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Rapid Analysis of Methanol in Grape-Derived Distillation Products Using Near-Infrared Transmission Spectroscopy

ROBERT G. DAMBERGS,*,† AMBROSIAS KAMBOURIS,‡ I. LEIGH FRANCIS,† AND MARK GISHEN†

The Australian Wine Research Institute, P.O. Box 197, Glen Osmond, SA 5064, Australia, and BRL Hardy Limited, P.O. Box 238, Berri, SA 5343, Australia

Samples of distillates derived from the production of wine-fortifying spirit were analyzed for methanol by gas chromatography (GC) and near-infrared spectroscopy (NIRS). NIRS calibration models were developed which could accurately predict methanol concentrations in samples of fortifying spirit that had been produced over a period of three years from four different commercial distillation facilities. The best accuracy of the predictive models, as measured by the standard error of prediction value, was 0.06 g/L methanol. Other distillation fractions, produced during preparation of commercial fortifying spirit, were also examined. The most useful NIRS calibration models used partial least squares regression on continuous spectra from a scanning instrument, but it was demonstrated that calibrations could also be developed with a smaller number of fixed wavelengths, using multiple linear regression models. NIRS offers the advantages of rapid analysis, with simple routine operation, and may offer the potential for in-line process control in the operation of a commercial distillation facility.

KEYWORDS: Methanol; alcohol; fortifying spirit; near-infrared spectroscopy

INTRODUCTION

In the production of fortified wines, Australian legislation demands the use of only grape-derived ethanol (Australian Food Standards Code, Regulation P4, 2001, Australia and New Zealand Food Authority). Wine-fortifying spirit, known as SVR (from the Latin *spiritus vini rectificatissimus*), is generally produced in commercial facilities from the distillation of byproducts of the winemaking process, rather than from finished wine. SVR commonly contains around 96% v/v ethanol with low concentrations of other volatile compounds. A major source of grape alcohol is from grape pomace (waste from a pressing step in wine production) and consists of predominantly skins, seeds, and stems, but contains sufficient ethanol or fermentable sugar to warrant recovery (*1*).

Methanol is one of the major undesirable contaminants in SVR. Methanol can occur in trace amounts in wine, possibly due to the action of naturally occurring pectin methyl-esterase in grapes (*2*), or by the use of exogenous enzymes added during the winemaking process (*3*, *4*). In pomace, as a result of the storage conditions before distillation, bacterial and fungal activity can result in production of methanol (*5*). The use of this type of material for the production of wine-fortifying spirit is therefore one of the major sources of methanol in wine.

In the commercial production of SVR, the distillation process must be carefully monitored to minimize methanol carry-over in the ethanol fractions, particularly when distilling material with high methanol concentration. A common method for measuring methanol in wine and wine-fortifying spirit is gas chromatography (*2*−*6*). This is a relatively complex and slow procedure, requiring an experienced analyst. Most large commercial spirit production facilities use continuous distillation equipment that requires careful adjustment to achieve a steady-state which produces spirit of the required low methanol content. Rapid analysis of the spirit composition is therefore required to expedite monitoring of the distillation process.

Enzyme electrodes have been suggested as a possibility for on-line determination of both ethanol and methanol during fermentation of wine, beer, or cider (*7*), but such electrodes are unlikely to remain stable at the high ethanol concentrations occurring in fortifying spirit, because of enzyme-denaturation effects. NMR spectroscopy has also been suggested as an analytical tool for measuring methanol in wine (*8*), but quantitative methods are complex, requiring multiple scans over a long period for good resolution at low methanol levels, and instrumentation is too expensive for cost-effective commercial application.

Near-infrared spectroscopy has gained wide acceptance within food and agriculture industries as a rapid analytical tool (*9*, *10*) and its main use in the wine industry has been for alcohol (ethanol) measurement in wines (*11*, *12*). NIRS has also been used for the measurement of alcohol (ethanol) in beer (*13*). It offers the advantage of rapid, nondestructive analysis, and, although calibrations can be difficult to prepare, routine operation is simple. To our knowledge, although NIRS has been

* To whom correspondence should be addressed (telephone +61-8-8303-6600; fax +61-8-8303-6601; e-mail bob.dambergs@awri.com.au). Formerly with BRL Hardy Limited.
† The Australian Wine Research Institute.
‡ BRL Hardy Limited.

