ELSEVIER

Analytica Chimica Acta 381 (1999) 257–264

ANALYTICA CHIMICA ACTA

# Authentication and differentiation of irish whiskeys by higher-alcohol congener analysis

Domingo González-Arjona[a], Victor González-Gallero[b], F. Pablos[b], A. Gustavo González[b,*]

[a]*Department of Physical Chemistry, University of Seville, 41012 Seville, Spain*
[b]*Department of Analytical Chemistry, University of Seville, 41012 Seville, Spain*

Received 14 July 1998; accepted 8 October 1998

**Abstract**

Four higher alcohols, namely, 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol and 2-methyl-1-butanol, selected as chemical descriptors, were determined by head space gas chromatography. Fifty eight samples of commercialized whiskeys consisting of 12 samples of irish whiskey, 20 samples of bourbon whiskey and 26 samples of single malt scotch whiskey were analyzed for their content in higher alcohols. The use of straightforward chemometric procedures showed that irish whiskeys are well characterized by the four higher alcohols and can be easily differentiated from other whiskeys. 

*Keywords:* Irish whiskey; Authentication; Higher alcohols; Gas chromatography

## 1. Introduction

The use of chemical descriptors for characterizing foods and beverages as an alternative to sensorial analysis is one of the fundamental aims of chemometrics [1]. Distilled alcoholic beverages such as whiskeys are products of choice for establishing authentication schemes. Whiskey is legally defined under European Community Council (ECC) regulation no. 1576/89 [2]. In the following, the term 'whiskey' will be applied to irish and american whiskeys.

Analytical profiles for scotch whiskey and bourbon whiskey are well known [3,4]. Among the chemical descriptors selected to confirm scotch whiskey authenticity, higher-alcohol congeners such as 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol and 2-methyl-1-butanol, also called *fusel oils*, are the most important ones [5,6]. Wilson et al. [7] state that the analysis of the fusel oils is sufficient to classify whiskeys as scotch, blended or sour mash/bourbon. Higher alcohols may be easily determined by gas chromatography (GC) with flame ionization detector and polar stationary phases [8]. GC analysis in combination with mass spectrometry (MS) is a powerful analytical tool that allows the separation and identification of fusel oils [5,9].

Albeit fusel oil profiles for scotch whiskeys and bourbon whiskeys have been widely discussed in the literature, data for irish whiskeys are scarce, if not absent. Aside from the spanish whiskey, the two

*Corresponding author. Tel.: +34-9-54-557-173; fax: +34-9-54-557-168; e-mail: agonzale@cica.es

0003-2670/99/$ – see front matter 
PII: S0003-2670(98)00764-8

principal types of whiskey in Europe are the scotch whiskey (pure malt, grain or blended) and the irish whiskey [10]. Irish whiskey is made either from malted barley or from a mixture of malted and unmalted barley and other cereals but with not less than 25% of malted barley. The malt is dried in closed Kilns unlike in Scotland, where malt is dried over open peat fires. Thus, the malting process used for the irish whiskey not only avoids the smoky taste but also ensures a smooth and natural flavor. In Ireland, whiskey is obtained only after three separated distillations. At the first stage, a pot still distillate called 'low wines' is obtained. This full-flavored product is then distilled in another pot still. The resulting product, called 'feints', requires one further distillation which is carried out in a patent Coffey still. As a consequence of the triple distillation, a final spirit of light and delicate character is obtained. The product is stored at not more than 63% alcohol (v/v) in oak casks, some of which have been used previously for sherry, for a period of five years or more [11–13]. The use of a mixture of partially malted barley, the absence of peat fire smoking and the application of a triple distillation procedure confer to irish whiskey peculiar features.

It is noticeable that the number of irish whiskey distilleries is limited compared with the hundreds of scotch and bourbon ones. Thus, formerly there were five irish distilleries only, namely, Jameson, John Powers, Cork (Paddy), Tullamore Dew and Old Bushmills. The four first ones joined together in 1966, constituting the Midleton Centre, in County Cork. Apart from Midleton Centre, Old Bushmills distilleries, located in North Ireland, produces its own whiskey by following a different elaboration [11]. Midleton whiskeys are elaborated according to the definition of irish whiskey by applying both discontinuous (pot stills) and continuous (Coffey stills) distillation. Old Bushmills produces a rather different whiskey by following the scottish recipe of using pure malted barley [14]. Besides, the triple distillation is discontinuously performed by using three pot stills. The produced liquor is maturated in sherry and american oak casks and in port wine pipes. The result is a 'single malt' irish whiskey, as claimed in the bottle label [12,14].

