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Full Paper

FTIR and chemometric tools for the classification of Thai wines

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Abstract: A simple and rapid Fourier transform infrared (FTIR) spectroscopic method was developed to determine the content in wines without sample preparation or use of organic solvents. This research aimed at classifying seven Thai wines from various regions by employing both instrumental and statistical analysis. FTIR spectra in the region between 650-4000 cm^{-1} were characterised and used for multivariate chemometric analysis by principal component analysis (PCA), discriminant analysis (DA) and hierarchical cluster analysis (HCA). Application of PCA to FTIR data revealed the pattern and relationship of each brand or trademark. Thai wines were effectively distinguished by DA according to their trademarks and can be divided into four main groups according to HCA. All of the multivariate analyses yield similar conclusions that Thai wines cannot be clearly classified in terms of geographical origin. However, additional samples may provide further insight into the geographical distribution of Thai wines.

Keywords: Thai wines, authentication, chemometrics, multivariate analysis, FTIR spectroscopy

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Introduction

The application of spectroscopic techniques in the study of the origin and differentiation of drink products has developed considerably in recent years [1, 2]. The advantage of these techniques lies in the almost complete lack of sample preparation required, which makes them especially rapid to apply.

In order to develop methods of classification and differentiation, spectra are treated with chemometric techniques that permit characterisation and subsequent construction of models. With regard to analysis methods of constituents in wine, a number of reports appear in the literature such as high performance liquid chromatography (HPLC) for the determination of phenolic acids [3], gas chromatography (GC) for the analysis of aroma compounds in wine [4], GC-MS (mass spectrometry) for trifluoroacetylated glycocides [5], nuclear magnetic resonance (NMR) for determination of minor compounds [6], Fourier transform infrared (FTIR) spectroscopy for the differentiation and classification of wines and brandies during their ageing process [7], and inductively coupled plasma optical emission spectroscopy (ICP-OES) for fast analysis of a number of elements of the periodic table [8]. There seems to be a problem, however, with treating a large quantity of data. Fortunately, chemometric methods can be used to solve such multivariate data analysis problems [9, 10]. The use of chemometric tools in data analysis, together with recent advances in computer technology which simplify complex mathematical calculations, leads to the development of multivariate data analysis as a powerful tool in the evaluation of food quality [11].

Wine production from many kinds of fruits has bloomed in Thailand under the One Tambon One Product project (the OTOP project), which also resulted in the formation of the Thai Wine Association in 2004, exactly ten years after the first Thai grape wine was launched. The Kingdom's leading wine producers set up the association to join forces and immediately established winemaking quality standards and labelling requirements for Thai grape wines. Members adhere to the Thai Wine Charter, which is in line with international standards. The objective is to create awareness and enhance the image of Thai wines, both in the domestic and international markets, and to educate Thai people about Thai grape wines and the health benefits associated with moderate wine drinking. The wineries are mostly located in the northern and north-eastern parts of Thailand as shown in Figure 1.

The purpose of this research is to associate some Thai red and white wines by FTIR data using multivariate analyses. Chemometric techniques were used to discriminate between very similar chemical components from which several groups could ideally be determined. Such methods are particularly suited for working with large data sets and may be used to classify Thai wines into distinct groups by the correlation of measurement data.

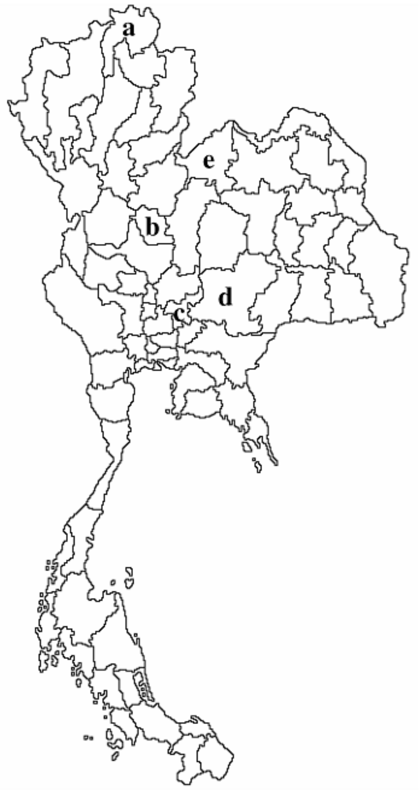

Figure 1. The location of wineries in Thailand. a) Chiang Rai province, b) Pichit province, c) Saraburi province, d) Nakornrachasima province, and e) Loei province

Materials and Methods

Samples

All Thai wines used in this study were commercial samples from the 2001-2004 vintage. Wine samples studied from different growing regions in Thailand are presented in Table 1, which included 2 white wines and 5 red wines belonging to three varieties, i.e. Shiraz, Chenin Blanc and a combination of 90% Shiraz and 10% Tempranillo. Two red Australian wines from the 2002-2003 vintage were also investigated for comparison.