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Table 1. Summary of GC Reference Data Statistics for Methanol Concentration in the Sample Sets Examined

distillate fraction	source of distillate	vintages	no. of samples	minimum (g/L)	maximum (g/L)	mean (g/L)	standard deviation (g/L)
SVR	producer A	1998, 1999, 2000	142	0.02	4.28	1.35	0.76
SVR	producer A	1998, 1999	123	0.02	4.28	1.29	0.42
SVR	producers B, C, D	1999	15	0.03	2.35	1.22	0.86
feints	producer A	1999	61	0.86	20.1	3.28	3.59
heads	producer A	1999	48	4.06	188.8	53.6	48.2

applied to ethanol measurement in beverages, it has not been applied to the rapid analysis of methanol in distilled spirits. The major objective of this study was to determine the feasibility of using NIRS for analysis of low levels of methanol in wine-fortifying spirit.

The total alcohol concentration is also an important standard measure for fortifying spirit and is normally done by densitometry, with the assumption that the major component is ethanol. We have also examined the use of NIRS at the high alcohol levels encountered in fortifying spirit to investigate the feasibility of the simultaneous measurement of methanol and total alcohol to provide a valuable process monitoring tool. The concept of distillation-process control aided by NIRS monitoring has been demonstrated previously in a study examining the recovery of solvent waste in the pharmaceutical industry (*14*).

MATERIALS AND METHODS

Samples. Samples of wine-fortifying spirit, known as SVR, derived from source material produced over a period of three vintages (1998, 1999, and 2000) were obtained from one commercial producer (producer A). The main source of distillation starting material for these samples was grape pomace.

NIRS methods require validation with a wide range of samples to check for sample matrix effects. The main validation and calibration work was done with samples from producer A, but further validation samples of fortifying spirit (SVR) were collected from three other commercial producers (B, C, and D) from the 1999 vintage.

Two other major distillation process fractions, "feints" and "heads", were also collected from one vintage (1999) from producer A. Feints are primary fractions from a first pass through the distillation columns and are the starting material for the final SVR fraction. Heads are low-boiling-point waste fractions collected from the top of the distillation columns. Samples required no pretreatment for either NIRS or GC analysis.

Reagents. Pure ethanol and methanol (analytical reagent grade) were obtained from BDH Chemicals.

Conventional Analyses. The method for methanol analysis was gas chromatography (GC) using a Varian 3400 G instrument with an SGE 25QC3/BP20, 25-meter polyethylene glycol-coated capillary column, with an internal diameter of 0.5 mm. Injection volume was 0.5 μL, with a 1/20 split ratio, and nitrogen was used as the carrier gas. The injector temperature was 220 °C. The starting column temperature was 55 °C with a 5 min hold, followed by an increase to 160 °C at 30 °C/min, with a final hold for 2 min at 160 °C. Peak detection was by flame ionization, with a detector temperature of 260 °C. External standards were used to create a 3-point calibration curve. Method validation indicated a measurement uncertainty of 3% and a standard error of 0.04 g/L methanol.

The method for determination of total alcohol was density measurement by hydrometry, corrected to 20 °C. The uncertainty of measurement in the method was 0.1% and the standard error was 0.07% v/v ethanol.

NIR Spectroscopy and Chemometric Analysis. Samples were scanned with a NIRSystems 6500 (Foss NIRSystems, Australia), from 400 to 2500 nm, in transmittance mode, and with a 1-mm path length. A reference scan was taken before each sample scan. To increase the signal to noise ratio, both reference and sample spectra were averaged from 32 scans. Samples were temperature equilibrated at 33 °C in the instrument before scanning. Temperature effects can often be accounted for in NIRS calibration methods, but temperature equilibration is important in a mixed alcohol system, where hydrogen bonding effects are very significant (*15*). Error introduced by such effects may be particularly significant at the low methanol concentrations encountered in these matrixes that could possibly be close to the limits of quantitative detection by NIRS.