The aim of the present paper is to characterize and differentiate irish whiskey from scotchs and bourbons by using the higher-alcohol congeners 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol and 2-methyl-1-butanol as chemical descriptors. For this purpose, a set of 58 samples of whiskeys containing 12 irish whiskeys, 20 bourbon whiskeys and 26 single malt scotch whiskeys was analyzed for fusel oils content by static head space GC–MS. The results in combination with pattern recognition procedures achieve a perfect differentiation of irish whiskey from the rest.

## 2. Experimental

### 2.1. Apparatus

A FISONS GC 8000 gas chromatograph coupled to a FISONS Trio 1000 mass spectrometer (FISONS Instrument, Valencia, CA, USA) and equipped with a J & W fused silica capillary column (J & W Scientific, Folsom, CA, USA) of 30 m×0.32 mm coated with a 1.8 μm film of DB-624 stationary phase was used. The oven was operated in isothermal mode at 32°C and the injector was held at 50°C. Helium was used as carrier gas at a flow rate of 1 ml/min through the column with a split ratio of 1/7. The mass spectrometer was operated in the electron impact mode at 70 eV. The GC–MS interface was held at 200°C and the ionization source at 250°C. Scan mode in the mass/charge range of 15–250 with a scan time of 0.90 and an interscan time of 0.01 s were used. Data acquisition began after a solvent delay of 4 min.

### 2.2. Reagents

Absolute ethanol (Merck, Darmstadt, Germany) and analytical grade 1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-methyl-1-butanol and 1-butanol (used as internal standard) (Fluka Chemie, Buchs, Switzerland) were used as received. Deionized water (18 MΩ/cm) purified by a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout. Standard solutions of the fusel oils for calibration were prepared in 40% ethanol/water (v/v) in order to match the aqueous alcoholic matrix of whiskey samples.

### 2.3. Samples

Fifty eight whiskey samples (bottles) commercially available were purchased from retail liquor stores. They consist of 12 irish whiskeys (I), 20 bourbon

Table 1
Sample codes and sources of the studied whiskeys

| Sample | Origin | Sample | Origin |
|---|---|---|---|
| S01 | Highlands | B04 | Kentucky, straight |
| S02 | Highlands | B05 | Kentucky, straight |
| S03 | Highlands | B06 | Tennessee, sour mash |
| S04 | Highlands | B07 | Kentucky, sour mash |
| S05 | Highlands | B08 | Kentucky, sour mash |
| S06 | Highlands | B09 | Kentucky, sour mash |
| S07 | Islay | B10 | Kentucky, straight |
| S08 | Highlands | B11 | Kentuchty, straight |
| S09 | Highlands | B12 | Kentucky, sour mash |
| S10 | Islay | B13 | Kentucky, sour mash |
| S11 | Highlands | B14 | Tennessee, sour mash |
| S12 | Highlands | B15 | Kentucky, sour mash |
| S13 | Skye | B16 | Kentucky, straight |
| S14 | Lowlands | B17 | Kentucky, sour mash |
| S15 | Orkney | B18 | Kentucky, straight |
| S16 | Islay | B19 | Kentucky, straight |
| S17 | Lowlands | B20 | Kentucky, sour mash |
| S18 | Highlands | I01 | Midleton |
| S19 | Highlands | I02 | Midleton |
| S20 | Highlands | I03 | Midleton |
| S21 | Highlands | I04 | Midleton |
| S22 | Islay | I05 | Midleton |
| S23 | Islay | I06 | Midleton |
| S24 | Skye | I07 | Midleton |
| S25 | Orkney | I08 | Midleton |
| S26 | Islay | I09 | Midleton |
| B01 | Kentucky, straight | I10 | Old Bushmills |
| B02 | Kentucky, straight | I11 | Old Bushmills |
| B03 | Kentucky, straight | I12 | Midleton |

whiskeys (B) and 26 single malt scotch whiskeys (S). An identification code was assigned to each sample. In Table 1, the code and source of the studied whiskey samples are depicted. Two single grain scotch whiskey samples were analyzed for the sake of comparison. Although the number of irish whiskeys seems to be smaller than the rest, the samples considered practically cover the most consumed brands issued from the irish distilleries.