FTIR analysis

A Perkin-Elmer FT-IR Spectrometre (Spectrum GX Series) equipped with a deuterated triglycine sulfate detector was used for FTIR analysis. The sampling station was equipped with an overhead horizontal attenuated total reflectance (ATR) accessory with multiple reflection comprising transfer optics within a chamber through which infrared radiation was directed to a detachable ATR zinc selenide crystal mounted in a shallow trough for sample containment [12-14]. The zinc selenide crystal was used to obtain data in the range of 650-4000 cm^{-1} with a resolution of 4.00 cm^{-1}. Single beam spectra (4000–650 cm^{-1}) of the samples were obtained (Figure 2) and corrected against the background spectrum of the zinc selenide crystal. The ATR crystal was carefully cleaned with water between measurements and dried with nitrogen gas after each experiment to ensure the best possible sample spectra. Commercial wines were used directly in

Table 1. Details of Thai wines under study

Code No.	Trademark	Type	Variety	Geographical region	Area in the map
1	Chateau de Loei	White	Chenin Blanc	Upper north-eastern Thailand (Loei province)	e
2	Chateau des Brumes	White	Chenin Blanc	Lower north-eastern Thailand (Nakornrachasima province)	d
3	Chateau de Loei	Red	Shiraz	Upper north-eastern Thailand (Loei province)	e
4	Chateau des Brumes	Red	Shiraz	Lower north-eastern Thailand (Nakornrachasima province)	d
5	Shala One	Red	Shiraz	Lower northern Thailand (Pichit province)	b
6	Lumphaya	Red	Shiraz	Central Thailand (Saraburi province)	c
7	Khao Yai	Red	Shiraz (90%) + Tempranillo (10%)	Lower north-eastern Thailand (Nakornrachasima province)	d
8	Rothbury	Red	Shiraz	New South Wales, Australia	-
9	Bilyara	Red	Shiraz	South Australia	-

200-µl ATR cell samples with the same temperature condition (24°C) as used for the Thai wines. Each wine sample was rerecorded 5 times for the multivariate analysis.

Data analysis

A data matrix was constructed with a column representing wine samples (45 objects) and rows corresponding to wavenumber (3350 variables) (Table 2). These variables, called ‘features’, formed a ‘data vector’ which represented a wine sample. Data vectors belonging to the same group were analysed. These groups were then termed a ‘category’. The chemometric tools used in this work were as follows.

Principal component analysis [15]

Principal component analysis (PCA), carried out with MATLAB 6.1 (MATLAB Inc, 1999), was mainly used for data reduction to identify a small number of factors that explain most of the variance observed in a much larger number of manifest variables. Such methods attempt to identify factors that explain the pattern of correlations within a set of observed variables. This permits a primary evaluation of the in-between category similarity and is very useful for visual inspection of complex data matrices. The information is compressed into a few components or directions in the

Table 2. Tabulation of FT-IR spectral transmittance of wine samples

Sample	Wavenumber (cm^{-1})									
	4000	**3999**	**3998**	**3997**	**3996**	……	**654**	**653**	**652**	**651**	**650**
W_Loei_1	93.365	93.361	93.353	93.342	93.327	……	84.760	85.633	87.039	90.230	97.292
W_Loei_2	93.130	93.116	93.104	93.096	93.094	……	79.567	85.731	90.890	93.440	96.536
W_Loei_3	93.028	93.016	93.008	93.003	92.998	……	73.313	79.884	86.343	92.315	100.290
W_Loei_4	92.923	92.917	92.913	92.907	92.897	……	71.122	76.368	83.804	92.426	101.020
W_Loei_5	92.771	92.759	92.751	92.745	92.738	……	74.166	79.460	85.981	92.150	98.865
⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮	⋮ ⋮
R_Bil_1	88.688	88.667	88.647	88.627	88.611	……	71.892	74.851	78.913	86.166	95.696
R_Bil_2	88.661	88.648	88.632	88.615	88.605	……	77.723	82.574	86.118	89.754	91.862
R_Bil_3	88.555	88.534	88.509	88.483	88.465	……	75.671	78.856	81.372	86.707	93.761
R_Bil_4	88.483	88.468	88.450	88.432	88.421	……	73.875	78.342	81.689	87.657	94.456
R_Bil_5	88.375	88.355	88.325	88.294	88.271	……	61.891	66.941	73.799	86.505	101.727