Chemometric analysis was performed with the Vision software package (Foss NIRSystems). Various combinations of wavelength ranges and mathematical treatments were tested resulting in selection of an optimal routine using a wavelength range of 1200−2450 nm and partial least squares (PLS) regression on the first derivative treated spectra. The coefficient of determination (R^2) relates to the NIRS predicted value regressed with the reference value obtained by analysis using the conventional method; the standard error of calibration (SEC) refers to the standard error of this regression. The standard error of cross validation (SECV) was calculated by a sequential removal of four cases from the calibration set and predicting them with the recalculated calibration model. The standard error of prediction (SEP) was calculated using a validation set separate from the calibration set. Samples in validation sets were independent of those in the calibration sets and represented different production runs or different distillation fractions from the same producer, or were from three other producers, representing the majority of the fortifying spirit production in Australia. The number of factors for PLS calibrations was determined by using the minimum prediction residual error sum of squares (PRESS) value.

RESULTS AND DISCUSSION

Reference Analyses. Reference data for methanol, obtained by GC analysis, are shown in **Table 1**. The fortifying spirit fractions (SVR) had the lowest average methanol concentration. The feints and heads fractions varied greatly in methanol levels, but heads had the highest average methanol concentrations. There was a wide range of methanol concentration for each of the fraction types, but the range was greatest for the heads fraction. Reference data for total alcohol in SVR samples ranged from 93.7 to 96.5% v/v, with a mean of 95.57% v/v, and a standard deviation of 0.36% v/v, for a set of 94 samples (all obtained from producer A from the 1999 vintage). The total alcohol range was clearly small, as is normally the case with this type of distillation fraction, because distillers aim for the highest possible alcohol concentration (the ethanol/water azeotrope mixture is 95.58% v/v).

Spectra. The NIR spectra of pure methanol and ethanol are compared in **Figure 1**. With these relatively simple organic structures, NIR band assignments are already known or can be proposed (see ref *8* for a summary of the NIR band assignments for the major functional groups). For example, peak 1 at 2080 nm is the combination band of OH stretch + OH deform: because methanol contains a higher concentration of OH on a molar basis, it will have a stronger signal, with a slight wavelength shift compared to ethanol, possibly due to differences in hydrogen bonding. Similarly, peak 2 at 2276 nm is common to both methanol and ethanol, but is elevated in the former and is most likely to be the combination band of CH stretch + CH deform from the CH_3 group, albeit with a small amount of wavelength shift. An example of a peak specific to ethanol is peak 3 at 2310 nm, which is most likely to be the

Table 2. Methanol PLS Regression[a] Calibration Statistics: Coefficient of Determination (R^2), Standard Error of Calibration (SEC), Standard Error of Cross Validation (SECV), and for Those Sample Sets Where a Separate Validation Set Was Used, the Standard Error of Prediction (SEP)

calibration set[b]	validation set	R^2	number of factors used	SEC (g/L)	SECV (g/L)	SEP (g/L)	SD/SECV[c]
1998, 1999, 2000 SVR ($n = 142$)		0.998	15	0.04	0.06		12.5
1998, 1999 SVR ($n = 123$)		0.998	15	0.04	0.07		11.1
1998, 1999 SVR ($n = 123$)	2000 SVR producer A	0.992	15			0.06	
1998, 1999, 2000 SVR	1999 SVR producers B, C, D	0.990	15			0.12	
1998, 1999, 2000 SVR	feints 1999, producer A	0.997	15			0.28	
1998, 1999, 2000 SVR	heads 1999, producer A	0.996	15			4.55	
feints ($n = 61$)		0.998	5	0.16	0.21		17.1
heads ($n = 48$)		0.998	3	2.14	2.40		20.1

[a] Wavelength range: 1200–2450 nm; math treatment: first derivative. [b] All samples used for calibration were from producer A. [c] Ratio of the standard deviation of methanol by GC to the SECV of methanol by NIRS.

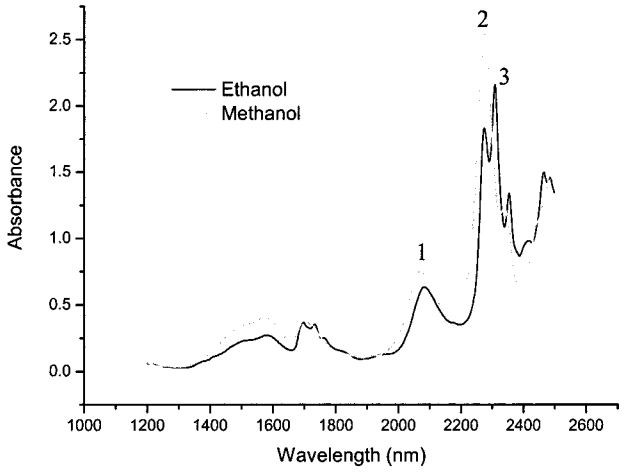

Figure 1. NIR spectra of pure methanol and ethanol, 1 mm path length.