The composition of the liquid phase influences directly the vapor composition in the head space. This may be envisaged as a matrix effect, which is different for each whiskey sample. Thus, for determining the fusel oils content of whiskey samples by static head space GC–MS, instead of using external calibration procedures, the method of standard additions was applied [15]. Unspiked samples and samples spiked at two levels were analyzed. The spiking procedure is indicated as follows: To 20 ml of whiskey, 10 μl of internal standard and 5 μl (1st level)/10 μl (2nd level) of each fusel oil were added. Five ml of the homogenized mixture were poured into a 20 ml head space vial and the analytical procedure was applied.

### 2.4. Analytical procedure

Five ml of sample (unspiked or spiked) or standard solution (prepared in 40% ethanol:water) containing 2.5 μl of internal standard was poured into a 20 ml head space vial that is sealed and then warmed up in the oven at 80°C for 30 min. 0.5 ml of the gas contained in the head space was injected on the chromatograph.

### 2.5. Data analysis

Each whiskey sample was considered as an assembly of four variables, i.e. the contents of each fusel oil congener, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol, which were the selected chemical descriptors. The corresponding data matrix whose rows are the whiskey samples and whose columns are the mentioned variables is presented in Table 2. All the results expressed, as mg/l, were the average of triplicate measurements. The results were rounded up to the last figure associated to random error (standard deviation).

In this study, pattern recognition (PR) procedures have been applied, involving principal component analysis (PCA) [16,17] and cluster analysis (CA) [18]. The statistical package CSS:STATISTICA from StatSoft™ (Tulsa, OK, USA) was used in PR calculations.

## 3. Results and discussion

### 3.1. Performance characteristics of the procedure

Typical chromatograms for single malt scotch whiskey, bourbon whiskey, irish whiskeys (Midleton and Bushmills) and single grain scotch whiskey are displayed in Fig. 1. As can be observed, the volatile profile of major constituents of the samples, aside from ethanol and methanol, consists of the following compounds by elution order: 1-propanol, ethyl acetate, 2-methyl-1-propanol, diethyl acetal (1,1-diethoxy ethane), 3-methyl-1-butanol and 2-methyl-1-butanol.