multivariate space. The first two of the principal components (PCs) of the wine data can be determined as follows:

$$PC1 = v1_1X_1 + v1_2X_2 + \ldots + v1_pX_p$$
$$PC2 = v2_1X_1 + v2_2X_2 + \ldots + v2_pX_p$$

where $PC1$, $PC2$ are the first and second principal component scores;
X_j is the observed variable of FTIR spectra at wavenumber j ($j = 1, \ldots, 3350$);
$v1_j$ is the eigenvector of the first principal component for variable j;
$v2_j$ is the eigenvector of the second principal component for variable j.

Discriminant analysis [16]

Discriminant analysis (DA) is a technique for classifying a set of observations into predefined classes. The main purpose of discriminant function analysis is to predict group membership based on a linear combination of the interval variables. The procedure begins with a set of observations where both group membership and the values of the interval variables are known. The end result of the procedure is a model that allows prediction of group membership when only the interval variables are known. The second purpose of discriminant function analysis is to understand the data set, as a careful examination of the prediction model that results from the procedure can give insight into the relationships between group membership and the variables used to predict group membership. This technique is a widespread parametric method for classification purposes that assumes a priori knowledge of the number of classes and the sample class membership. The model is built based on a set of observations by which the classes are known. The technique constructs a set of linear functions of the predictors, known as discriminant functions (L), such that

$$L = b_1x_1 + b_2x_2 + \ldots + b_nx_n + c$$

where the b's are discriminant coefficients, the x's are the predictor variables and c is a constant.

These discriminant functions are used to predict the class of a new observation. For a k class problem k discriminant functions are constructed. Given a new observation, all the k discriminant functions are evaluated and the observation is assigned to class i if the i^{th} discriminant function has the highest value. In our study we used all PCs as the input matrix. The DA was performed using SPSS 10.0 (SPSS Inc, 1999).

Hierarchical cluster analysis [17]

A general approach to cluster analysis is hierarchical cluster analysis (HCA) [18], the purpose of which is to group together objects or records that are 'close' to one another. The cluster method of complete linkage and the distance measured by the Euclidean squared distance were used. The dendrogram is a tree-like plot where each step of hierarchical clustering is represented as a fusion of two branches of the tree into a single one. The branches represent clusters obtained from each step of hierarchical clustering. The HCA was done using SPSS 10.0 (SPSS Inc, 1999).

Results and Discussion

Characterisation of FTIR spectra

Figure 2 presents the FTIR spectra of different Thai wines showing absorbance bands at 3264 cm^{-1} (O−H stretching), 2984 cm^{-1} (C–H stretching), 2123 cm^{-1} (C≡N stretching), 1636 cm^{-1} (C=C stretching), 1454 cm^{-1} (CH_2−methylene group), 1328 cm^{-1} (CH_3−methyl group), 1044 cm^{-1} (C−OH stretching), and 900-690 cm^{-1} (=C−H out of plane (oop) bending). The spectra of all wines showed similar peaks. Most wines contain water, alcohols, aldehydes, glycerol, sorbitol, mannitol, sulfites, amino acids, esters, minerals, phenols, sugars, organic acids such as tartaric, malic and citric acids, as well as volatile acids as common ingredients [19]. Similarity of the major ingredients gave rise to similar peak positions in the ATR spectra of the Thai wines studied. The broad peak found at 3264 cm^{-1} is mainly due to the stretching vibration of O-H bond of water, whereas the 2884 cm^{-1} peak is most likely due to the stretching vibration of bonds from multiple constituents of the wines. These vibrations include C–H stretching of hydrocarbons, O–H stretching of carboxylic acids and most importantly asymmetric stretching vibration of C–H bonds of methyl (–CH_3) groups. Acids give wine the sour or sharp note that enhances flavour when in balance with other components. Of the three organic acids that originate in grapes, tartaric acid is prevalent as the base measure of total acidity in wine, followed by malic and citric acids. Three other acid, namely succinic, lactic and acetic acids (the volatile acids), are produced by fermentation. The region between 1000 and 2200 cm^{-1} contains five peaks at 1044, 1328, 1454, 1636 and 2123 cm^{-1}, which can be correlated with the C−OH stretching, CH_3 bending, CH_2 bending, C=C stretching and C≡N stretching of the groups in compounds such as, phenols, alcohols, aldehydes, higher alcohols, polyols, acids, sugars, volatile acids and amino acids. The full spectrum of peaks was used for the chemometric analysis of the wines.