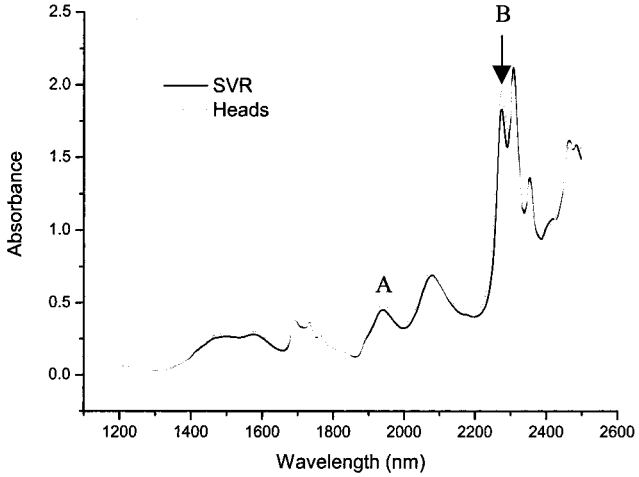

Figure 2. NIR spectra of an SVR sample (1 g/L methanol) and a heads sample (114 g/L methanol), 1 mm path length.

combination band of CH stretch and CH deform from the CH_2 group. However, even with a relatively simple system, such as mixtures of ethanol and methanol, interpretation of NIR spectra can be complicated because of hydrogen bonding related shifts and possible vibrational bands arising from intermolecular interaction (*16*). NIR absorbance bands rely on anharmonicity in the overtones of fundamental vibrations with energies in the infrared region and as such are very matrix dependent; although it can be difficult to assign wavelengths to structures, because of matrix-dependent wavelength shifts, chemometrics can be used to correlate spectral features with analyte concentrations (*9*).

Examples of spectra from distillate fractions are shown in **Figure 2**. The samples represent the extremes of methanol levels, with an SVR sample at 1 g/L methanol and a heads sample at 114 g/L methanol. In comparison with the spectra of pure methanol and ethanol, a major difference in the distillate samples is a broad peak at 1940 nm (region A), related to the small amount of water present in the distillates. Close examination of expanded spectra revealed many small differences, but major differences occur at the region marked B, possibly related to the CH_3 group, as discussed with **Figure 1**.

Methanol PLS Calibration Model. Calibration results are given in **Table 2**. A PLS calibration model for NIRS prediction of methanol in SVR was prepared using samples from three vintages. The correlation plot comparing NIRS with GC results is shown in **Figure 3** and was linear over the range measured from 0.02 to 4.28 g/L ($R^2 = 0.998$). The SEC for this model was similar to the standard error for the GC reference method. The more relevant value is the SECV, which was acceptable at 0.06 g/L, considering that this represents an error of 2% of the upper limit for the methanol concentration allowed in the commercial product (3 g/L, Australian Food Standards Code, Regulation P3, 2001, Australia and New Zealand Food Authority).

SVR represents the low range of methanol levels encountered, but the heads samples represent the high range (4.06−188.8 g/L methanol). The NIRS calibration for heads samples was linear over this range, with an R^2 of 0.998 and an SECV of 2.40 g/L methanol (**Table 2**).

The number of factors used in the SVR methanol calibration was relatively high, but with PLS models, absorbance nonlinearities caused by hydrogen bonding in such a mixed alcohol system can be compensated for by using a large number of factors (*15*); this may be particularly significant at the low methanol concentrations in SVR, where the precision of the calibration must be maximized. To avoid overfitting, the number of factors was optimized using the PRESS value (the first minimum PRESS before an increase). The validity of this

