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Research Note

Application of the Statistical Multivariate Analysis to the Differentiation of Whiskies of Different Brands

ABSTRACT

A study was made to test the authenticity of whisky that is offered from opened bottles in Spanish public establishments. It is based on 100 genuine Scotch whisky samples from five labels and 38 genuine Spanish whisky samples of high quality; two standard populations were formed. The major volatile components and absorbances were determined from all samples. Principal Component and Stepwise Discriminant Analysis are used in the statistical treatment applied to these data to determine the differences between the Spanish whiskies and the Scotch whiskies. Also analyzed were 113 samples from bottles of Scotch whisky with one of the five standard labels, already opened in the establishment inspected. A method for identifying outliers was applied to these 113 test samples, and the contents of 41% of the bottles agreed with the characteristics of their labels, but 28% of the Scotch whiskies had been substituted by Spanish whiskies of similar quality.

INTRODUCTION

One of the tasks which the Municipal Laboratories in Spain have to undertake consists in controlling the spirits which are served in public establishments. In order to complete their supervision activities, these Laboratories should have an efficient analytical method which will ensure that the contents of a bottle previously opened are, or are not, what is

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TABLE 1
The Use of Multivariate Techniques for the Characterization of Spirits

Samples	*Objective*	*Statistical treatment*	*References*
Major volatiles			
Fruit distillates, brandies, cognacs and whiskies	Differentiation	DA	Schreier & Reiner (1977)
Whiskies	Detection of counterfeit samples	PR	Saxberg *et al.* (1978)
Whiskies, rums, brandies and fruit distillates	Relationship between composition and identity	DA and KNN	Lisle *et al.* (1978)
Spanish brandies, whiskies, wine distillates, and wines intended for distillation	Differentiation	DA	Cabezudo *et al.* (1981)
French brandies	Classification	DA	Wenker *et al.* (1981*a* and *b*)
Hungarian brandies	Differentiation	PR	Donath-Jobbagy *et al.* (1982)
Minor volatiles			
French and German brandies, and cognacs	Differentiation	DA	Schreier & Reiner (1979)
French and German brandies	Classification	PR	Leegwater & Leegwater (1981)
Sherry brandies	Classification	CA	Diez *et al.* (1985)
Brandies	Differentiation	PCA	Bataglia, 1986
Awamori	Differentiation	DA & PCA	Tamaki *et al.* (1986)
Phenols			
Whiskies, brandies and rums	Differentiation	DA	Lehtonen (1983*a* and *b*)
Major and Minor volatiles			
Pisco	Influence of technical parameters	DA & PCA	Loyola *et al.* (1987)
Cognacs and brandies	Differentiation	PCA	Cantagrel (1986)

DA = Discriminant Analysis; PCA = Principal Component Analysis; CA = Cluster Analysis; PR = Pattern Recognition methods.

expressed on the label. The most convenient way to do this is by calculating a mathematical model which may reflect a series of characteristics fitted for each drink and each brand. This has been done already with brandy (Zel'venskii *et al.*, 1974).

The distilled drinks (brandy, Cognac, Armagnac, Calvados, whisky, rum, awamori and the different fruit brandies) have, in common, the volatile components of alcoholic fermentation, of which the concentrations change according to the substrate from which they proceed and the yeasts. That is why the study of these distilled drinks has been made, resorting, in a large number of cases, to the major volatiles and in others to some minor volatile components (Table 1).

The most important major components and absorbance measures are used in this study in order to establish the differences which exist between five brands of Scotch whiskies and four brands of Spanish ones, by means of Principal Component Analysis and Stepwise Discriminant Analysis. An outliers detection procedure is applied to other samples which have been found open during inspection in order to know if they are imported whiskies of the brand mentioned on their label, if they are national quality whiskies, or if they are actually outliers.

MATERIALS AND METHODS

A total of 254 samples has been analyzed. One hundred of them correspond to closed and sealed bottles of five brands of Scotch whisky (labelled A, B, C, D and E; 20 bottles in each group), which are sold in large quantities in Spain, and 38 samples which have the same characteristics as Spanish quality brands. Two standard groups have been established with these 138 samples: Scotch whiskies and Spanish whiskies. The test group was composed of 113 other samples from bottles which have been found open in the controlled establishments and which had labels of the brands A, B, C, D and E (respectively, 46, 18, 17, 16 and 16 bottles) and three samples of Scotch whisky, deliberately kept half-full during 20 days (brand B), 6 months (brand E) and 12 months (brand D).

