Prediction of Enological Parameters and Discrimination of Rice Wine Age Using Least-Squares Support Vector Machines and Near Infrared Spectroscopy

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The use of least-squares support vector machines (LS-SVM) combined with near-infrared (NIR) spectra for prediction of enological parameters and discrimination of rice wine age is proposed. The scores of the first ten principal components (PCs) derived from PC analysis (PCA) and radial basis function (RBF) were used as input feature subset and kernel function of LS-SVM models, respectively. The optimal parameters, the relative weight of the regression error γ and the kernel parameter σ^2, were found from grid search and leave-one-out cross-validation. As compared to partial least-squares (PLS) regression, the performance of LS-SVM was slightly better, with higher determination coefficients for validation (R_{val}^2) and lower root-mean-square error of validation (RMSEP) for alcohol content, titratable acidity, and pH, respectively. When used to discriminate rice wine age, LS-SVM gave better results than discriminant analysis (DA). On the basis of the results, it was concluded that LS-SVM together with NIR spectroscopy was a reliable and accurate method for rice wine quality estimation.

KEYWORDS: Near-infrared spectroscopy; least-squares support vector machines; enological parameter; rice wine age

INTRODUCTION

Authenticity of foods and, in particular, of wine has been extensively investigated because wine is an easily adulterated product due to its strong chemical basis (high alcohol content, low pH) and its availability throughout the world (*1*). Meticulous and continuous controls are required to maintain the quality and the authenticity of wine, mainly in terms of variety, geographical origin, vintage, and wine age. Quality determination of wine is usually performed according to wet chemical methods, high-performance liquid chromatography (HPLC), gas chromatography (GC), and so on. Discrimination of wine age has been performed according to chemical features analyzed by HPLC, such as pigment composition (*2, 3*), phenolic compounds (*4, 5*), and flavonoids (*6*). However, the methods mentioned above are relatively labor-intensive and time-consuming. The potential of near-infrared (NIR) spectroscopy as a fast analysis, good precision, and accuracy as a multiparameters analytical tool in estimating quality of wine has been recognized for many years.

It has been applied to predict methanol in wine-fortifying spirit (*7*), to determine trace metals in white wine and rice wine (*8, 9*), to evaluate alcohol content (*10*), to determine phenolic compounds in red wine fermentations (*11*), to determine alcohol content, original and real extract and titratable acidity in beer (*12, 13*), to screen enological parameters in different types of wines (*14, 15*), and to determine concentration of enological parameters of rice wine (*16*). It has also been applied to discriminate varietal origin (*17*), geographical origin (*18, 19*), and rice wine age (*20*).

The NIR spectroscopic technique is based on measurement of the frequencies of the vibrations of chemical bonds in functional group such as C—C, C—H, O—H, C=O and N—H upon absorption of radiation in the NIR region. The measured frequencies are processed through a series of mathematical procedures to an absorbance spectrum, which in turn is correlated to the actual concentration of the relevant component in the sample matrix through a calibration process that involves multivariate statistical procedures such as principal component analysis (PCA), principal component regression (PCR), and partial least-squares (PLS) regression, which are the most commonly used multivariate methods (*21*). Recently, support vector machines (SVM), a learning algorithm based on the statistical learning theory (*22*), have been introduced as promis-

ing alternatives to the existing linear and nonlinear multivariate statistical procedures. SVM has the advantage that it can deal with ill-posed problems and can lead to global models that are often unique. Furthermore, because of its specific formulation, sparse solutions can be found, and both linear and nonlinear regression can be performed (*23*). As a powerful tool for data classification and regression, SVM has only recently been used for NIR spectroscopy analysis. In the aspect of classification, Langeron et al. (*24*) used SVM for classification of textile products; Polat et al. (*25*) used least-squares support vector machines (LS-SVM) for discrimination of breast cancer; Chen et al. (*26*) used SVM for identification of green, black, and Oolong teas. In the aspect of regression, Chauchard et al. (*27*) applied LS-SVM for prediction of total acidity in fresh grapes; LS-SVM regression showed more accurate prediction than PLS and multivariate linear regression (MLR); Borin et al. (*28*) quantified common adulterants in powdered milk using LS-SVM, with low prediction errors and superior performance in relation to PLS; Kovalenko et al. (*29*) determined amino acid composition of soybeans and concluded that the performance of PLS and LS-SVM was better than that of artificial neural network (ANN). Yet, in the field of wine quality determination, no applications of SVM on classification or regression have been reported.

