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ARTICLES

Investigation of the Potential Utility of Single-Bounce Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy in the Analysis of Distilled Liquors and Wines

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A new Fourier transform infrared (FTIR) spectroscopic method based on single-bounce attenuated total reflectance (SB-ATR) spectroscopy was developed for the analysis of distilled liquors and wines. For distilled liquors, a partial least-squares (PLS) calibration was developed for alcohol determination based on the SB-ATR/FTIR spectra of mixtures of ethanol and distilled water. An independent set of 12 different distilled liquor samples was predicted from the PLS calibration, and a standard deviation of the differences for accuracy (SDD_a) between actual and predicted values of 0.142% (v/v) was obtained. The potential utility of SB-ATR/FTIR spectroscopy for the analysis of wines was initially evaluated based on a comparison with Fourier transform near-infrared (FT-NIR) spectroscopy and FTIR spectroscopy using a flow-through transmission cell. PLS calibrations for alcohol, total reducing sugars, total acidity and pH were developed using pre-analyzed wine samples ($n = 28$), and for SB-ATR/FTIR spectroscopy, the SDD_a for the leave-one-out cross-validation statistics were of the order of 0.100% (v/v), 0.707 g L^{-1}, 0.189 g L^{-1} (H_2SO_4), and 0.230, respectively. Overall, the SB-ATR/FTIR results were better than those obtained using FT-NIR spectroscopy and comparable to those obtained with transmission FTIR spectroscopy. A PLS calibration based on preanalyzed wine samples ($n = 72$) for the prediction of 11 different components and parameters in wines by SB-ATR/FTIR spectroscopy was subsequently developed and validated using an independent sample set ($n = 77$). Good coefficients of correlation between the reference and predicted values for the validation set were obtained for most of the components and parameters except citric acid, volatile acids, and total SO_2. The results of this study demonstrate the suitability of SB-ATR/FTIR spectroscopy for the routine analysis of distilled liquors and wines.

KEYWORDS: Wine; SB-ATR; FTIR; distilled liquors; PLS

INTRODUCTION

Spirits are largely alcohol/water mixtures with only minor levels of added or developed constituents present. Wines, on the other hand, can have a complex provenance, and their quality depends on both volatile (e.g., ethanol and aromatic compounds) and nonvolatile (e.g., sugars, organic acids, tannins, nitrogen compounds, and mineral matter) constituents (*1*, *2*). As a consequence, whereas the analysis for alcohol in spirits and wines is routine for industrial quality control and government regulatory purposes, more detailed analysis for other constituents in wines is also commonplace (*3*, *4*). Such analyses tend to be tedious, and the availability of a simple and rapid means of obtaining most of the relevant information using a single method of analysis would clearly be desirable.

Near-infrared (NIR) spectroscopy might be considered a likely candidate to meet this demand as it is a well-established technique for multicomponent analysis of agricultural and food products (*5*). Its utility for the analysis of alcohol in wines was initially demonstrated using filter-based NIR reflectance spectrometers, employing wavelengths of 2270, 2230, 2180, and 1778 nm (*6*). Since then, NIR spectroscopic methods have also been developed for the analysis of alcohol in spirits using transmission measurements (*7*, *8*) and flow injection analysis (*9*), for monitoring alcohol and sugars during wine fermentation (*3*), and for analyzing alcohol, sugars, and glycerol in botrytized-grape sweet wines using filter-based reflectance spectrometers (*10*). Recently, an FT-NIR transmission method was developed

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for the analysis of methanol in grape-derived distillation products (*11*) and a reflectance NIR method was developed for the analysis of 15 parameters in wines employing partial least-squares (PLS) regression (*12*). Overall, although NIR spectroscopy is an adequate analytical tool for predicting the alcohol content in wines and spirits, it is limited in its ability to analyze other wine components. For example, although NIR methods for the determination of sugar content have been developed for sweet wines (*10*), the major NIR absorption bands of sugars are highly overlapped by the OH stretching and deformation combination bands of water, making the measurement of sugars imprecise below 30 g L^{-1} (*13*).