Table 2
Fusel oils content for the whiskey samples studied

| Sample | 1-Propanol | 2-Methyl-1-propanol | 3-Methyl-1-butanol | 2-Methyl-1-butanol |
|---|---|---|---|---|
| S01 | 169.8 | 368.5 | 315.2 | 248.1 |
| S02 | 186.8 | 423.9 | 409.4 | 231.3 |
| S03 | 203.5 | 353.3 | 368.2 | 152.1 |
| S04 | 270.2 | 425.1 | 410.2 | 162.3 |
| S05 | 289.6 | 398.2 | 415.4 | 216.5 |
| S06 | 269.6 | 378.6 | 345.6 | 201.8 |
| S07 | 258.3 | 452.3 | 398.7 | 200.2 |
| S08 | 213.2 | 484.1 | 379.8 | 195.9 |
| S09 | 280.5 | 420.1 | 502.4 | 179.5 |
| S10 | 247.7 | 464.6 | 450.9 | 284.7 |
| S11 | 249.4 | 424.4 | 548.6 | 300.4 |
| S12 | 341.3 | 395.3 | 398.5 | 213.6 |
| S13 | 290.6 | 402.5 | 425.6 | 215.4 |
| S14 | 215.7 | 561.8 | 426.4 | 282.7 |
| S15 | 258.3 | 523.4 | 386.5 | 302.5 |
| S16 | 226.8 | 428.8 | 525.3 | 238.9 |
| S17 | 191.2 | 453.4 | 374.6 | 210.2 |
| S18 | 241.3 | 395.8 | 415.2 | 268.4 |
| S19 | 228.6 | 512.4 | 378.5 | 298.1 |
| S20 | 233.6 | 359.2 | 358.7 | 201 |
| S21 | 253.3 | 400.5 | 440.1 | 365.4 |
| S22 | 232.6 | 392.4 | 445.3 | 187.5 |
| S23 | 290.2 | 483.1 | 512.6 | 270 |
| S24 | 214.1 | 561.4 | 558.4 | 348.1 |
| S25 | 212.8 | 507.2 | 339.9 | 212.8 |
| S26 | 242.3 | 502.5 | 432.2 | 350.2 |
| B01 | 117.6 | 448.3 | 1514.4 | 438.9 |
| B02 | 152.5 | 532.1 | 1461.1 | 457 |
| B03 | 98.3 | 478.2 | 1283.1 | 424.2 |
| B04 | 59.1 | 493.2 | 1244.2 | 466.3 |
| B05 | 105.4 | 375.7 | 1353.3 | 606.2 |
| B06 | 91.9 | 587.7 | 1666.3 | 533.7 |
| B07 | 130.6 | 428.4 | 1277.4 | 577.5 |
| B08 | 129.6 | 417.5 | 1389.6 | 421.7 |
| B09 | 115.8 | 400.5 | 1459 | 465.2 |
| B10 | 102.6 | 398.6 | 1504.2 | 524.7 |
| B11 | 99.5 | 504.2 | 1389.9 | 503.1 |
| B12 | 125.8 | 545.5 | 1478.8 | 484.5 |
| B13 | 130.5 | 584.1 | 1253.3 | 482.4 |
| B14 | 128.5 | 415.2 | 1515.2 | 588 |
| B15 | 130.2 | 425.9 | 1497.2 | 528.5 |
| B16 | 111.1 | 419.8 | 1556.3 | 520.1 |
| B17 | 102.8 | 485.4 | 1498.7 | 430.2 |
| B18 | 146.2 | 475.3 | 1358.4 | 452.2 |
| B19 | 154.4 | 387.8 | 1335.2 | 444.8 |
| B20 | 108.9 | 415.5 | 1565 | 453 |
| I01 | 211.1 | 154.5 | 289.1 | 88.4 |
| I02 | 242.3 | 168.9 | 315.2 | 90.2 |
| I03 | 218.5 | 152.3 | 330.1 | 81.5 |
| I04 | 225.3 | 150.8 | 298.4 | 84.7 |
| I05 | 258.4 | 162.5 | 335.5 | 89.3 |
| I06 | 260 | 145.8 | 286.3 | 81.5 |
| I07 | 234.8 | 158 | 340.2 | 80.2 |
| I08 | 220.2 | 142.3 | 329.5 | 91.5 |
| I09 | 237.5 | 171.2 | 301.4 | 83.2 |
| I10 | 202 | 427.9 | 941.2 | 250.9 |
| I11 | 208.5 | 430.2 | 950 | 254.8 |
| I12 | 244.8 | 160.1 | 288.8 | 89.1 |

According to Wilson et al. [7], 1-butanol was used as internal standard. The presence of the above mentioned components was confirmed from the mass spectra, and the superior alcohols were also confirmed by using standard solutions. Due to the high content of ethanol in the whiskeys, a solvent delay of 4 min was set before starting the data acquisition for the sake of proper outputs.

In all cases, a non-drifted baseline was obtained. Peak tailing [19] was less than 1.35 in all cases. Resolution between chromatographic peak pairs was always higher than 1.5 except for the peaks corresponding to 3-methyl- and 2-methyl-1-butanol, that ranged within 1.1–1.3 depending on the relative amounts of these two alcohols. A linear relationship between concentration and the ratio of (analyte peak height)/(internal standard peak height) was obtained, from 40% ethanol/water standard solutions of the fusel oils, in the range 100–1000 mg/l. Good linearities were found with correlation coefficients higher than 0.990 for all the fusel oils. Limits of detection (LOD) were obtained from the calibration straight line according to Miller and Miller [20] as LOD=3$s/b$, $s$ being the standard deviation of the calibration line and $b$ its corresponding slope. The calculated LODs were as follows: 19 mg/l of 1-propanol, 13 mg/l of 2-methyl-1-propanol, 35 mg/l of 2-methyl-1-butanol and 52 mg/l of 3-methyl-1-butanol.