LS-SVM is very well suited for high-dimensional problems with few data, as is often the case in NIR applications (*30*); in this study, LS-SVM combined with NIR spectra was used to predict enological parameters and to discriminate wine age of rice wine. In addition, the prediction performances of LS-SVM in the case of regression and classification were compared with PLS and discriminant analysis (DA), respectively.

MATERIALS AND METHODS

Sample Preparation. Rice wine samples from 147 bottles were sourced from "Pagoda" brand Shaoxing rice wine brewery (Zhejiang cereal, oils, and foodstuffs import and export Co., Ltd. "Pagoda" brand Shaoxing rice wine brewery. Shaoxing, Zhejiang, China). Among them, 50 were of aged 1 year, 48 were of aged 3 years, and 49 were of aged 5 years.

Shaoxing rice wine is the most well-known rice wine, which is known by the generic name "Shaoxing", a sort of denomination of origin. It is made from high-quality glutinous rice and wheat. Glutinous rice has higher protein and lower fat contents as compared to non-glutinous rice, and wheat serves as an abundant carbon, nitrogen, and microelement source for yeast in fermentation. The unique brewing technology passed down through many generations provides Shaoxing rice wine with a bright brown color, subtle sweet flavor, and low alcohol content (*31, 32*). These wines are typically aged between 1 and 20 years. The rice wine samples used in this study were selected from different batches of production for each age group.

In multivariate analysis, such as PLS, DA, and LS-SVM, the rice wine samples were divided into two parts. One part was used for training the model (calibration set), another part was used to evaluate the performance of the model (validation set). For enological parameter prediction, the concentrations of each enological parameter were arranged in ascending order, and then one validation sample was chosen from every three samples. Thus, 98 samples were for the calibration set, and the remaining 49 samples were for the validation set. For wine age discrimination, 16 samples of each age group were used for the validation set, and the remaining 34, 32, and 33 samples of 1-, 3-, and 5-year aged wines were used for the calibration set, respectively. The validation samples were randomly selected.

Chemical Analysis. Each sample was analyzed for alcohol content, titratable acidity, and pH. Reference analyses were in accordance with the Official Methods of Analysis for Chinese Rice Wine and Official Methods of Analysis for Shaoxing Rice Wine (GB/T 13662–2000 and GB 17946–2000) (*33, 34*). (GB means national standard; 13662 and 17964 were the codes of the two official methods; and 2000 was the

Table 1. Enological Parameters and Reference Methods

enological parameter	reference method
alcohol content	distillation and aerometry
titratable acidity	titration with NaOH up to 8.20
pH	potentiometry

year in which the methods were revised.). All analyses were done in duplicate. The reference methods for the three enological parameters are shown in **Table 1**.

Spectral Measurement. Samples taken from freshly opened bottles of rice wine were scanned in transmission mode using a commercial FT-NIR spectrometer (Thermo Nicolet Corp., Madison, Wisconsin) and a liquid cell of 1 mm optical path-length. The spectrometer consisted of an interferometer, an InGaAs detector with a spectral range of 800–2500 nm, a wide-band light source (50 W quartz tungsten halogen), and a transmission accessory.