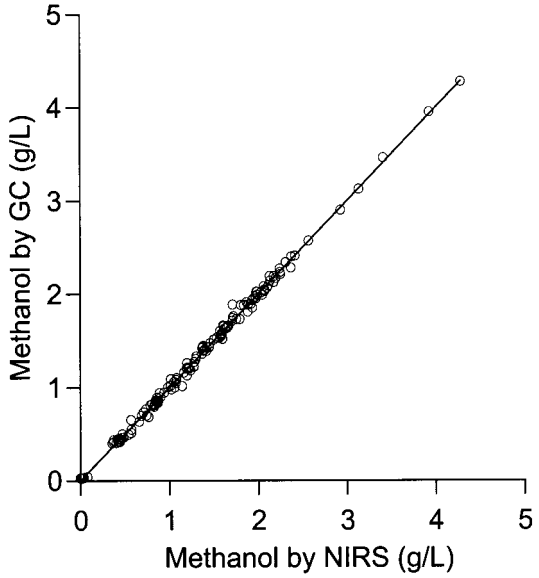

Figure 3. Relationship of methanol determination by NIRS and by GC in SVR samples from producer A from the 1998, 1999, and 2000 vintages ($n = 142$) (see **Table 2** for more details). Wavelength range 1200–2450 nm; math treatment first derivative, PLS; calibration statistics $R^2 = 0.998$, SEC = 0.04 g/L, SECV = 0.06 g/L.

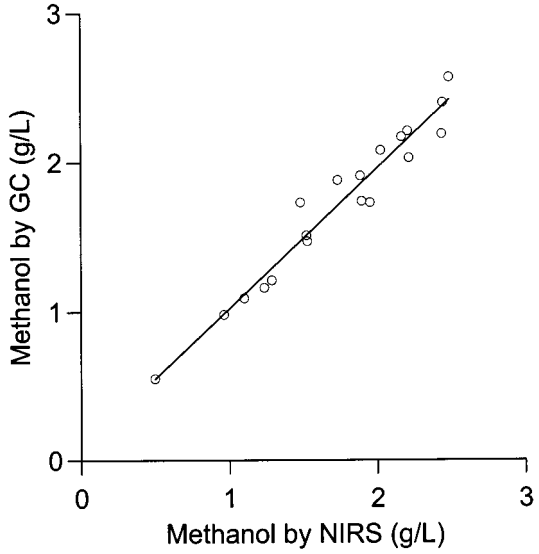

Figure 4. Relationship of methanol determination by NIRS and by GC in SVR samples from a validation set from the 2000 vintage from producer A using an MLR calibration model developed from 1998 and 1999 vintage SVR samples from producer A. Wavelengths used: 1732 nm, 2192 nm, 2412 nm, 2276 nm, 2290 nm, 1718 nm, 2308 nm, 2204 nm; math treatment first derivative, MLR; validation statistics $R^2 = 0.98$, SEP = 0.12 g/L.

calibration model is further demonstrated with the prediction of 2000 vintage samples with a calibration model prepared with 1998 and 1999 samples (**Table 2**).

The ability of calibrations to predict other sample sets can be estimated by examining the ratio of the standard deviation of the reference analysis data to the NIRS calibration SECV. A ratio greater than three indicates a robust calibration (*17*). The methanol calibrations had ratios ranging from 11.1 to 20.1 (**Table 2**), providing further evidence of their ability to be applied to samples outside the calibration set.

Sample Matrix Effects. Production of fortifying spirit by distillation is often a seasonal event and process conditions may vary from year to year, with the possible introduction of matrix effects that can increase errors in NIRS calibrations. As discussed above, methanol in SVR calibrations could predict across vintages and a combined calibration could be produced (**Table 2**).

Other matrix effects could be introduced with samples from different producers. This was examined with samples from three other Australian production facilities using different source materials and distillation units. Although the SEP value was increased, it was still acceptable for commercial use and presumably can be improved by incorporation of further samples into the calibration set. In this study, insufficient samples from other distillers were available to further develop a more robust, global calibration. Variation among distillers may not be a significant issue in Australia, as the number of producers is small.

Other examples of matrix variation are demonstrated by prediction of the feints and heads fractions with calibrations derived from SVR fractions. The feints fractions are similar in composition to the final product and this is reflected in the ability of a calibration model derived from SVR samples for predicting the methanol concentration in feints: the SEP was similar to the SECV obtained with a feints-only calibration model. Heads represent an extreme example of matrix variation in this system: although similar in total alcohol to fortifying spirit, they have relatively high methanol, acetaldehyde, and ethyl acetate levels (*18*). As expected, the SEP for an SVR calibration model predicting heads (SEP = 4.55 g/L) was greater than the SECV for a calibration model developed for heads only (SECV = 2.40 g/L) − a complicating factor could be nonlinearity of the NIR spectra of methanol over the large concentration range encountered when comparing SVR with heads. Artificial neural network (ANN) calibration models can improve the accuracy of NIRS calibrations in situations of nonlinearity and have been successful in the measurement of methanol in model systems (*15*), but the size of this data set may have to be significantly increased in order to effectively develop a robust ANN model.