The following analytical determinations have been carried out for each sample: alcoholic degree (aerometry), colour (absorbance, 420 nm) and major volatiles (methanol, ethyl acetate, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol + 3-methyl-1-butanol) through GC (column: 4 m × 1/8 in internal diameter, packed with Chromosorb W, 80–100 mesh, coated by Carbowax, 1500, 15%).

The statistical methods used for the data processing have been: Principal Component Analysis (PCA), Stepwise Discriminant Analysis (SDA) and

Outliers Detection Technique (ODT). The following statistical formula (Afifi & Azen, 1979) was applied in order to know if a whisky sample, from an open bottle, of a certain Scotch brand, is or is not an outlier of the group which corresponds to this brand:

$$F = \frac{n(n-p)}{(n^2-1)p} D^2 \tag{1}$$

where n is the number of samples corresponding to the standard group, p the number of analyzed variables, and D^2 is the Mahalanobis distance between the sample mean vector and the sample to be checked whether it is or is not an outlier. If the population values are multinormally distributed, F follows a Snedecord distribution, with p and $n-p$ degrees of freedom. Then, when $\Pr(F > F_{\alpha,p,n-p}) < \alpha$ the sample can be considered as an outlier at an α significant level.

The BMDP package (1983) was used for PCA (BMDP4M) and SDA (BMDP7M). For the calculations related with the Outliers Detection Technique a specific FORTRAN program has been prepared. All these programs were run in a CDC Cyber 180/855 computer.

RESULTS AND DISCUSSION

Standard samples

Table 2 contains the average, maximum, minimum and standard deviation values of the variables analyzed for both standard populations: Scotch whiskies ($n = 100$) and Spanish whiskies ($n = 38$). The values shown for the first ones are in accordance with Lisle *et al.* (1978) for the blended.

If the Principal Component Analysis is applied to these 138 standard samples, then the variance percentage explained by the first two principal components is 80%. 1-propanol and methanol are strongly correlated with the first principal component and 2-methyl-1-propanol and ethyl acetate are correlated with the second principal component. The samples are represented in the space defined by these two principal components, as is shown in Fig. 1. The Spanish whiskies occupy an area which is completely separated from the Scotch whiskies, one with the peculiarity that the latter are subdivided according to the different brands, except for the brands A and D which are very similar.

The Stepwise Discriminant Analysis (SDA) has also been applied in order to differentiate the groups of Spanish whiskies of each of the Scotch whisky subgroups A, B, C, D and E. The discriminant variables are those contained in Table 3 and it has been possible to classify correctly (in every case) 100%

TABLE 2
Distribution of the Variables in the Standard Populations of Scotch and Spanish Whiskies

Variable	*Total frequency*	*Mean*	*Standard deviation*	*Smallest value*	*Largest value*
Scotch whiskies (five labels)					
Methanol[a]	100	11·1	2.00	6·50	14·3
Ethyl acetate[a]	100	33·3	4·30	24·2	43·7
1-Propanol[a]	100	54·4	7·56	35·1	69·5
2-Methyl-1-propanol[a]	100	66·9	10·0	47·4	88·2
Isoamyl alcohols[a]	100	80·7	4·67	69·3	94·6
Absorbance[b]	100	0·58	0·22	0·32	0·91
Spanish whiskies (four labels)					
Methanol[a]	38	5·58	0·60	4·40	6·60
Ethyl acetate[a]	38	27·6	4·55	22·1	42·0
1-Propanol[a]	38	25·9	3·65	18·0	33·9
2-Methyl-1-propanol[a]	38	44·58	7·21	29·3	55·9
Isoamyl alcohols[a]	38	88·8	8·23	68·8	104
Absorbance[b]	38	0·39	0·06	0·25	0·49

[a] mg/100 ml; [b] 420 nm.