Samples were scanned in the liquid cell at room temperature. A reference spectrum was acquired for an empty cell without sample, and the reference spectrum was subtracted from the sample spectra to remove background noise. OMNIC v6.1 software (Thermo Nicolet Corp., Madison, Wisconsin) was available for spectrometer setup and spectra acquiring operation. The spectrometer was configured for spectra acquisition using the parameters provided as follows: mirror velocity, 0.9494 cm s^{-1}; resolution, 16 cm^{-1}; and scan number, 32 times. The transmission spectra were saved as absorbance.

Multivariate Modeling. For enological parameter prediction, PLS and LS-SVM were used to establish calibration models. For rice wine age discrimination, the prediction performance of DA and LS-SVM were compared.

PCA. PCA is a powerful tool in explorative data analysis. It was used here to extract information from the data, and to reduce the dimensionality of the spectra. Explorative data analysis is the first fundamental step for obtaining information about the variables, the objects, and their relations. The explorative analysis and representation techniques are useful for identifying general data features, finding similarities between the samples or the variables by which they are characterized, and detecting anomalies or errors, to devise the appropriate classification or correlation strategies (*35*). By calculating the eigenvectors of the covariance matrix of the original inputs, PCA transforms the original independent variables (wavelengths) into new axes and calculates the principal components (PCs) as new variables by a relevant algorithm to replace the original data. The PCs are orthogonal and account as much as possible for the variability in the original variables (*17*). The PC plot can indicate the interrelationships between different variables.

In this study, spectra were exported from the OMNIC software into a commercial software package, TQ Analyst v6.2.1 (Thermo Nicolet Corp., Madison, Wisconsin) for PCA.

PLS. PLS is a method for relating two data matrices, **X** and **Y**, by a linear multivariate model, but it goes beyond traditional regression in that it also models the structure of **X** and **Y**. PLS derives its usefulness from its ability to analyze data with many, noisy, collinear, and even incomplete variables in both **X** and **Y**. PLS has the desirable property that the precision of the model parameters improves with the increasing number of relevant variables and observations (*36*). The properties of PLS and examples of its use have been dealt with extensively in the refs *37*.

PLS and leave-one-out cross-validation were used for establishing calibration models for alcohol content, titratable acidity, and pH of rice wine. Leave-one-out cross-validation estimated the prediction error by splitting all samples into two groups. One was reserved for validation, and the other was used for calibration. The process was repeated until all samples had been used once in the validation set. The optimum number of factors used in PLS was determined by the lowest value of predicted residual error sum of squares (PRESS). In this study, PLS were performed using TQ Analyst.

LS-SVM. LS-SVM has been proposed as a class of kernel machines related to many other well-known techniques (e.g., kernel Fisher discriminant analysis, PCA, canonical correlation analysis, PLS, or

Rice Wine Quality Estimation Using LS-SVM and NIR

J. Agric. Food Chem., Vol. 56, No. 2, 2008 **309**

Table 2. Statistics of Chemical Analysis Results for Alcohol Content, Titratable Acidity, and pH of the 1-, 3-, and 5-Years Aged Sample Set

enological parameter	1-year aged		3-year aged		5-year aged		F-value ($F_{0.05}$ = 3.14)
	range	average	range	average	range	average	
alcohol content (%(V V^{-1}))	17.64~18.20	17.91	17.05~17.55	17.29	17.16~18.01	17.65	126.9
titratable acidity (g L^{-1})	4.05~4.43	4.25	4.43~4.89	4.52	4.22~4.51	4.41	103.1
pH	4.25~4.30	4.28	4.20~4.35	4.26	4.34~4.41	4.38	135.1

recurrent neural networks). It is also closely related to Gaussian processes and regularization networks but uses an optimization approach as in SVM. Therefore, LS-SVM encompasses similar advantages as SVM, but its additional advantage is that it requires solving a set of only linear equations (linear programming), which is much easier and computationally very simple (*23*). For detailed in-depth theoretical background on LS-SVM for both regression and classification, the reader is referred to the introductions of refs *38 and 39*.