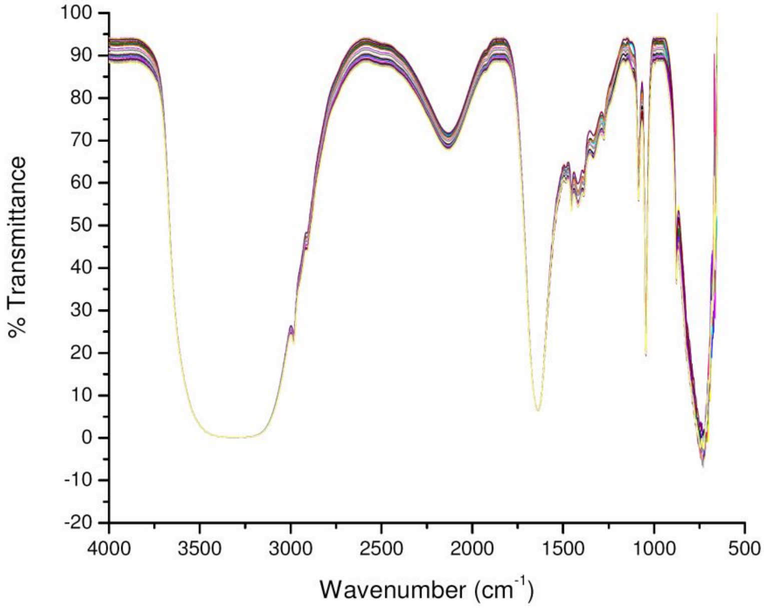

Figure 2. FT-IR spectra of different Thai wines

Principal component analysis

PCA allows the visualisation of the information in the data set in a few principal components while retaining the maximum possible variability within that set. The scores for each sample on the first two principal components, which contain 67.3% of the total variance, are represented in Figure 3. On the first principal component at the bottom left of the graph, the majority of the samples are the white wine of Chateau des Brumes, which has a higher negative score than the white wine of Chateau de Loei. The red wine samples fell into the same area on the right of the PC plots. Chateau des Brumes, Shala One, and Lumphaya were quite clearly distinguishable according to their own trademarks, whereas the red and white wines of Chateau de Loei could not be distinctly classified. PC1 and PC2 might differentiate better if the variance explained was high (more than 80%). Such overlap represents the closer relationship between these two wines which come from the same province and share the same trademark of Chateau de Loei. It can be seen that the samples of Australian red wines (Rothbury and Bilyara) at the top right of the graph are separated from the remaining samples. The Thai wine closely located near the Australian wine is the reserve red Khao Yai. A combination of 90% Shiraz (red) and 10% Tempranillo (white) varieties in Khao Yai was used in the wine production. The cluster of samples found on the right of PC1 may be due to the higher percentage of red wine variety. The first principal component is therefore most likely related to the wine type, i.e. white or red wine. Although no classification or grouping of wine by geographical origin is clearly seen in the plot, the grouping can be more related to the wine trademark and variety. The Shiraz's are grouped together towards the right while the Chenin Blanc's are located on the left. For the second principal component, it can be seen that the samples of red wine of Chateau de Loei have higher scores than the white wine of the same vineyard; however, they can be grouped in the same cluster. It can be concluded that using these first two principal components, we can clearly distinguish among the wine samples according to their brand or trademark. Although the wines of different brands or trademarks were of the same variety, the PC plots of FTIR data show that the components of these wines are different and are clustered in their own individual groups which are apparently differentiated by their geographical origin or process of production.

