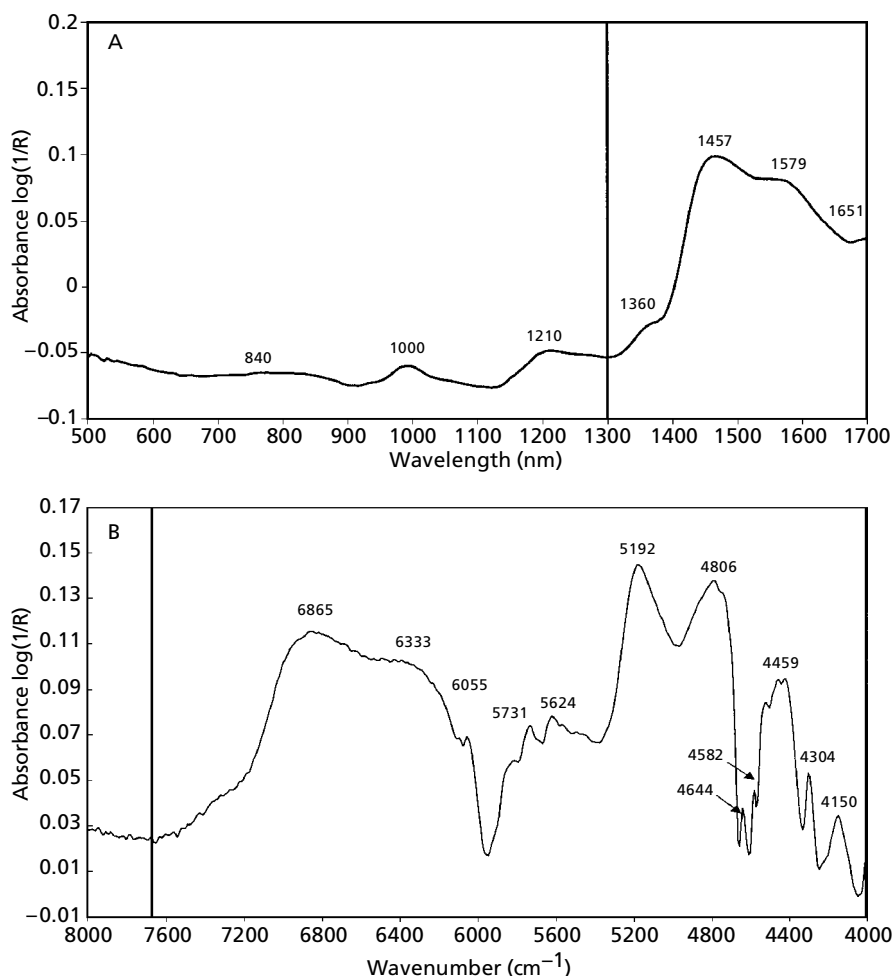
Figure 2   Plots of NIR spectra (A) and FT-NIR spectra (B) of vitamin C in binary mixtures.

FTIR-PAS

The assignment of major peaks in the FTIR-PAS spectra (Figure 1C) is given in Table 1. Although the intensities of these peaks in the FTIR-PAS spectra increased as the concentration of vitamin C decreased, the contours of the peaks in the FTIR-PAS spectra (Figure 1C) did not change as those in the DRIFTS spectra (Figure 1B). Although the major peaks of the FTIR-PAS and DRIFTS were similar, the contours of FTIR-PAS spectra were different from DRIFTS, especially in the fingerprint region between 1800 and 500 cm^{-1}. The differences may be due to the different mechanisms involved in the two techniques. DRIFTS measures the radiation that is diffusely reflected from the (powdered) sample. FTIR-PAS, on the other hand, uses a sensitive microphone to measure the photoacoustic signal that is produced by the sample in a sealed system when the modulated radiation strikes the sample.

Similar peaks were also observed in the FTIR-ATR spectra (Figure 1A), but the contours of FTIR-ATR were different from those acquired by the other two techniques. For example, the peak at 1041 cm^{-1} that had a prominent

absorbance in both the FTIR-ATR and FTIR-PAS was almost absent in the DRIFTS spectra (Figure 1B). Only a weak shoulder was observed at higher concentration of vitamin C (Figure 1B).