Proper kernel function and optimum kernel parameters are the crucial elements in LS-SVM. Kernel functions typically used are the polynomial function $\langle x_i, x \rangle^d$ and the radial basis function (RBF) exp($-\|x_i - x\|^2/\sigma^2$), which is a Gaussian curve. As can be seen, each kernel function is associated with a kernel specific parameter. For the polynomial and RBF kernels, these parameters are the degree of the polynomial (d) and the width of the Gaussian function (σ^2), respectively. So instead of calculating a specific mapping for each dimension of the data, the problem comes down to selecting a proper kernel function and optimizing its specific parameter.

In this study, PCA was used to derive the first ten PCs from the spectral data to ensure that all variability is considered by the analysis. The scores of these PCs were used as the inputs of the LS-SVM models. The often used Gaussian kernel (RBF) was used, because it was a nonlinear function and a more compact supported kernel and could reduce the computational complexity of the training procedure while giving good performance under general smoothness assumptions. The optimal parameters, the relative weight of the regression error (γ) and the kernel parameter (σ^2), were found from an intensive grid search and leave-one-out cross-validation. In practice, this numerical approach was the most common one used. Grid search is a two-dimensional (2D) minimization procedure based on exhaustive search in a limited range. In each iteration, one leaves out one point, and fits a model on the other data points. The performance of the model is estimated based on the point left out. This procedure is repeated for each data point. Finally, all of the different estimates of the performance are combined.

All LS-SVM algorithms were implemented with MATLAB v7.0 (The MathWorks, Natick, Massachusetts) and a free LS-SVM toolbox for MATLAB (LS-SVM v1.5, Suykens, Leuven, Belgium) under Windows XP.

DA. DA is a supervised pattern recognition method, which seeks to find a linear transformation by maximizing the between-class variance and by minimizing the within-class variance. The discriminant function obtained in this way produces a new variable, which is a linear combination of the original variables. This variable is called the canonical variable. When there are g classes, only ($g - 1$) discriminant functions can be determined (*35*). In this study, DA was performed using TQ Analyst.

For enological parameter prediction, statistics include determination coefficients for validation (R_{val}^2, eq 1), and root-mean-square error of validation (RMSEP, eq 2).

$$R_{\text{val}}^2 = \left[1 - \frac{\sum\limits_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum\limits_{i=1}^{n}(y_i - y_m)^2} \right] \times 100\% \qquad (1)$$

$$\text{RMSEP} = \sqrt{\frac{1}{n}\sum\limits_{i=1}^{n}(y_i - \hat{y}_i)} \qquad (2)$$

Where y_i is the reference value of the ith sample, $\hat{y}_i$ is the predicted value of the ith sample, y_m is the average of the reference value of

the validation set, and n is the number of samples in the validation set.

For wine age discrimination, the percentage of samples correctly classified was used to evaluate the prediction performance of models developed by DA and LS-SVM.

RESULTS AND DISCUSSION

Chemical Analysis Results. The statistical data for alcohol content, titratable acidity, and pH of the 1-, 3-, and 5-year aged sample groups are listed in **Table 2**. To compare statistically, the *F*-test was performed on the reference data of the three sample groups. As listed in **Table 2**, the *F*-values of the three enological parameters are all higher than $F_{0.05}$, which indicates that the values of alcohol content, titratable acidity, and pH of the 1-, 3-, and 5-year aged sample groups are significantly different.

Spectra Analysis. Figure 1, panels **a** and **b**, shows the average spectra and standard deviation, respectively, of spectral data for the 1-, 3- and 5-year aged sample groups. The main features of the rice wine spectra are absorption bands at 1455, 1900–1950, 2266, and 2300 nm. The absorption bands at 1455 and 1900–1950 nm are related to the first overtone of the O—H stretch of H_2O and a combination of stretch and deformation of the O—H group in water and ethanol, respectively. The band around 2300 nm is associated with the CH_2 group of ethanol (*16*). The spectra in the region of 1900–1950 nm are off scale, and therefore are not used in further analysis.