TABLE 3
Application of SDA to the Groups formed by all the Spanish Whiskies and each of the Scotch Whisky subgroups

Groups to be differentiated	*Correct classification percentage*	*Variables with high discriminant power*
Spanish and A	100	1-propanol methanol isoamyl alcohols
Spanish and B	100	Absorbance 1-propanol isoamyl alcohols
Spanish and C	100	1-propanol ethyl acetate isoamyl alcohols
Spanish and D	100	1-propanol methanol isoamyl alcohols
Spanish and E	100	methanol 1-propanol isoamyl alcohols

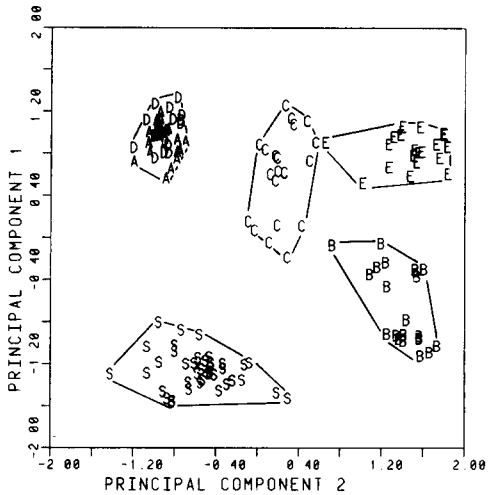

Fig. 1. Representation of the samples in the space delimited by the first two principal components. Scotch whiskies, A, B, C, D and E; Spanish whiskies, S.

of the samples. The 1-propanol appears in the Spanish whiskies in a much lower quantity than in the Scotch whiskies; on the other hand, the Spanish samples have slightly higher concentrations of isoamyl alcohols. Previously one of the isoamyl alcohols (3-methyl-1-butanol) had also contributed to the differentiation between Bourbon-, Scotch- and cheap Scotch-whiskies, according to Schreier & Reiner (1977). The isoamyl alcohols, together with ethyl acetate, are also the most important variables for the differentiation between very well known brands of Scotch whisky (Saxberg *et al.*, 1978). Moreover, 1-propanol, together with isobutanol, 1-hexanol and methanol, contributes to the differentiation of samples of cognac and French brandies (Cantagrel, 1986).

Test samples

This group of samples has been reserved to prove the outliers detection technique. First of all each subgroup of the test population is compared with the equivalent subgroup of the Scotch whisky standard group. The samples which initially result in outliers are compared with the Spanish whisky population, owing to the suspicion that some Scotch-labelled bottles would have been filled with Spanish whiskies. The results obtained for $\alpha = 0{\cdot}01$ are shown in Table 4. The test population consists of 113 samples, which are found open in the establishments subjected to inspection, and three genuine samples, maintained with an appreciable head space, for a certain time. From this total, 48 bottles, which represent 41%, correspond to their brand, 32 bottles, i.e. 28% prove to be Spanish quality whisky and the

TABLE 4
Application of the Equation (1) to the Test Population for Detection of Outliers

Scotch whisky label	*Number of samples in test group*	*Results*		
		In accordance with their label	*Spanish whiskies*	*Outliers*
A	46	16	18	12
B	18 + 1[a]	8 + 1[a]	3	7
C	17	9	3	5
D	16 + 1[a]	5 + 1[a]	7	4
E	16 + 1[a]	7 + 1[a]	1	8
Total	113 + 3[a]	45 + 3[a]	32	36

[a] Genuine bottles kept opened with a variable headspace, during 20 days, 6 months and 12 months, respectively.

remaining 31% are definitely outliers. It is particularly interesting to notice that the three genuine bottles kept half-full have not lost their identity and prove to belong to the brand from which they come: respectively B, D and E.

CONCLUSIONS

The analysis of the major volatiles and the absorbance measures of the whiskies are determinations of simple and quick execution. They make easier the control of a large number of samples. If this information is used, two principal components are obtained and explain 80% of the total variance; they show the mutual differences between Spanish whiskies and Scotch whiskies of various brands. By means of the Stepwise Discriminant Analysis, it is found that the main differences between the two kinds of whiskies are the contents in 1-propanol and isoamyl alcohols. When the outliers detection method is applied, the results show that, in a large number of cases, it is possible to confirm that the contents of the bottles offered in Spanish establishments are genuine imported whisky, or otherwise that they have been replaced by Spanish whiskies of an equivalent quality, or else the samples are doubtful.

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A. Herranz, P. de la Serna, C. Barro
Laboratorio Municipal de Higiene de Madrid, Bailén 41, 28005 Madrid, Spain

P. J. Martin* & M. D. Cabezudo
Instituto de Fermentaciones Industriales, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

(Received 30 October 1987; revised version received and accepted 7 March 1988)

* To whom correspondence should be addressed.