When FTIR-PAS spectra are used for quantitative analysis, the regions 3718–2800 cm^{-1} and 1728–400 cm^{-1} show a high correlation with respect to vitamin C concentration. The lowest PRESS value of 0.018 was obtained with 9 factors in the PLS calibration model. An R^2 of 0.966 and 0.985, and an SECV and SEE of 1.95% and 1.45% were obtained for calibration and validation sets, respectively. The results of both FTIR-PAS and DRIFTS were similar. FTIR-PAS could be an alternative to DRIFTS for vitamin C determination in food powders.

NIR

Figure 2A shows the dispersive visible/NIR spectra of vitamin C in binary mixtures. The vibrations of C—H and O—H groups in the NIR region were noted (Table 3) with their corresponding assignments (Murray & Williams 1987;

Osborne et al 1993). Unlike the narrower MIR peaks that occur due to fundamental vibration of molecules in each functional group (Table 1), most of the bands in NIR are very broad. This makes assessment of changes in the shape or pattern very difficult. For quantitative analysis, the region between 1300 and 1700 nm that contains the C—H and O—H groups was chosen because of the high correlation between the spectra and the corresponding concentrations. A minimal PRESS value of 0.028 corresponding to 5 factors was chosen for the PLS calibration model. An R^2 of 0.988 and 0.973, and an SECV and SEE of 1.35% and 1.23% were respectively obtained for calibration and validation models, respectively.

FT-NIR

FT-NIR spectra of vitamin C in binary mixtures are shown in Figure 2B. The region considered was 8000–4000 cm^{-1} (1250–2500 nm). The vibrational modes of major peaks are given in Table 3 and the spectra presented in Figure 2B. The peaks were much narrower beyond 1700 nm. The region from 1300 to 2500 nm (7692–4000 cm^{-1}) was selected from the PLS spectral correlation plot for building the model because of its high correlation with the vitamin C concentration. The optimal number of factors corresponding to the lowest PRESS value was 3. An R^2 value of 0.992 (SECV = 0.96%) for calibration and 0.980 (SEE =

Table 3 Chemical assignment of bands in NIR region.

Wavelength (nm)	Wavenumber (cm^{-1})	Vibration of mode	Intensity
2409	4150	Combination of C—H, C—C, and C—O—C stretching	m
2323	4304	Combination of C—H stretching and bending and C—O—C stretching	m
2242	4459	Combination of C—H stretching and bending	s
2182	4582	Combination of C—H stretching and bending	sh
2153	4644	Combination of C—H stretching and bending	m
2080	4806	Combination of O—H stretching and bending and second of C=C stretching	s
1926	5192	Combination of O—H stretching and bending and second overtone of C=O stretching	s
1778	5624	First overtone of C—H stretching	w
1744	5731	First overtone of C—H stretching	w
1651	6055	First overtone of C—H stretching	w
1579	6333	First overtone of O—H stretching	w, br
1457	6865	First overtone of O—H stretching	w, br
1360	7353	Combination of C—H stretching and bending	sh
1210	8264	Second overtone of C—H stretching	w, br
1000	10000	Second overtone of O—H stretching	w, br
840	11905	Third overtone of C—H stretching	w, br

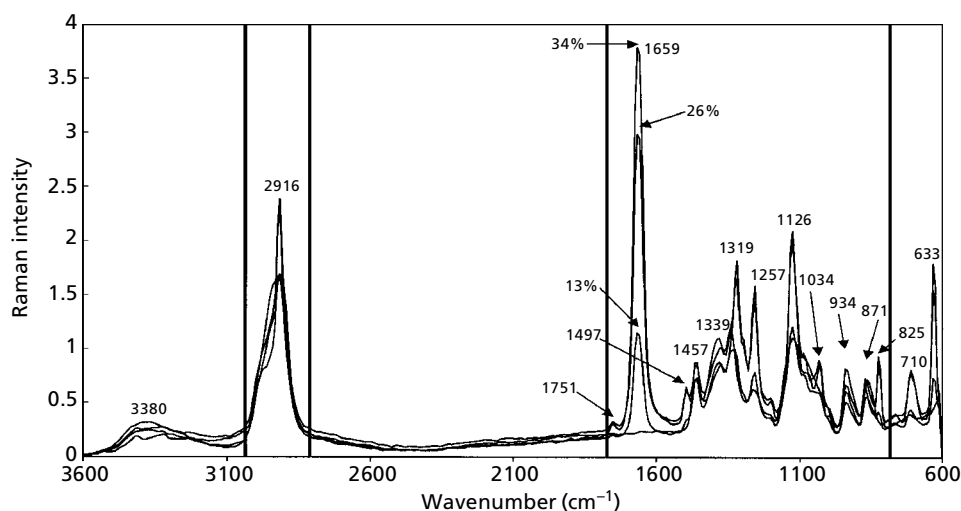s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Figure 3 Plot of FT-Raman spectra of vitamin C in binary mixtures.