The spectral differences between the 1-, 3- and 5-year aged sample groups can be observed from 2250 to 2320 nm, as shown in **Figure 1(a)**. The sequence for the absorbance intensity of the three sample groups is in accordance with that of alcohol content (**Table 2**). The highest is the 1-year aged sample group, next is the 5-year aged, and then the 3-year aged. The standard deviation of spectral data for the 1-, 3- and 5-year aged groups is shown in **Figure 1(b)**. It can be seen that the largest deviations are in the region of 1900–1950 nm and the deviations of other regions are small.

PCA. PCA was performed on the full spectral region, 800–2500 nm. The spectra of the first three PCs for alcohol content analysis are shown in **Figure 2**. The loadings of the first three PCs account for 92.81% of the variation in the spectra. PC1 accounts for 49.55% of the total variance, and PC2 explains 30.56% of the total variance. The highest eigenvectors of the first two PCs are found at 1410 and 1884 nm, both related to O—H overtones due to water, and the highest eigenvectors of PC3 are at 2266 and 2300 nm, associated with the CH_2 group of ethanol.

Although PCA itself can not be used as a classification tool, it may indicate the data trend in visualizing dimension space. **Figure 3** shows the three-dimensional (3D) PC score plot using the first three score vectors, PC1, PC2, and PC3, derived from raw spectra of the samples. The initial three factors, which account for 92.82% of the spectral variations (49.68, 30.48, and 12.66% for PC1, PC2, and PC3, respectively) related to chemical quality and are indicated as positive or negative, are used to make differentiation clearer. As can be seen, the samples with
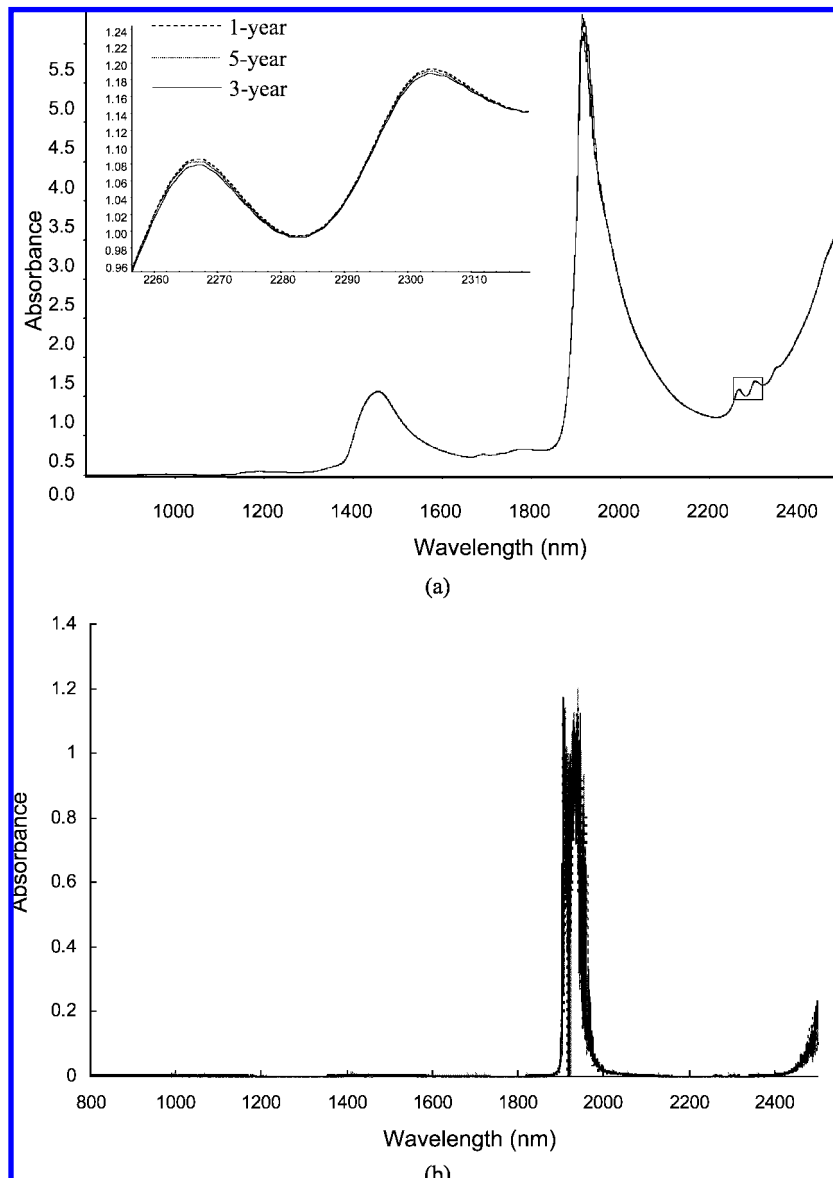
Figure 1. (**a**) Average spectra of 1-, 3- and 5-year aged rice wine sample groups and (**b**) standard deviation of spectral data for 1-, 3- and 5-year aged rice wine sample groups.
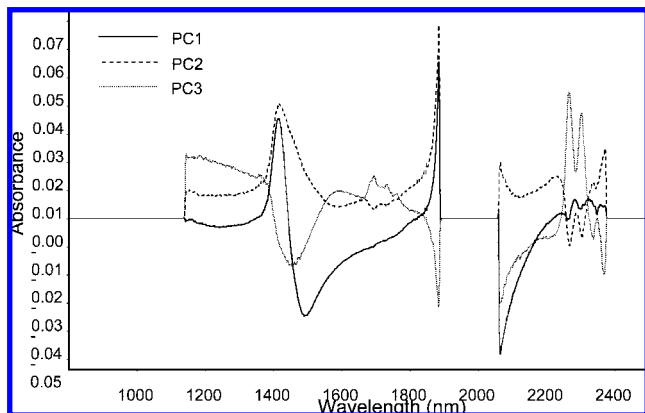