In order to evaluate the reproducibility of the procedure, five injections of a blend of standards were daily made over a two-month period. The reproducibilities expressed as percent relative standard deviation (RSD) for all the fusel oils lie within 3–5%. As was indicated above, to avoid matrix effects on the content of volatile compounds in the vapor phase of head spaces, the method of standard additions [17] was applied to quantify the fusel oils in samples. Each

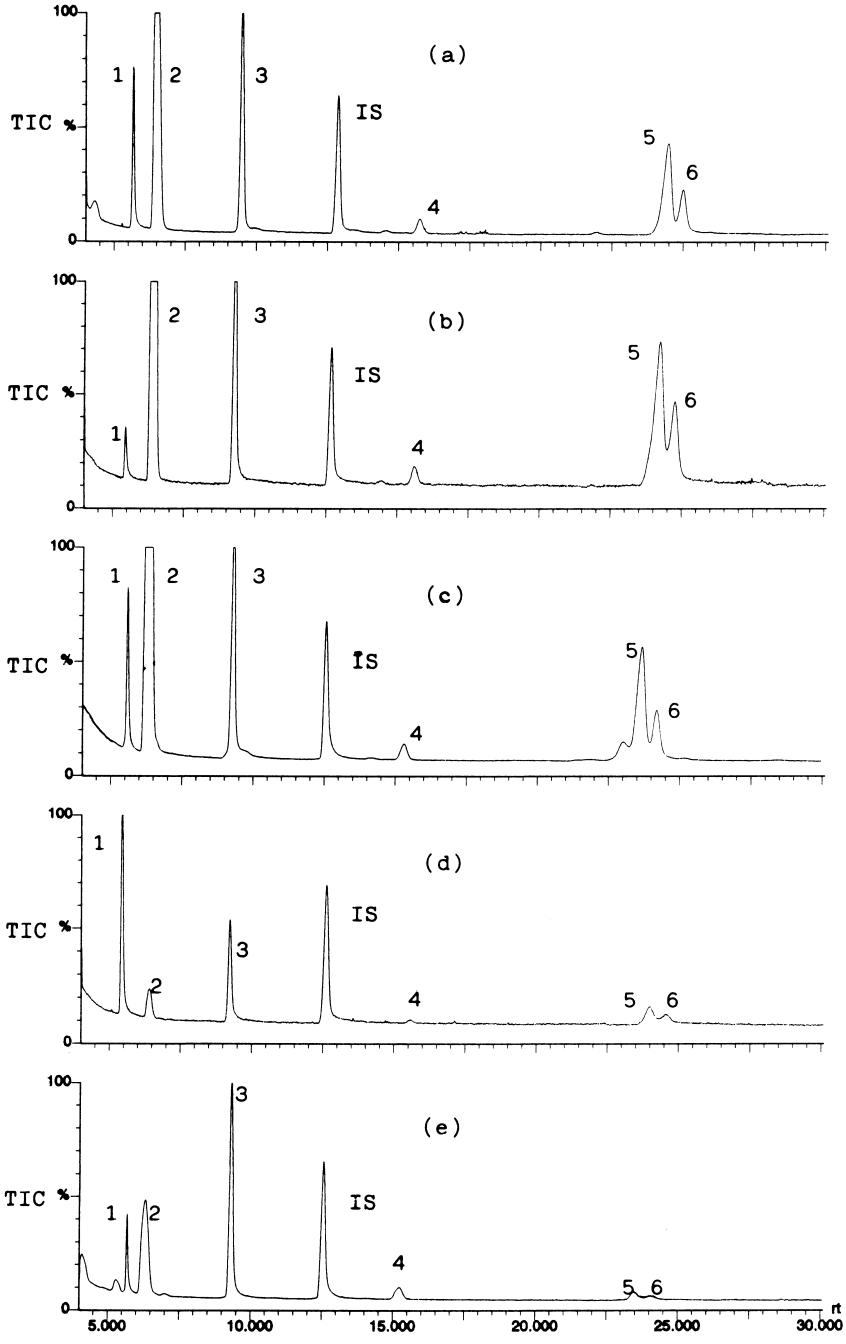


Fig. 1. Chromatograms corresponding to samples representatives of: (a) single malt scotch whiskey; (b) bourbon whiskey; (c) irish whiskey (Old Bushmills); (d) irish whiskey (Midleton); and (e) grain scotch whiskey. Key for peaks: 1: 1-propanol; 2: ethyl acetate; 3: 2-methyl-1-propanol; IS: internal standard (1-butanol); 4: ethyl acetal (1,1-diethoxyethane); 5: 3-methyl-1-butanol; 6: 2-methyl-1-butanol; TIC refers to the total ion current and tr to retention time, in min.

Table 3
Mean values and standard deviations of the fusel oils for the three classes of whiskey

| Class | 1-Propanol | 2-Methyl-1-propanol | 3-Methyl-1-butanol | 2-Methyl-1-butanol |
|---|---|---|---|---|
| Scotch | 243±38 | 441±60 | 422±64 | 244±59 |
| Bourbon | 117±23 | 461±64 | 1430±116 | 490±56 |
| Irish[a] | 235±17 | 156±9 | 311±21 | 86±4 |

[a]Samples I10 and I11 coming from the Old Bushmills distilleries were not considered according to their outlying behavior compared to typical irish whiskeys.

sample was spiked at two levels as described in Section 2. From the results of spiked samples, recoveries were calculated for establishing the accuracy of the procedure. Averaged recoveries, calculated as the mean of the recoveries obtained at each fortification (spike) level, ranged within 0.97–1.05. According to these results, one can conclude that the procedure is accurate and then it may be considered as suitably validated.