Although mid-IR spectroscopy has generally found much less practical application than NIR spectroscopy in the analysis of agricultural and food products, it has been successfully employed in the analysis of alcohol in alcoholic beverages (*14*, *15*) and has recently been shown to be a suitable technique for the analysis of multiple components in wines, including tartaric acid, malic acid, lactic acid, total acidity, pH, volatile acidity, reducing sugars, fructose, glucose, and glycerol (*16*−*18*). However, at present, Fourier transform infrared (FTIR) wine analysis is basically restricted to proprietary commercial instrumentation dedicated to this application but based on the design of FTIR milk analyzers. The sample-handling accessory integrated into these systems incorporates a temperature-controlled flow-through transmission cell equipped with CaF_2 windows and having a fixed path length of ~50 μm. Despite this short path length, which is required to limit the overwhelming IR absorptions of water (*18*), products containing high levels of alcohol and/or sugar would require dilution prior to analysis in order to keep the major absorption bands of these components on scale. The present work was undertaken to develop FTIR analytical methodology that utilizes a more versatile single-bounce attenuated total reflectance (SB-ATR) sample-handling accessory and a standard benchtop FTIR spectrometer, thereby reducing the cost of implementing FTIR wine analysis. The advantages of the recently developed SB-ATR accessories (*19*) were exploited in previous work in our laboratory for the quantitative analysis of sugars during lactose hydrolysis in milk (*20*). These include higher energy throughput (*19*) and more precise temperature control by comparison with the multiple-reflection devices traditionally employed for ATR measurements. Furthermore, a ZnSe SB-ATR accessory provides access to much more spectral information than the transmission cell employed in commercial FTIR wine analyzers owing to its very short path length, as well as the much lower transmission cutoff of ZnSe compared to that of CaF_2. On the basis of these considerations, the present study was undertaken to evaluate the utility of SB-ATR/FTIR spectroscopy for the analysis of distilled liquors and wines. In the first part of the study, alcohol determination in spirits, which are relatively simple matrices, was assessed. Subsequently, a comparative evaluation of SB-ATR/FTIR spectroscopy relative to FT-NIR and FTIR transmission methods for the analysis of wines was carried out. Finally, the simultaneous determination of 11 constituents in wines by SB-ATR/FTIR spectroscopy was investigated.

MATERIALS AND METHODS

Samples, Chemicals, and Reagents. Anhydrous alcohol (ethanol) was obtained from Commercial Alcohols Inc. (Brampton, ON, Canada), and 12 distilled liquor samples (rum, gin, vodka, brandy, scotch, and whiskey) were obtained from local liquor stores. A total of 177 wine samples were obtained courtesy of the central laboratory of the Société des alcools du Québec (SAQ), all of which had been analyzed for alcohol content by distillation and densitometry, for pH by potentiometry, and for total reducing sugars, total acidity, volatile acidity, and total SO_2 by colorimetry using an automated system (Skalar Analytical Inc., Tinstraat, The Netherlands). The products included red and white, dry, semisweet, and sweet wines from a wide variety of countries including Italy, France, Spain, the United States, South Africa, Germany, Canada, and Australia. All reagents were obtained from Fisher Scientific (Montreal, PQ, Canada) and were of analytical grade.

Instrumentation. All quantitative IR analyses were carried out using an ABB Bomem (Québec City, PQ, Canada) MB-150 dual-range (NIR/mid-IR) FTIR spectrometer equipped with a deuterated triglycine sulfate detector. The spectrometer was purged with dry air from a Balston air drier (Lexington, MA) to avoid spectral contributions from atmospheric water vapor and carbon dioxide. SB-ATR spectra were recorded with the use of a Harrick (Ossining, NY) ZnSe accessory equipped with a temperature controller (Watlow System Integrators, Decorah, IA). During sample analysis, the SB-ATR crystal was covered with a glass microscope slide to avoid any alcohol evaporation during spectral recording, and the sample temperature was maintained at 30 ± 0.1 °C to minimize spectral changes due to temperature variation. For purposes of comparison, FT-NIR and FTIR analyses were carried out with a 1000-μm quartz cell and a 50-μm CaF_2 cell, respectively, both thermostated at 30 ± 0.1 °C using an Omega temperature controller (Omega Engineering, Stamford, CT). Spectral collection parameters for FT-NIR, transmission FTIR, and SB-ATR/FTIR analyses were 16, 32, and 32 co-added scans at resolutions of 16, 8, and 8 cm^{-1}, respectively. The spectra of all samples were ratioed against a background single-beam spectrum recorded immediately prior to collection of the spectrum of the sample.

HPLC analysis of wines for glycerol, fructose, and organic acids (citric acid, malic acid, tartaric acid, and lactic acid) was carried out employing a Hewlett-Packard 1050 HPLC system, equipped with an ultraviolet detector set to 192 nm. Separation was carried out isocratically on a 7.8 mm × 300 mm Rezex ROA-Organic Acid column manufactured by Phenomenex Inc. (Torrance, CA) using 0.0025 N sulfuric acid at a flow rate of 0.5 mL min^{-1} and a column temperature of 52 ± 0.1 °C.

Calibration Development and Validation. For the determination of alcohol in spirits, calibration standards were prepared by blending anhydrous ethanol with distilled water to cover a range of 25−75% (v/v) alcohol, and the validation set comprised 12 distilled liquor samples. Both standards and validation samples were analyzed using an Anton Paar density meter (Graz, Austria) according to the Association of Official Analytical Chemists' method 982.10 (*21*). For wines, an initial set of 28 samples that had been analyzed for alcohol content, pH, total acidity, and total reducing sugars by standard methods was used for comparing the utility of the SB-ATR method to more conventional FT-NIR and FTIR transmission methods. A larger set of 149 wines was then used to assess the feasibility of employing FTIR/SB-ATR spectroscopy for the simultaneous determination of 11 components (alcohol, total reducing sugars, fructose, total acidity, volatile acidity, tartaric acid, malic acid, citric acid, lactic acid, glycerol, and SO_2), with 72 of the wines used for calibration and 77 serving as validation samples.