1.64%) for the validation model were obtained. Results indicate that FT-NIR was more accurate and reliable than dispersive NIR spectroscopy due to the rich information content, especially between 1700 to 2500 nm (Figures 2A and 2B). Secondly, FT mathematics gives a more precise and reproducible spectra than NIR (McClure et al 1996).

FT-Raman

Raman spectroscopy gives bands related to fundamental vibrations and provides fingerprints of components that can be used for quantitative and qualitative characterization. Figure 3 shows the Raman spectra of vitamin C in powders and Table 4 gives the major peak assignments. The intensities of most of the major peaks, such as 1659 cm^{-1}, increased as the concentration of vitamin C increased. Compared with MIR spectra, the Raman peaks were narrow; however, infrared and Raman methods are two different techniques. For example, polar O—H groups have a strong absorbance in the infrared spectra (Table 1) but are weak in the Raman (Table 4) region. Non-polar C—C groups have strong Raman absorbance (Table 4), but absorb weakly in the infrared spectra (Table 1). Therefore, FT-Raman and FTIR techniques are generally considered as complementary methods.

FT-Raman spectra in the 3000–2800 cm^{-1} and 1750–800 cm^{-1} regions were selected for building the PLS model (Figure 3) due to their high correlation with vitamin C concentrations. An R^2 value of 0.950 (SECV = 2.47%) for calibration using 5 PLS factors (PRESS = 0.0219) and 0.941 (SEE = 2.68%) for validation were obtained. Results demonstrate that FT-Raman spectroscopy is a viable alternative for quantitative estimation of vitamin C. The Raman technique has been used for on-line determination (Kip et al 2000), hence its potential in an on-line setting appears promising.

Table 4   Chemical assignment of bands for the FT-Raman spectra.

Wavenumber (cm^{-1})	Vibration of mode	Intensity
3380	O—H stretching	w, br
2916	C—H stretching	s
1751	C=O stretching	w
1659	C=C ring stretching	s
1497	C—H bending	sh
1457	C—H bending	m
1339	C—H bending (wagging)	sh
1257	C—H bending (twisting)	m
1126	C—O—C stretching	m
1034	C—O—H bending	w
934	C—C ring stretching	m
871	C—C ring stretching	m
825	C—C ring stretching	m
710	C—C ring stretching	m
633	C—C ring stretching	m

s, strong; m, medium; w, weak; sh, shoulder; br, broad.

Conclusion

DRIFTS, FTIR-PAS, NIR, FT-NIR and FT-Raman techniques were used to predict vitamin C concentration in powdered mixtures, while the FTIR-ATR procedure was used to predict vitamin C concentration in aqueous solutions. The methods adopted are simple and do not require sample preparation. Of all the methods, FTIR-ATR gave the best prediction rate (R^2 = 0.999) and the lowest error (SECV = 0.23%) of determination. In general, infrared methods give a better prediction rate compared with Raman. The measurement could be completed in about 5 s using NIR and 3 min with FT-Raman.

References

Arya, S. P., Mahajan, M., Jain, P. (1998) Photometric methods for the determination of Vitamin C. *Anal. Sci.* **14**: 889–895

Arya, S. P., Mahajan, M., Jain, P. (2000) Non-spectrophotometric methods for the determination of Vitamin C. *Anal. Chim. Acta* **417**: 1–14

Bjørsvik, H., Martens, H. (1992) Calibration of NIR instruments by PLS regression. In: Burns, D. A., Ciurczak, E. W. (eds) *Handbook of near-infrared analysis.* New York, Marcel Dekker Inc., pp 159–180

Blanco, M., Coello, J., Iturriaga, H., Maspoch, S., Pezuela, C. (1993) Determination of ascorbic-acid in pharmaceutical preparations by near-infrared reflectance spectroscopy. *Talanta* **40**: 1671–1676

Blitz, J. P. (1998) Diffuse reflectance spectroscopy. In: Mirabella, F. M. (ed.) *Modern techniques in applied molecular spectroscopy.* New York, John Wiley & Sons Inc., pp 185–219