### 3.2. Typification and differentiation of irish whiskey samples

According to the results given in Table 2, the mean values and standard deviations for each class of whiskey are presented in Table 3.

In order to visualize the data structure and the discriminating efficiency of the selected features, PCA based display methods were applied. The data matrix was subjected to PCA and two principal components (PC1 and PC2) were selected. These PCs explain up to 94% of the data variance and lead to communalities higher than 0.91 for all the considered variables. According to the PC loadings, the variables 1-propanol, 3-methyl-1-butanol and 2-methyl-1-butanol are dominant in PC1, whereas for PC2 the main contribution corresponds 2-methyl-1-propanol. The scores plot for the whiskey samples is depicted in Fig. 2. As can be seen, three groups appear that nearly correspond to the three classes of whiskey analyzed with the exception of two samples of irish whiskey coming from Old Bushmills distilleries, which were located close to the scotch cloud. Typical irish whiskeys produced by Midleton distillery form a compact isolated clump. This indicates that the higher-alcohol congeners are promising descriptors for the typification and differentiation of irish whiskey. For assessing this statement, a hierarchical cluster analysis of samples was performed using the euclidean distance as similarity measurement and the Ward's method as amalgamation rule. The resulting dendrogram is depicted in Fig. 3. For distances of about 10% of the maximum distance, three clusters appear corresponding to the three considered classes of whiskey. In