All calibrations were developed by applying PLS regression (*22*) using Omnic TQ Analyst software (Nicolet Instrument, Madison, WI). The correlation, variance, and pure component spectra generated from the PLS software package were used to select regions in developing and optimizing the calibration model for each component. The optimal number of factors used for each component was determined from the minimum point on the predicted residual error sum of squares (PRESS) plot. The overall suitability of the calibration model ultimately developed was assessed by calculating the mean difference for accuracy (MD_a), standard deviation of the differences for accuracy (SDD_a), and standard error of cross-validation (SECV) between the leave-one-out cross-validation predictions and values obtained by the reference method(s). For validating the FTIR/SB-ATR method employing 77 preanalyzed wine samples, the performance of the method was evaluated by calculating the MD_a, SDD_a, and standard error of prediction (SEP) between the predicted and reference values.

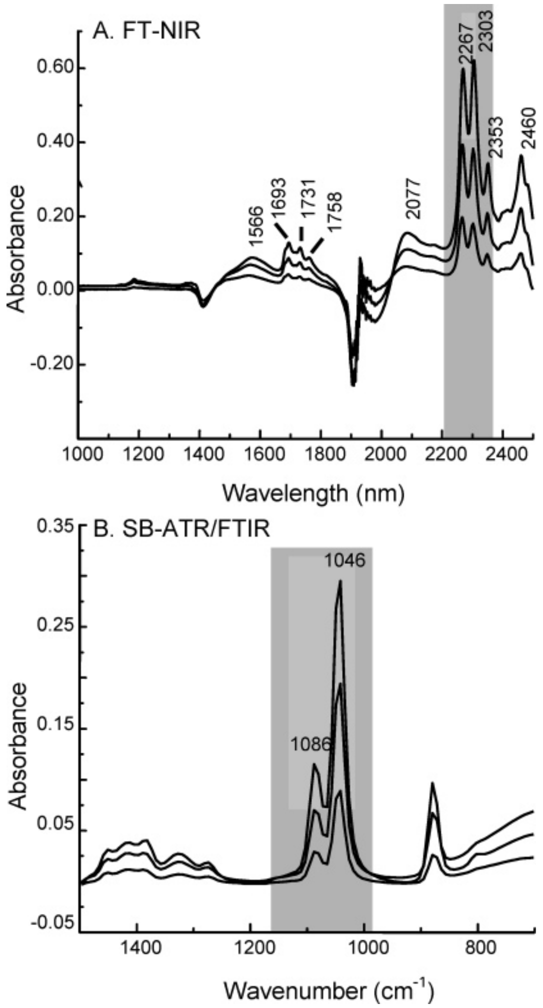

Figure 1. FT-NIR (**A**) and SB-ATR/FTIR (**B**) spectra of 20, 40, and 60% (v/v) solutions of ethanol after subtraction of water absorptions. The shaded area represents the spectral region ultimately used for PLS calibration.

RESULTS AND DISCUSSION

Distilled Liquor Analysis. Although there are many ways of measuring alcohol in distilled liquors, the most commonly used official methods are those involving physical measurements (*21*, *23*−*25*). NIR (*7*−*9*) and mid-IR (*14*, *15*) transmission methods have also been investigated and developed, with NIR methods dominating. Owing to the simplicity of the distilled liquor matrix, the NIR spectra of distilled liquors exhibit some fairly well-defined combination and first overtone bands of the O−H, C−H, and C−O stretching and bending vibrational frequencies of ethanol (*8*), whereas the mid-IR spectra exhibit two strong bands at 1046 and 1086 cm^{-1} due to the fundamental C−O stretching vibrations (**Figure 1**). Because transmission FT-NIR spectroscopy has been shown to be a suitable technique for the determination of alcohol in distilled liquors (*7*, *8*), it was used as a basis of comparison in the evaluation of an SB-ATR/FTIR method. The spectra of ethanol/distilled water mixtures were used to develop PLS calibrations for the transmission FT-NIR and SB-ATR/FTIR procedures, and the spectral regions ultimately used to derive the PLS calibrations are shown in **Figure 1**. The calibrations were assessed by leave-one-out cross-validation, and linear regression of the cross-validation predictions versus the actual values yielded an *R* value of 0.999 for both methods with an SECV of 0.065 and 0.080% (v/v) for the FT-NIR and SB-ATR/FTIR methods, respectively.

Table 1. Regions Employed in FT-NIR, Transmission FTIR, and SB-ATR/FTIR PLS Regressions for a Comparative Study Employing 28 Wine Samples

		FTIR regions (cm^{-1})	
component	FT-NIR regions (nm)	transmission	SB-ATR
alcohol	2368–2207	1000–1500	850–1500
reducing sugar	1851–1666	1108–1500	956.7–1500 3000–2800
total acidity	2368–2207	1108.3–1500 1700–1800	1108.3–1500 1700–1800
pH	1851–1389	1000–1500	956.7–1500 3000–2800