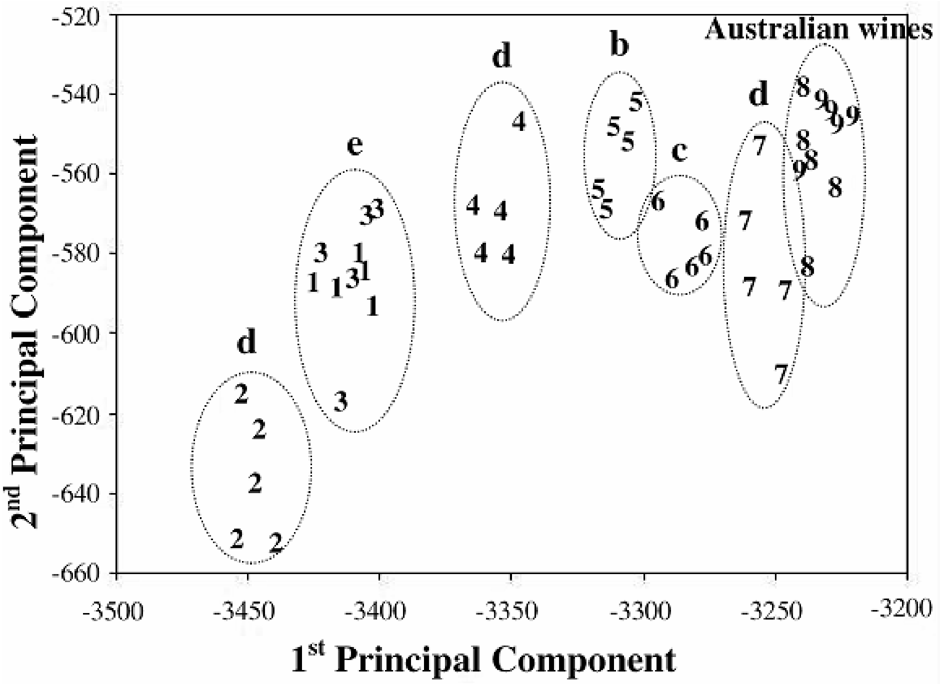

Figure 3. Scores of the wine samples on the first two principal components: 1 (white Chateau de Loei), 2 (white Chateau des Brumes), 3 (red Chateau de Loei) , 4 (red Chateau des Brumes), 5 (red Shala One), 6 (red Lumphaya), 7 (reserve red Khao Yai), 8 (red Rothbury) and 9 (red Bilyara). The letters b-d indicate the locations of wineries as defined in Figure 1

Discriminant analysis

In all, 45 PCs were used to populate the input matrix in our study. Since there are 9 discriminant functions, the charts present scatter plots showing the discriminant scores of the cases on the 9 discriminant functions with 30 PCs (eigenvalues more than 1) used in the classification. Figure 4 shows that DA resulted in better classification of Thai wines according to their brand or trademark. In the replication experiments, each wine sample was plotted at almost exactly the same point, demonstrating that the wines of different trademarks can be reproducibly separated and clearly classified. The overlap between the Rothbury and Bilyara Australian wines at the right corner indicates the close relationship of the wines which were from the same vineyard. Cross-validation was used to assess how well the discriminant function worked and whether it worked equally well for each group of the dependent variable. In this case, it correctly classified 100% of the original grouped cases and 100% of cross-validated grouped cases for Thai wines. About 80.0% of cross-validated grouped cases were correctly classified for Australia's Rothbury due to the overlapping with the Bilyara. Similar results were derived for DA and PCA, but neither of them could classify the wines clearly in terms of their geographical origin.

To investigate the potential of chemical components for wine classification, a table of equality of group means (Table 3) was generated by selected Univariate ANOVAs. This indicates whether there is a statistically significant difference among the dependent variable means (group) for each independent variable. The Wilks' Lambda was used as a statistical criteria to add or remove variables from the analysis. In the ANOVA, the smaller the Wilks' Lambda is, the more important the independent variable to the discriminant function becomes. In our case, Wilks' Lambda was significant by the F test with significant values for PC1, PC3, PC8, PC10 and PC16 (Table 3), which correctly classified about 88.9% of the cross-validated group cases. They were the main discriminate parameters among all wines. The important variables indicated by the higher component values in these PCs were related to the absorbance regions in the FTIR spectrum. As a result, we found that the O-H stretching and the C=C stretching vibrations of water, alcohols, higher alcohols, acids, sugars and volatile acids mainly made the wine different and separable into different areas of the scatter plot in Figure 4.