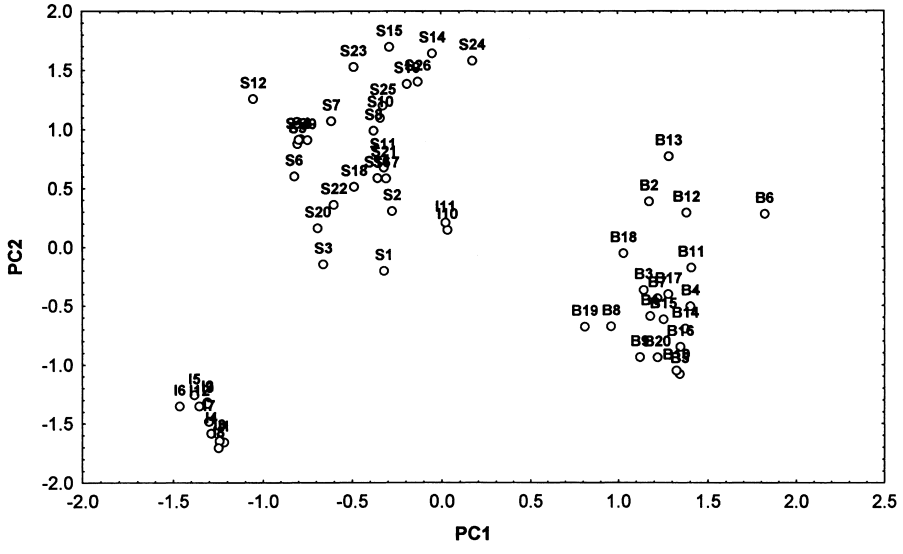


Fig. 2. Scores plot of the studied samples for the first two PCs.

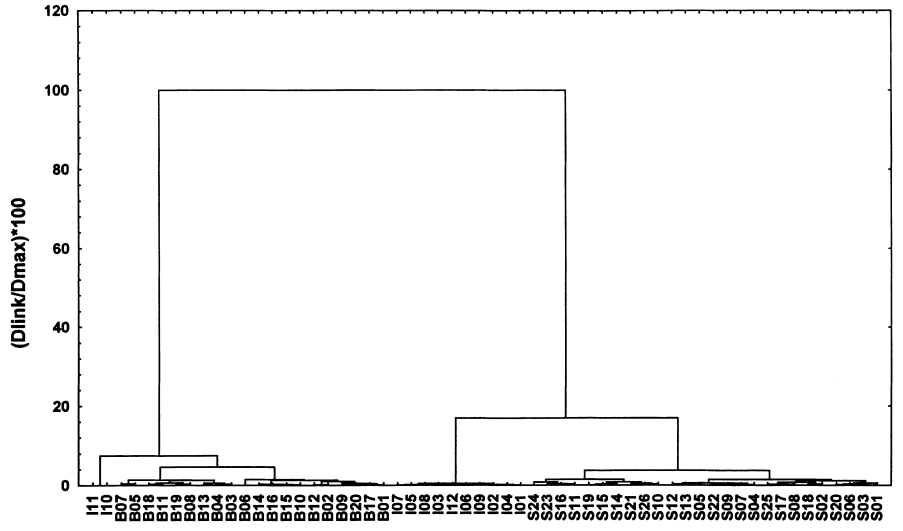


Fig. 3. Dendrogram corresponding to the hierarchical clustering of whiskeys using the fusel oils as variables. Similarity measurement: Euclidean distance. Amalgamation rule: Ward's method.

this case, irish whiskeys from Old Bushmills are grouped into the bourbon cluster. Thus, it can be concluded that with the exception of these two apparently outlying irish samples, the separation of the three classes of whiskeys was very good.

Taking into account both the excellent separation attained and the number of chemical descriptors chosen (only four), a very straightforward way to select the best discriminating features by direct inspection is to draw the corresponding six variable–variable plots. The couple 2-methyl-1-propanol and 3-methyl-1-butanol lead to the best separation between the classes. As can be observed in Fig. 4, irish-Midleton whiskeys, scotchs and bourbons are grouped homogeneously, the clusters being located at separate zones in the chart. It is remarkable that the presence of an isolated cluster