Table 2. Cross-Validation Results for PLS Calibration Models Developed for the Determination of Alcohol, Reducing Sugar, Total Acidity, and pH by FT-NIR, FTIR, and SB-ATR/FTIR Spectroscopy Based on a Calibration Set of 28 Wine Samples, Including Linear Regression Equations and Values of *R*, SECV, MD$_a$, and SDD$_a$

component	method	equation	*R*	SECV	MD$_a$	SDD$_a$
alcohol [% (v/v)]	FT-NIR	$Y = 0.231 + 0.982X$	0.991	0.110	0.00	0.109
	FTIR	$Y = 0.059 + 0.996X$	0.991	0.111	0.01	0.109
	SB-ATR	$Y = 0.061 + 0.995X$	0.993	0.102	0.00	0.100
reducing sugar (g L^{-1})	FT-NIR	$Y = 1.479 + 0.341X$	0.500	0.764	−0.04	1.123
	FTIR	$Y = 0.946 + 0.584X$	0.735	0.697	−0.01	0.863
	SB-ATR	$Y = 0.605 + 0.711X$	0.837	0.613	−0.06	0.707
total acidity (g L^{-1} H_2SO_4)	FT-NIR	$Y = 2.874 + 0.152X$	0.270	0.167	0.00	0.304
	FTIR	$Y = 0.453 + 0.863X$	0.882	0.142	−0.01	0.146
	SB-ATR	$Y = 1.164 + 0.656X$	0.787	0.156	0.00	0.189
pH	FT-NIR	$Y = 2.107 + 0.390X$	0.548	0.202	0.01	0.283
	FTIR	$Y = 1.213 + 0.654X$	0.706	0.222	0.02	0.246
	SB-ATR	$Y = 1.416 + 0.582X$	0.713	0.190	−0.01	0.230

The PLS calibrations were used to evaluate the alcohol content of 12 distilled liquors representing a variety of products. The predicted alcohol contents were compared to the results obtained using the Anton Paar density meter giving MD$_a$ and SDD$_a$ values of 0.03 and 0.163% (v/v) for FT-NIR and 0.02 and 0.142% (v/v) for SB-ATR/FTIR; however, regression was not performed as there was inadequate variability in the alcohol content [ranging from 40 to 41% (v/v)] to produce meaningful regression data. The MD$_a$ and SDD$_a$ data indicate that the alcohol content of the distilled liquor products investigated could be predicted to within 0.17% (v/v) of the density meter values, with no significant bias indicated between the reference and IR methods, and that the FT-NIR and SB-ATR/FTIR methods performed comparably.

These results indicate that the SB-ATR/FTIR method is readily able to quantify alcohol content in spirits to a similar, if not higher, degree of accuracy as the FT-NIR procedure. The results are also comparable to those reported in publications on both NIR (*7*−*9*) and mid-IR (*14*, *15*) methods for the analysis of distilled liquors. With respect to the previous mid-IR methods, which were based on the use of transmission cells, the SB-ATR procedure has the advantage that sample dilution is not required.

Comparison of Transmission FT-NIR, Transmission FTIR, and SB-ATR/FTIR Methods for Wine Analysis. A preliminary comparative feasibility study was carried out by developing PLS calibrations for four parameters (alcohol content, total reducing sugars, total acidity, and pH) in wines by using transmission FTIR and FT-NIR as well as SB-ATR/FTIR spectra of 28 preanalyzed wine samples. The spectral regions employed in the optimized PLS calibration models for each of the four components are presented in **Table 1**. **Table 2** summarizes the leave-one-out cross-validation results in terms of the linear regression equations relating the cross-validation predictions to the values obtained by the reference methods, together with the corresponding values for *R*, SECV, MD_a, and SDD_a. The FT-NIR cross-validation data indicated poor agreement between the predicted and reference method values for all of the components except alcohol. Better overall agreement between the predicted and reference method values was obtained with both the transmission FTIR and SB-ATR/FTIR calibrations. Again, the best results were obtained for alcohol, whereas the results for reducing sugars, total acidity, and pH are very much in line with what has been reported in the literature for FTIR wine analysis using a transmission cell (*16*, *17*).

The performance of the SB-ATR calibrations was generally comparable to that obtained with the conventional transmission cell, despite the much shorter effective path length of the SB-ATR accessory, and is in fact superior in the case of reducing sugars. This is likely due to the lower transmission cutoff of the ZnSe crystal as compared to CaF_2 windows, through which the transmission of IR energy declines rapidly between 1110 and 1000 cm^{-1}, where the strongest absorption bands for sugars and alcohol are found (*13*). In addition, owing to the short effective path length of the SB-ATR accessory, all of the spectral information in the regions where water absorbs is available, and the CH stretching (3000−2800 cm^{-1}) and carbonyl stretching bands (1800−1600 cm^{-1}) are on scale. **Figure 2** illustrates the "pure component" spectra generated by the Turbo Quant Analyst software, each of which corresponds to the first loading spectrum in a PLS calibration for the component in question. The pure component spectra reveal that there is significantly less spectral information available in the transmission cell spectra. This is especially the case for total acidity, where the region between 1750 and 1600 cm^{-1} is totally "blanked out" due to off-scale water absorptions, whereas the SB-ATR spectra exhibit the characteristic carbonyl stretching absorption of carboxylic acids.