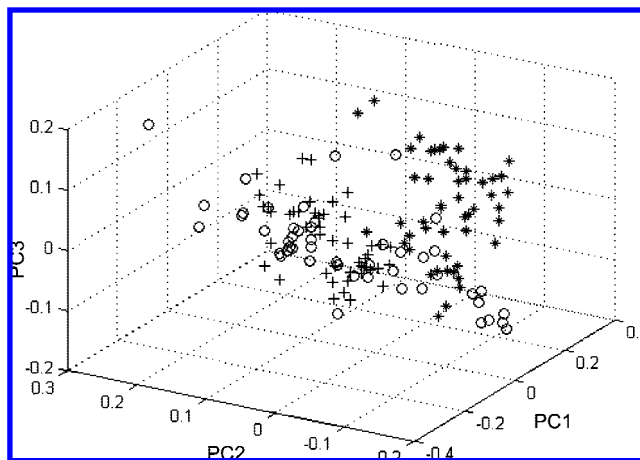**Figure 2.** Eigenvectors for principal component analysis for rice wine samples.

Figure 3. Score cluster plot with the first three PCs for rice wine sample sets of 1-year aged (*), 3-years aged (O), and 5-years age (+) wines.

the same years of aging gather together; 1- and 5-years aged groups separate clearly; however, there is not a clear separation between 1- and 3-years aged groups, as well as 3- and 5-years aged groups, respectively.