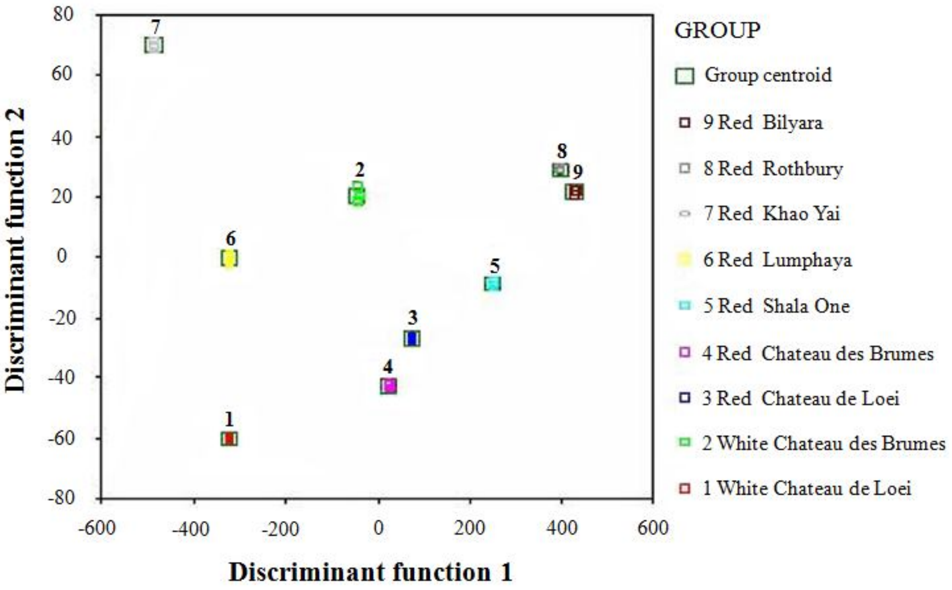

Figure 4. Group centroid and scatter plot of 9 groups of known wines

Hierarchical cluster analysis

Results from the HCA for 7 Thai wines and 2 Australian wines were reported in the form of a dendrogram using complete linkage and Euclidean squared distance (Figure 5). As a criterion for similarity on the basis of the connecting distances between parameters and their positions on the dendrogram, four distinctive clusters of wines were defined as follows:

Cluster 1, comprising a group of red wines: Australian wines, Shala One and some red wine samples of Chateau des Brumes;

Cluster 2, comprising the red wine of Chateau de Loei, white wine of Chateau des Brumes and some red wine samples of Chateau des Brumes;

Cluster 3, comprising the red wine of Lumphaya and white wine of Chateau de Loei;

Cluster 4, consisting of the red wine of Khao Yai only.

Table 3. Tests of equality of group means

PCs	Wilks' Lambda	F test	Significant value
PC1	.006	690.109	.000
PC2	.902	.491	.854
PC3	.282	11.469	.000
PC4	.731	1.657	.143
PC5	.770	1.342	.255
PC6	.811	1.046	.421
PC7	.764	1.386	.236
PC8	.357	8.089	.000
PC9	.804	1.098	.387
PC10	.359	8.021	.000
PC11	.804	1.096	.388
PC12	.735	1.623	.153
PC13	.708	1.853	.099
PC14	.852	.782	.621
PC15	.834	.895	.531
PC16	.573	3.359	.006
PC17	.698	1.950	.082
PC18	.891	.552	.809
PC19	.791	1.192	.331
PC20	.863	.715	.677
PC21	.908	.454	.880
PC22	.924	.372	.929
PC23	.898	.510	.841
PC24	.839	.866	.554
PC25	.860	.734	.661
PC26	.939	.293	.964
PC27	.891	.550	.811
PC28	.757	1.446	.212
PC29	.952	.228	.983
PC30	.968	.150	.996
PC31	.869	.677	.708
PC32	.992	.037	1.000
PC33	.926	.360	.934
PC34	.966	.159	.995
PC35	.992	.038	1.000