One consideration arising in the use of the ATR technique for quantitative analysis is the dependence of the effective path length on the depth of penetration (d_p) of the evanescent IR radiation emerging from the surface of the ATR crystal. The depth of penetration, in turn, is dependent on the refractive index of the sample in accordance with the equation

$$d_p = \lambda/\{2\pi n_1[\sin^2(\theta) - (n_2/n_1)^2]^{1/2}\}$$

where λ is the wavelength of the IR radiation, n_1 is the refractive index of the ATR crystal, n_2 is the refractive index of the sample, and θ is the angle at which the IR radiation strikes the ATR crystal face (*26*). The effective path length thus may vary from sample to sample, depending on the refractive index of the sample material, whereas the calibration model is based on the assumption of a linear relationship between IR absorbance and concentration and, hence, a constant path length. In the case of distilled liquors, the value of the refractive index is almost invariant as the amount of alcohol in these types of products is almost always between 40 and 41% (v/v), with extremely low concentrations of other constituents. For wines, the refractive index is almost entirely dependent on the levels of alcohol and sugar, ranging from 1.34 for low-alcohol, dry wines to almost 1.36 for high-sugar, high-alcohol wines. According to the equation above, for the SB-ATR accessory employed in the present study, which employs a ZnSe crystal and a 45° angle of incidence, this range corresponds to a variation of ~2.6% in the effective path length. Because the effective path length represented by the calibration model would correspond to an intermediate refractive index value, the errors in predicted concentrations resulting from this variability in the effective path length may be estimated to be <1.5%, which can be considered to be acceptable in relation to the errors presented in **Table 2** for the alternative FT-NIR and FTIR transmission methods. Overall, on the basis of the initial comparative results in **Table 2**, it was concluded that SB-ATR/FTIR spectroscopy has the potential to serve as a means by which multicomponent analysis of wines can be carried out.

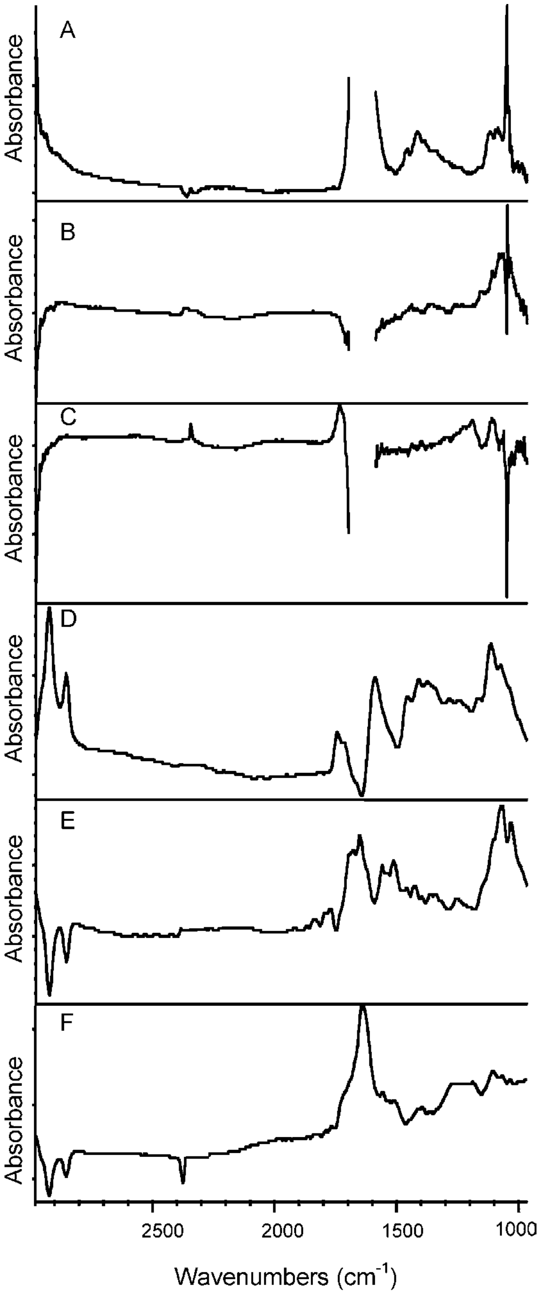

Figure 2. "Pure component" spectra derived for (**A**) pH, (**B**) total reducing sugar, and (**C**) total acidity from FTIR transmission spectra and for (**D**) pH, (**E**) total reducing sugar, and (**F**) total acidity from SB-ATR spectra of 28 wine samples.

Multicomponent Wine Analysis by SB-ATR/FTIR Spectroscopy. Winemakers, enologists, and governments have an interest in a variety of components and parameters that affect the quality of wine, are indicative of adulteration or provenance, or affect revenue. In this study, PLS calibrations were developed for a total of 11 components and parameters using a diverse set of 149 wine samples, for which reference values were obtained by combining data from the Société des alcools du Québec and

Table 3. Regions Employed in PLS Regressions for the Analysis of 11 Components in Wines by SB-ATR/FTIR Spectroscopy

	region				
component	1500–850 cm^{-1}	1500–957 cm^{-1}	1500–1108 cm^{-1}	1801–1500 cm^{-1}	3000–2800 cm^{-1}
alcohol	+	−	−	−	−
fructose	−	+	−	−	+
citric acid	+	−	−	+	+
tartaric acid	+	−	−	+	+
malic acid	−	−	+	+	−
glycerol	+	−	−	+	−
lactic acid	+	−	−	+	−
reducing sugar	−	+	−	−	+
volatile acidity	−	+	−	+	−
total acidity	−	−	+	+	−
total SO_2	+	−	−	−	−

HPLC analyses performed in our laboratory. About half of the samples were employed as calibration standards, with the balance serving as an independent validation set.