In this study, regression and classification models developed by LS-SVM were tested using the full spectral range of the NIR
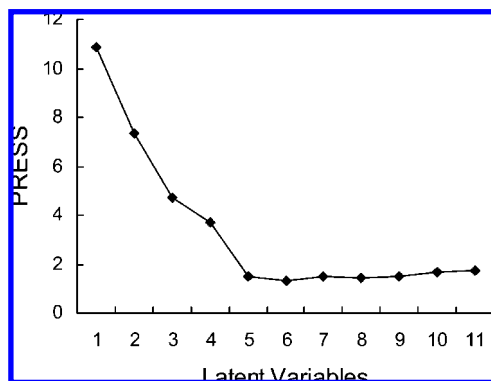
Rice Wine Quality Estimation Using LS-SVM and NIR

J. Agric. Food Chem., Vol. 56, No. 2, 2008 **311**

Figure 4. Latent variables for PLS model for alcohol content.
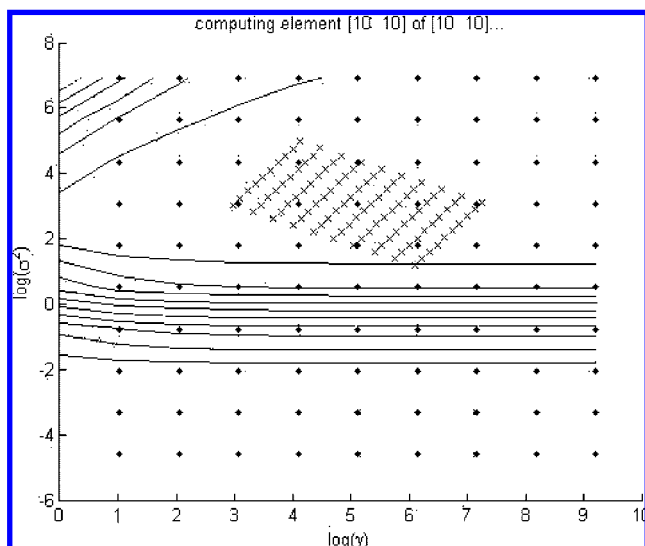

Figure 5. Contour plot of the optimization the parameters γ and σ^2 for the prediction of alcohol content.

Table 3. Performance Comparison Results for Alcohol Content, Titratable Acidity, and pH Models Developed by PLS and LSV-SVM

	PLS		LS-SVM	
enological parameter	R^2_{val}	RMSEP	R^2_{val}	RMSEP
alcohol content (%(V V^{-1}))	0.90	0.109	0.91	0.099
titratable acidity (g L^{-1})	0.79	0.061	0.82	0.056
pH	0.94	0.016	0.96	0.013

sensor as input and the first ten PCs scores as input, respectively. The performance of the models using full spectral range of the NIR sensor was worse than that using the first ten PCs scores. Therefore, the first ten PCs scores were used as the inputs of LS-SVM in further analysis.

Enological Parameters Prediction by PLS and LS-SVM. By means of full cross-validation with one sample omitted, the number of latent variables for alcohol content is obtained according to the smallest PRESS, as **Figure 4** shows. The number of latent variables for alcohol content, titratable acidity, and pH was 5, 6, and 10, respectively.

As discussed above, optimizing parameters γ and σ^2 was the first step in obtaining the optimal LS-SVM models. The contour plot of the optimization the parameters γ and σ^2 for the prediction of alcohol content is shown in **Figure 5**. The grids "•" in the first step is 10×10, and the searching step in the first step is large. The optimal search area is determined by the error contour line. The grids '×' in the second step is 10×10, and the searching step in the second step is smaller. The optimal
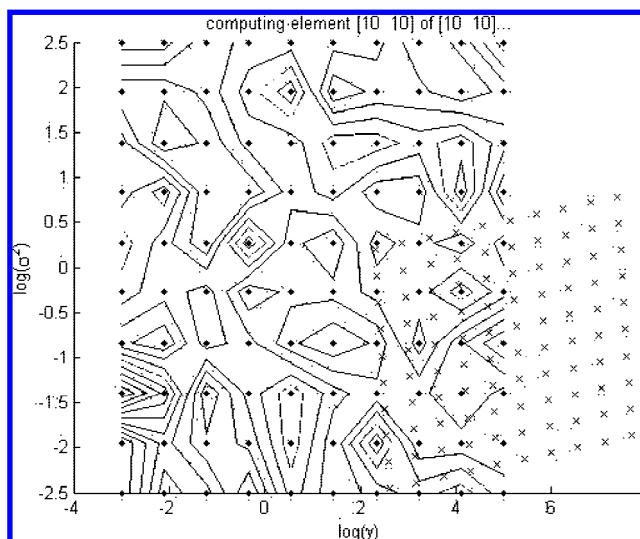