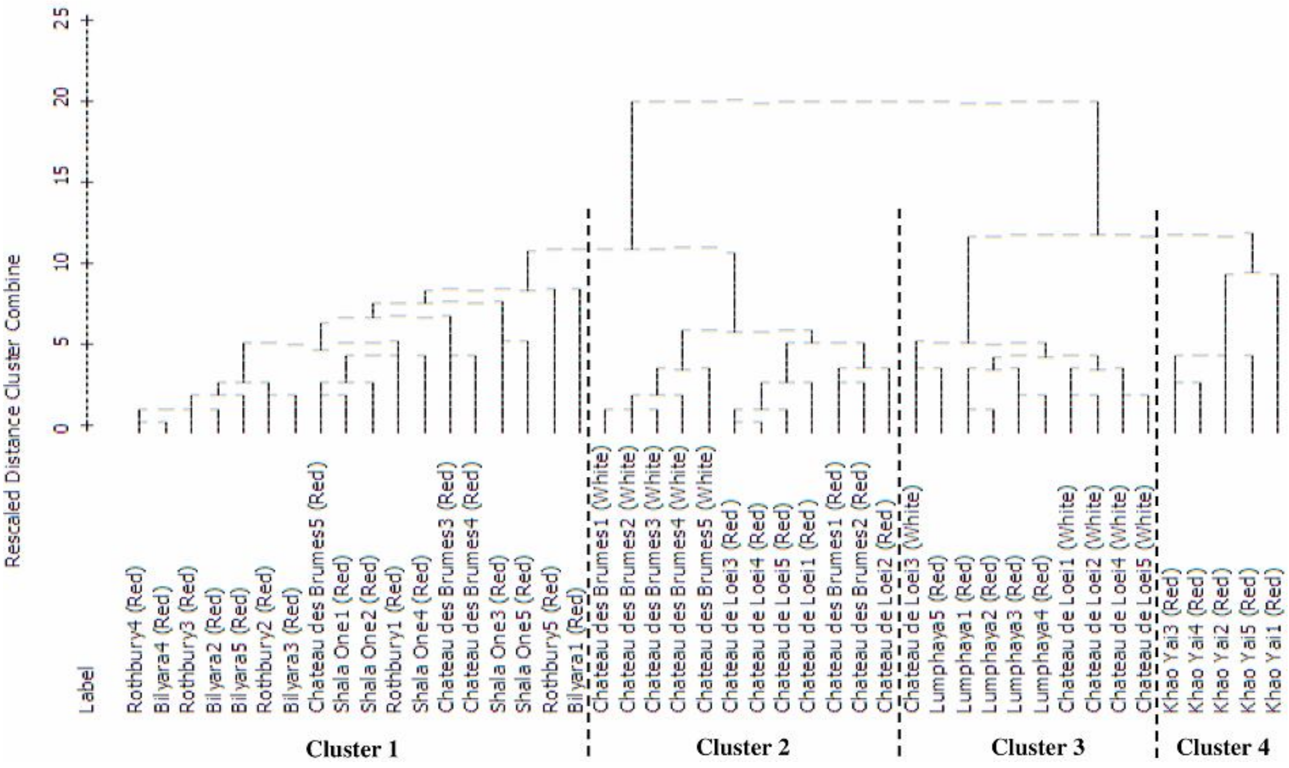

Figure 5. Dendrogram built with all variables using complete linkage and Euclidean squared distance

In comparison with the PC1/PC2 plot in Figure 3, such clusters can be visualised and similar conclusions derived although HCA gives a broader and less definitive classification than PCA, since the clustering and interpretation based on the dendrogram are largely subjective. The red wine of Chateau des Brumes is separated into the two groups in clusters 1 and 2. Red and white wines of Chateau des Brumes are located in different groups in clusters 1 and 2, while red and white wines of Chateau de Loei are located in clusters 2 and 3. Thus, this method cannot clearly classify the wines by their geographical origin.

Conclusions

A rapid and simple FTIR procedure has been developed, which can be directly applied for wine analysis. Chemometric techniques were used to distinguish between very similar chemical components of multivariate FT-IR data of red and white Thai wine samples. The PC1/PC2 plot could be used to separate Thai wines into their own individual trademarks. However, the trademark pattern could be differentiated better by DA, which was one of the supervised methods of distinguishing the group from the selected parameters. From these results, the difference in the wines studied mostly stemmed from the differences in the amount of water, alcohols, higher alcohols, acids, sugars and volatile acids. The application of the unsupervised HCA method gave a broader and less definitive classification of the wines in four main clusters which highly correlated with the PC plot. All of the above multivariate analyses demonstrate that the wine varieties have not been differentiated by their geographical origin, although the wines were effectively distinguished by their trademarks.

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