In the development of the PLS calibration models, five broad spectral regions were initially selected by examining the pure component spectra. The optimal spectral region or combination of spectral regions for the prediction of each of the 11 parameters was chosen by evaluating the cross-validation statistics. The regions ultimately selected are summarized in **Table 3**. The optimized calibration models were validated by comparing the PLS-predicted values for the 77 preanalyzed wines in the validation set to the reference method values. **Table 4** summarizes the data obtained for all 11 parameters, including the ranges of the values spanned by the validation set and the linear regression equations relating the PLS predicted values to the reference method values as well as the values for *R*, SEP, MD_a, and SDD_a. For purposes of comparison, the SEP and SDD_a values reported by Patz et al. (*16*) and Dubernet and Dubernet (*17*), respectively, for FTIR wine analysis using a commercial wine analyzer are also included in **Table 4**.

The predicted values for the parameters evaluated in the initial trial (alcohol, reducing sugars, and total acidity) corresponded well to the reference method values for the validation samples; compared to the initial trial set in **Table 2**, higher *R* values were obtained (>0.90) because the data set in **Table 4** spanned a larger range of concentration values. A high correlation value (0.987) was also obtained for fructose. It may be noted that the validation set was uniformly distributed over the entire range of alcohol content, whereas for sugars, most of the wines were dry with only a few of them being semisweet or sweet. The possibility of simplifying the calibration process by developing PLS calibration models for the prediction of these two parameters based simply on mixtures of ethanol, glycerol, fructose, and glucose as calibration standards was investigated. However, large biases were obtained when wines were analyzed using these calibrations, indicating that these simple calibration standards did not adequately model the spectra of wines. This finding is consistent with results obtained by Schindler et al. (*4*) in their investigation of a calibration set consisting of model solutions as an alternative to preanalyzed wines.

Satisfactory agreement between the FTIR-predicted and reference values was also obtained for glycerol, a component present in wines as a fermentation byproduct (*27*), and for the individual organic acids, with the exception of citric acid. Better results were obtained for total acidity ($R = 0.925$) than for the individual organic acids, which may be attributed to differences in the precision of the reference methods as well as to possible inadequacy of the FTIR method in differentiating among the various organic acids. The poor results for citric acid are due to its very low concentration, as naturally occurring levels in wine are typically below 0.1 g L^{-1} (*27*), and very few of the samples available for this study contained >0.30 g L^{-1}. However, citric acid is sometimes added to wines to increase the total acidity content or to prevent casse, a winemaking term used to describe cloudiness or formation of a precipitate due to an excess of certain metal salts (*27*). If quantitation of citric acid in these types of samples is required, a calibration model based on wines spiked with known amounts of citric acid to extend the concentration range and enhance the spectral response can be developed.

In addition to citric acid, volatile acidity and total SO_2 were poorly predicted. Volatile acidity levels were too low and spanned too narrow a range of concentration (0.2−0.8 g L^{-1} H_2SO_4) to develop an adequate calibration, whereas total SO_2, present at the parts per million level in wines, does not produce an adequate signal to calibrate on at concentrations of <100 ppm (*16*), and its spectrum is complicated by its multiple ionic states, which are sensitive to the sample matrix pH (*17*).

A detailed comparison between the SEP and SDD_a values obtained in this study and the values from the literature given in **Table 4** would not be informative because the analytical performance achieved for each component is highly dependent on the precision of the reference method used to analyze the calibration and validation samples and the number and types of wine samples used in the calibration and validation sets. However, overall, the data in **Table 4** indicate that the SB-ATR/FTIR results are comparable to those obtained in studies using a commercial FTIR wine analyzer equipped with a CaF_2

Table 4. Linear Regression Equations Relating PLS Predictions to the Reference Values for a Validation Set of 77 Wine Samples Ranked in Terms of Decreasing *R* Value with Comparison of SEP and SDD_a to Data Published from Studies Using a CaF_2 Transmission Flow-through Cell

component	range of concentration	equation	R	SEP	SEP[a]	MD_a	SDD_a	SDD_a[b]
alcohol	7.3–17.0% (v/v)	$Y = -0.235 + 1.020X$	0.997	0.099	0.21	0.01	0.101	0.08
reducing sugar	1.3–116.6 g L^{-1}	$Y = -0.729 + 0.970X$	0.992	2.180	0.86	–0.94	2.231	2.41
fructose	0–64.48 g L^{-1}	$Y = -0.179 + 1.040X$	0.987	1.606	0.62	–0.08	1.630	
total acidity	2.7–6.3 g L^{-1} (H_2SO_4)	$Y = 0.172 + 0.906X$	0.925	0.178	0.13[c]	–0.17	0.182	0.07
lactic acid	0.03–3.47 g L^{-1}	$Y = 0.366 + 0.821X$	0.901	0.291	0.20	0.12	0.317	0.30
glycerol	2.07–15.53 g L^{-1}	$Y = 2.136 + 0.796X$	0.864	0.824	0.49	0.84	0.894	1.315
malic acid	0–4.54 g L^{-1}	$Y = 0.498 + 0.700X$	0.768	0.651	0.16	0.26	0.727	0.12
tartaric acid	0.43–3.81 g L^{-1}	$Y = 0.432 + 0.764X$	0.709	0.388	0.38	–0.09	0.404	0.11
volatile acidity	0.21–0.83 g L^{-1} (H_2SO_4)	$Y = 0.281 + 0.472X$	0.625	0.105	0.071[c]	0.04	0.14	0.022
total SO_2	0–250 ppm	$Y = 54.27 + 0.307X$	0.569	21.1	17	–5.9	38.8	
citric acid	0–3.37 g L^{-1}	$Y = 0.126 + 0.081X$	0.384	0.104		–0.11	0.497	