Figure 6. Contour plot of the optimization the parameters γ and σ^2 for rice wine age discrimination.

Table 4. Performance Comparison Results for Rice Wine Age Discrimination Models Developed by DA and LSV-SVM

		DA		LS-SVM	
data set	wine age	number of samples misclassified	percentage of samples correctly classified	number of samples misclassified	percentage of samples correctly classified
calibration set	1-year aged	1	97.06%	0	100%
	3-years aged	3	90.63%	1	96.88%
	5-years aged	2	93.94%	0	100%
validation set	1-year age	1	93.75%	0	100%
	3-years aged	1	93.75%	1	93.75%
	5-years aged	1	93.75%	0	100%

search area is determined based on the first step. The optimal pair of (γ, σ^2) for alcohol content, titratable acidity, and pH was found at the value of (30.40, 95.16), (24.69, 53.94), and (77.97, 62.25), respectively.

Using the optimum parameters for PLS and LS-SVM, the calibration models for alcohol content, titratable acidity, and pH was established by the two multivariate methods, respectively. Performance comparison results for PLS and LSV-SVM are listed in **Table 3**. From **Table 3** it can be observed that the prediction performance of LV-SVM is slightly better than that of PLS, with higher R^2_{val} values of 0.91, 0.82, and 0.96, and lower RMSEP values of 0.099% (V V^{-1}), 0.056 g L^{-1}, and 0.013 for alcohol content, titratable acidity, and pH, respectively. On the basis of the results, it was concluded that LS-SVM was a reliable and accurate method for prediction of enological parameters of rice wine.

Rice Wine Age Discrimination by DA and LS-SVM. Before establishing the wine age discrimination models, the reference values and the spectra of the whole sample set were checked. It was observed that there was no outlier sample. The contour plot of the optimization the parameters γ and σ^2 for wine age discrimination for LS-SVM is shown in **Figure 6**. The optimal pair of (γ, σ^2) for wine age discrimination was found at the value of (24.13, 0.09).

Calibration and validation models for wine age discrimination were developed by DA and LS-SVM, respectively. The results are listed in **Table 4**. From **Table 4** it can be observed that the calibration and validation results for LS-SVM are better than

Table 5. Reference Data of Samples Misclassified in the Rice Wine Age Discrimination Model Developed by LS-SVM

number	actual age (year)	calculated age (year)	alcohol content (%(V V^{-1}))	titratable acidity (g L^{-1})	pH
1	3	5	17.31	4.5	4.35
2	3	5	17.43	4.51	4.2

those for DA, with the percentage of samples correctly determined being 100%, 96.88%, and 100% for 1-year aged, 3-years aged and 5-years aged validation sample sets, which indicate that LS-SVM is suitable for wine age discrimination. In the calibration and validation analysis results for LS-SVM, one sample of 3-years aged wine is classified in the 5-years aged group, respectively. Comparing the reference data of the samples (**Table 5**) with the average data listed in **Table 2**, it can be observed that the alcohol content, titratable acidity, and pH of the two samples are not only between the range of the 3-years aged group but also between that of the 5-years aged group. The superposition of the 3- and 5-years aged groups might be the reason that the 3-years aged group is harder to classify.

The good performances of the quantitative and qualitative models developed by LS-SVM indicated that LS-SVM was a promising method to use in estimation of the quality of rice wine from indirect but fast and reliable measurements such as NIR spectra.

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