Note that when comparing relative error (expressed as percentage of mean value), matrix-specific calibrations for SVR, feints, and heads were similar, but the feints and heads calibrations used fewer factors, possibly a reflection of the higher methanol concentrations in these fractions.

Multiple Linear Regression Calibration Model. The data shown in **Table 2** were derived from PLS calibration models, using continuous spectral data produced with a relatively expensive scanning instrument. Photodiode array based instruments offer a cheaper alternative at lower wavelengths, but in the long-wavelength range required for optimal methanol calibrations, a fixed wavelength instrument may be a cost-effective option for a routine, commercial application. A multiple linear regression (MLR) calibration model was tested using fixed wavelengths derived from the continuous spectral data (**Figure 4**). The wavelengths were chosen at points of maximum correlation with the methanol reference value, combined with minimum sensitivity to slight wavelength shifts (i.e., minimum loss of correlation caused by deviation around the selected wavelength). The SEP for this calibration model was twice that of a PLS model, but was at a level where commercial application was still viable. The wavelengths used in the MLR calibration model all related to areas of spectral differences between methanol and ethanol, the major components in this system (**Figure 1**).

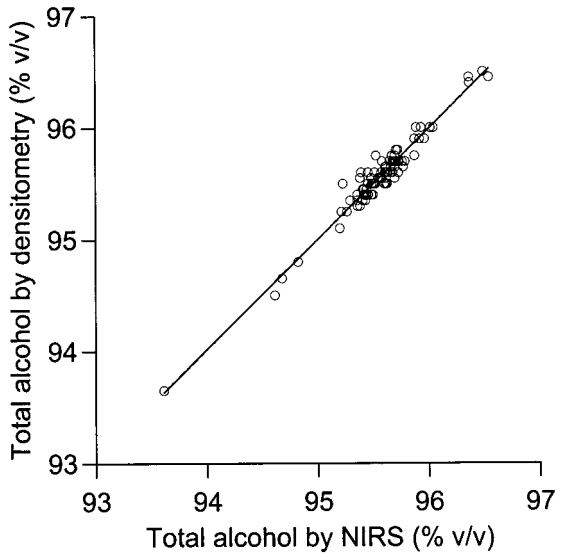

Figure 5. Total alcohol by NIRS vs densitometry (SVR samples). Wavelength range 1200–2450 nm; math treatment first derivative, PLS; calibration statistics $R^2 = 0.96$, SEC = 0.08 g/L, SECV = 0.08 g/L.

Total Alcohol Calibration Model. Although it was not one of the initial aims of this study, an NIRS calibration model for "total alcohol" determination was tested. The compositional variable "total alcohol" in fortifying spirit, based on the assumption that the major components of fortifying spirit are ethanol and water, is normally measured by densitometric methods using conversion tables based on ethanol/water mixtures. The total alcohol is an important parameter in distillation control and is required in the final product for the calculation of wine fortification rates and for government regulatory control. Despite the very small range of alcohol concentrations in SVR, a good calibration model for alcohol in SVR was developed, using samples from three vintages (**Figure 5**). It is noted that this model used only four PLS factors and had an SECV of the same magnitude as the SEC, indicating that it was likely to be a robust model. This degree of accuracy would be adequate for simultaneous monitoring of both methanol and total alcohol for control of the distillation process.

In summary, rapid analysis of wine-fortifying spirits for the determination of methanol and total alcohol can be performed by NIRS. Using this methodology, analysis time can be reduced from hours to minutes, with minimal operator training. Errors introduced by sample matrix variation are relatively minor and could be further reduced with improved calibration methods and increased calibration set size. The concentrations of the primary analytes, methanol and total alcohol, can be determined simultaneously, with a degree of accuracy that is sufficient to allow process control in a commercial distillation operation.

ABBREVIATIONS USED

GC, gas chromatography; NIRS, near-infrared spectroscopy; SVR, *spiritus vini rectificatissimus;* PLS, partial least squares; R^2, coefficient of determination; SEC, standard error of calibration; SECV, standard error of cross validation; SEP, standard error of prediction; PRESS, prediction residual error sum of squares; ANN, artificial neural network; MLR, multiple linear regression.

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