[a] SEP values from Patz et al. (*16*). [b] SDD_a values from Dubernet and Dubernet (*17*). [c] SEP values for total acidity and volatile acidity in Patz et al. (*16*) expressed as g L^{-1} tartaric acid and g L^{-1} acetic acid, respectively.

flow-through cell (*16, 17*) (**Table 4**). Given the results in **Table 2** for the SB-ATR accessory and a 50-μm CaF_2 transmission cell, which can be directly compared with each other because they are based on a common sample set, and in **Table 4**, it may be concluded that SB-ATR/FTIR spectroscopy can provide comparable sensitivity to commercial FTIR wine analyzers, capable of measuring concentrations of components at levels of >0.1 g L^{-1} (*16*, *17*).

Conclusion. This study has demonstrated the suitability of SB-ATR/FTIR spectroscopy for the analysis of distilled liquors and wines. The determination of alcohol in distilled liquors is a simple analytical procedure, and calibration can be performed using a small set of ethanol/distilled water mixtures as standards. In contrast, multicomponent wine analysis is a complex undertaking, requiring a very careful selection of the wines used as calibration standards to represent the population of interest and substantial investment in quality reference method analyses. This drawback pertains equally to commercially available FTIR wine analyzers (*16*, *17*). In this context, the use of gravimetrically prepared solutions containing the pure components of interest as calibration standards would clearly be advantageous. However, an investigation of this possibility in the present work indicated that such an approach was not viable owing to the complexity of the wine matrix, corroborating the findings of a previous study (*4*).

As an alternative to the transmission cell employed in FTIR wine analyzers, the SB-ATR accessory yielded comparable analytical performance. In addition, it provided a very simple means of sample handling, as only a drop of sample is required to cover the surface of the ATR crystal for analysis and the sample can simply be wiped off the crystal, which is then ready for the next analysis after a quick rinse with water. Furthermore, the SB-ATR sample-handling accessory can be adapted for automated flow-through analysis, which would avoid the need to cover the crystal to prevent evaporation and to clean the surface of the crystal between samples. Generally speaking, this method provides a means of analyzing a wide range of alcoholic beverages, including products high in alcohol and/or sugar content without any need for prior dilution of the sample. The proven suitability of an SB-ATR accessory for wine analysis makes it possible to readily implement FTIR wine analysis methodology on a standard benchtop FTIR spectrometer, furnishing a less costly alternative to the purchase of a dedicated analyzer. Furthermore, the standard SB-ATR accessory can be adapted to a flow-through configuration to accommodate high-volume analytical applications in distilleries, wineries, and commercial and regulatory laboratories.

ABBREVIATIONS USED

ATR, attenuated total reflectance; FTIR, Fourier transform infrared; FT-NIR, Fourier transform near-infrared; HPLC, high-performance liquid chromatography; IR, infrared; MD_a, mean difference for accuracy; NIR, near-infrared; PLS, partial least squares; *R*, coefficient of correlation; SB-ATR, single-bounce attenuated total reflectance; SDD_a, standard deviation of the differences for accuracy; SECV, standard error of cross-validation; SEP, standard error of prediction.

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LITERATURE CITED

(1) *Encyclopedia of Food Science, Food Technology and Nutrition*; Macrae, R., Ed.; Academic Press: San Diego, CA, 1993; pp 4921−4941.

(2) Amerine, M. A.; Ough, C. S. In *Methods for Analysis of Musts and Wines*, 1st ed.; Wiley: New York, 1980.

(3) Davenel, A.; Grenier, P.; Foch, B.; Bouvier, J. C.; Verlaque, P.; Pourcin, J. Filter, Fourier transform infrared, and areometry, for following alcoholic fermentation in wines. *J. Food Sci.* **1991**, *56* (6), 1635−1638.

(4) Schindler, R.; Vonach, R.; Lendl, B.; Kellner, R. A rapid automated method for wine analysis based upon sequential injection (SI)-FTIR spectrometry. *Fresenius' J. Anal. Chem.* **1998**, *362*, 130−136.

(5) Li-Chan, E. C. Y.; Ismail, A. A.; Sedman, J.; van de Voort, F. R. Vibrational spectroscopy of food and food products. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; Wiley: Chichester, U.K., 2002; pp 3629−3662.