Cutmore, E. A., Skett, P. W. (1993) Application of Fourier-transform Raman-spectroscopy to a range of compounds of pharmaceutical interest. *Spectroschim. Acta A* **49**: 809–818

Du, D., Sun, S., Zhou, Q., Liang, X., Yang, X. (2000) Quantitative analysis of rutin and vitamin C by NIR FTIR. *Spectrosc. Spect. Anal.* **20**: 474–476

Findlay, W. P., Bugay, D. E. (1998) Utilization of Fourier transform Raman spectroscopy for the study of pharmaceutical crystal forms *J. Pharmaceut. Biomed.* **16**: 921–930

Hancewicz, T. M., Petty, C. (1995) Quantitative analysis of Vitamin A using Fourier transform Raman spectroscopy. *Spectroschim. Acta A* **51**: 2193–2198

Kip, B. J., Berghmans, T., Palmen, P., van der Pol, A., Huys, M., Hartwig, H., Scheepers, M., Wienke, D. (2000) On the use of recent developments in vibrational spectroscopic instrumentation in an industrial environment: quicker, smaller and more robust. *Vib. Spectrosc.* **24**: 75–92

McClure, W. F., Maeda, H., Dong, J., Liu, Y., Ozaki, Y. (1996) Two-dimensional correlation of Fourier transform near-infrared and Fourier Transform Raman spectra I: mixtures of sugar and protein. *Appl. Spectrosc.* **50**: 467–475

Murray, I., Williams, P. C. (1987) Chemical principles of near-infrared technology. In: Williams, P. C., Norris, K. H. (eds) *Near-infrared technology in the agricultural and food industries.* Am. Assoc. Cereal Chem., St. Paul, MN, pp 17–34

Osborne, B. G., Fearn, T., Hindle, P. H. (1993) In: *Practical NIR spectroscopy with applications in food and beverage analysis.* Singapore, Longman Scientific & Technical, pp 13–35

Oskin, K. E. (2000) *Near infrared and visible spectroscopy for predicting beef palatability.* MS Thesis, Penn State University

Ozaki, Y., Cho, R., Ikegaya, K., Muraishi, S., Kawauchi, K. (1992) Potential of near-infrared Fourier-transform Raman-spectroscopy in food analysis. *Appl. Spectrosc.* **46**: 1503–1507

Özgür, M. Ü., Sungur, S. (1995) Third order derivative spectrophotometric determination of ascorbic acid in fruits and vegetables. *Talanta* **42**: 1631–1640

Reeves, J. B., Zapf, C. M. (1998) Mid-infrared diffuse reflectance spectroscopy for discriminant analysis of food ingredients. *J. Agric. Food Chem.* **46**: 3614–3622

Rubens, P., Snauwaert, J., Heremans, K., Stute, R. (2000) In situ observation of pressure-induced gelation of starches studied with FTIR in the diamond anvil cell. *Carbohydr. Polym.* **39**: 231–235

Schrader, B. (1996) Raman spectroscopy in the near infrared – a most capable method of vibrational spectroscopy. *Fresen. J. Anal. Chem.* **335**: 233–239

Silverstein, R. M., Bassler, G. C., Morrill, T. C. (eds) (1991) Infrared spectroscopy. In: *Spectrometric identification of organic compounds.* 5th edn, New York, John Wiley & Sons Inc., pp 91–164

Sivakesava, S., Irudayaraj, J. (2000) Determination of sugars in aqueous mixtures using mid-infrared spectroscopy. *Appl. Eng. Agric.* **16**: 543–550

Williams, P. C., Norris, K. H. (1987) Qualitative applications of near-infrared reflectance spectroscopy. In: Williams, P. C., Norris, K. H. (eds) *Near-infrared technology in the agricultural and food industries.* Am. Assoc. Cereal Chem., St. Paul, MN, pp 241–288

Wojciechowski, C., Dupuy, N., Ta, C. D., Huvenne, J. P., Legrand, P. (1998) Quantitative analysis of water-soluble vitamins by ATR-FTIR spectroscopy. *Food Chem.* **63**: 133–140

Yang, H., Irudayaraj, J. (1999) Estimation of particle size by DRIFTS and FTIR-PAS. *Particul. Sci. Technol.* **17**: 269–282

Yang, H., Irudayaraj, J. (2000) Characterization of semisolid fats and edible oils by Fourier transform infrared photoacoustic spectroscopy. *J. Am. Oil Chem. Soc.* **77**: 291–295