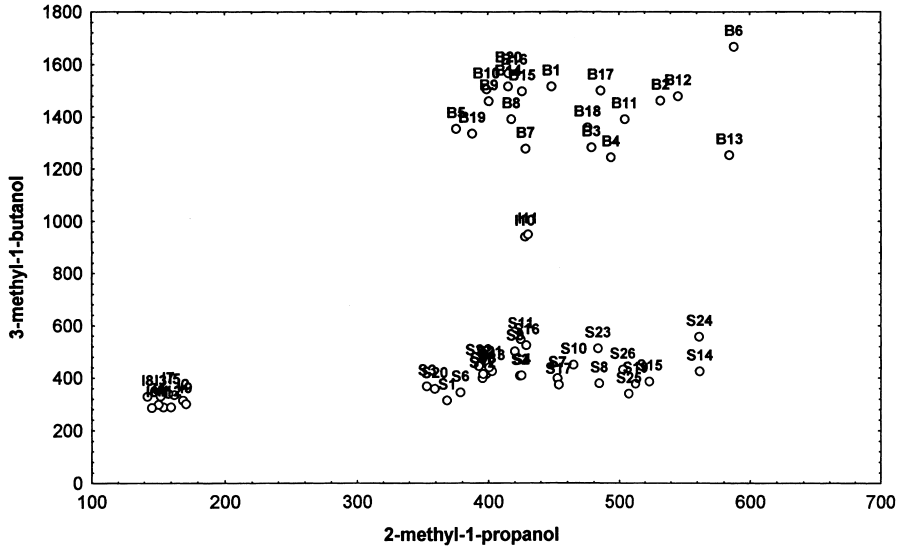


Fig. 4. Scatter plot of the studied whiskeys using as coordinate variables the contents in 2-methyl-1-propanol and 3-methyl-1-butanol.

halfway scotchs and bourbons contain the two samples of irish-Bushmills whiskeys.

The reason for the different behavior of the samples coming from the irish Old Bushmills distilleries may be explained taking into account the differences in the distillation process: In Old Bushmill distilleries the triple distillation is carried out by using pot stills always. In Midleton distilleries, the last distillation is performed by employing a patent Coffey still, where a continuous distillation takes place. The liquor resulting from the patent still has a low content of higher alcohols, such as 2-methyl and 3-methyl-1-butanol [11]. Pure grain scotch whiskeys are produced from continuous distillation and accordingly they show lower contents in higher alcohols. As can be seen in Fig. 1, chromatograms corresponding to typical irish whiskey and pure grain scotch whiskey are similar, as expected.

## 4. Conclusion

Higher-alcohol profiles provided a valuable method for checking irish whiskey authenticity, with particular attention being paid to 2-methyl-1-propanol and 3-methyl-1-butanol.

## References

[1] M.C. Ortiz, J.A. Sáez, J. López Palacios, Analyst 118 (1993) 801.
[2] Council Regulation (EEC) No. 1576/89 of May 1989, Off. J. Eur. Commun. (1989) No. L160, p. 1.
[3] R.L. Schoeneman, R.H. Dyer, E.M. Earl, J. Assoc. Off. Anal. Chem. 54 (1971) 1247.
[4] R.L. Schoeneman, R.H. Dyer, J. Assoc. Off. Anal. Chem. 56 (1973) 1.
[5] R.I. Aylott, A.H. Clyne, A.P. Fox, D.A. Walker, Analyst 119 (1994) 1741.
[6] W.A. Simpkins, J. Sci. Food Agric. 36 (1985) 367.
[7] L.A. Wilson, J.H. Ding, A.E. Woos, J. Assoc. Off. Anal. Chem. 74 (1991) 248.
[8] L.M. González, R. González-Lara, J. Chromatogr. Sci. 32 (1994) 195.
[9] L.M. Headly, J.K. Hardy, J. Food Sci. 57 (1992) 980.
[10] J. Muñoz Ramos, Enciclopedia de los Alcoholes, Editorial Planeta, 1996.
[11] P. Casamayor, M.J. Colombani, El libro del amante del whisky, El Cuerno de la Abundancia, Barcelona, 1985.
[12] G. Delos, Les whiskies du monde, Studio, Paris, 1996.
[13] Web sites: http://www.indigo.ie/ipress/jhc/whiskey.htm; http://www.mindspring.com/-mccathys/whiskey/irish.htm.
[14] Web sites: http://www.bushmills.com/compare.htm; http://www.bushmills.com/distilling.htm.
[15] L. Cuadros-Rodríguez, M. García-Campaña, F. Alés-Barrero, C. Jiménez-Linares, M. Román-Ceba, J. AOAC Int. 78 (1995) 471.
[16] C. Chatefield, A.J. Collins, Introduction to Multivariate Analysis, Chapman & Hall, London, 1981.
[17] R. Henrion, G. Henrion, Multivariate Datenanalyse, Springer, Heidelberg, 1995.
[18] D.L. Massart, L. Kaufman, Interpretation of Analytical Data by Use of Cluster Analysis, Wiley, New Yark, NY, 1983.
[19] J.W. Dolan, LC-GC Int. 10 (1997) 788.
[20] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, Ellis Horwood, Chichester, 1988, pp. 115–117.