(6) Cabanis, M. T.; Cabanis, J. C.; Raffy, J.; Peyronnenche, M.; Viotte, O.; Leboeuf, J. P. L'Infralyzer 400: une détermination automatique du titre alcoolmétrique des vins. *Rev. Fr. Oenol.* **1983**, *89*, 75−79.

(7) van den Berg, F. W. J.; van Osenbruggen, W. A.; Smilde, A. K. Process analytical chemistry in the distillation industry using near-infrared spectroscopy. *Process Control Qual.* **1997**, *9*, 51−57.

(8) Gallignani, M.; Garrigues, S.; de la Guardia, M. Direct determination of ethanol in all types of alcoholic beverages by near-infrared derivative spectrometry. *Analyst* **1993**, *118*, 1167−1173.

(9) Tipparat, P.; Lapanantnoppakhum, S.; Jakmunee, J.; Grudpan, K. Determination of ethanol in liquor by near-infrared spectrophotometry with flow injection. *Talanta* **2001**, *53*, 1199−1204.

(10) Garcia-Jares, C. M.; Medina, B. Application of multivariate calibration to the simultaneous routine determination of ethanol, glycerol, fructose, glucose and total residual sugars in botrytized-grape sweet wines by means of near-infrared reflectance spectroscopy. *Fresenius' J. Anal. Chem.* **1997**, *357*, 86−91.

(11) Dambergs, R. G.; Kambouris, A.; Francis, I. L.; Gishen, M. Rapid analysis of methanol in grape-derived distillation products using near-infrared transmission spectroscopy. *J. Agric. Food Chem.* **2002**, *50*, 3079−3084.

(12) Urbano-Cuadrado, M.; Luque de Castro, M. D.; Pérez-Juan, P. M.; Garcia-Olmo, J.; Gomez-Nieto, M. A. Near infrared reflectance spectroscopy and multivariate analysis in enology. Determination or screening of fifteen parameters in different types of wines. *Anal. Chim. Acta* **2004**, *527*, 81−88.

(13) Bouvier, J. C. Réflexion sur l'analyse oenologique par spectrométrie infrarouge. *Rev. Fr. Oenol.* **2001**, *191*, 16−17.

(14) Mahia, P. L.; Gandara, J. S.; Losada, P. P. Validation of ethanol determination in alcoholic beverages by infrared spectrophotometry using orthogonal and derivative functions to correct for water absorption. *Vibr. Spectrosc.* **1992**, *3*, 133−138.

(15) Gallignani, M.; Garrigues, S.; de la Guardia, M. Derivative Fourier transform infrared spectrometric determination of ethanol in alcoholic beverages. *Anal. Chim. Acta* **1994**, *287*, 275−283.

(16) Patz, C. D.; David, A.; Thente, K.; Kurbel, P.; Dietrich, H. Wine analysis with FTIR spectrometry. *Vitic. Enol. Sci.* **1999**, *54* (2−3), 80−87.

(17) Dubernet, M.; Dubernet, M. Utilisation de l'analyse infrarouge à transformée de Fourier pour l'analyse oenologique de routine. *Rev. Fr. Oenol.* **2000**, *181*, 10−13.

(18) Andersen, S. T.; Hansen, P. W.; Andersen, H. V. Vibrational spectroscopy in the analysis of dairy products and wine. In *Hanbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, P. R., Eds.; Wiley: Chichester, U.K., 2002; pp 1−10.

(19) Brierley, P. R. Imaging stage for Fourier transform infrared spectrometer. U.S. Patent 5,965,889, 1999.

(20) Cocciardi, R. A.; van de Voort, F. R.; Sedman, J.; Ismail, A. A. Monitoring of lactose hydrolysis in milk by single-bounce attenuated total reflectance Fourier transform infrared spectroscopy. *Milchwissenschaft* **2004**, *59* (7−8), 403−407.

(21) Association of Official Analytical Chemists. In *Official Methods of Analysis*, 16th ed.; AOAC International: Arlington, VA, 1995; sec. 982.10.

(22) Haaland, D. M.; Thomas, E. V. Partial-least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information. *Anal. Chem.* **1988**, *60*, 1193−1201.

(23) Association of Official Analytical Chemists. In *Official Methods of Analysis*, 16th ed.; AOAC International: Arlington, VA, 1995; sec. 942.06.

(24) Association of Official Analytical Chemists. In *Official Methods of Analysis*, 16th ed.; AOAC International: Arlington, VA, 1995; sec. 950.04.

(25) Association of Official Analytical Chemists. In *Official Methods of Analysis*, 16th ed.; AOAC International: Arlington, VA, 1995; sec. 957.03.

(26) Noiseux, I.; Long, W.; Cournoyer, A.; Vernon, M. Simple fiber-optic-based sensors for process monitoring: an application in wine quality control monitoring. *Appl. Spectrosc.* **2004**, *58* (8), 1010−1019.

(27) Amerine, M. A.; Berg, H. W.; Kunkee, R. E.; Ough, C. S.; Singleton, V. L.; Webb, A. D. Legal restrictions on wine making. In *The Technology of Wine Making*, 4th ed.; Avi Publishing: Westport, CT, 1980; pp 715−755.

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