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Multi-method analysis of matured distilled alcoholic beverages for brand identification

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Abstract The aim was to achieve a simple method or methods by which different countries' and regions' brands of whisky, brandy and rum could be identified on the basis of chemical composition, ultraviolet-visible (UV-vis) absorption, and/or pH. The analytical results were processed statistically using principal components analysis. To determine whether the concentrations of chemical components in a particular brand remain constant, samples of batches bottled over a period of 3–4 years and those bottled within the same year were compared. In study 1 (14 whiskies, 7 rums and 9 brandies) the main distinguishing factors among the three categories of beverages were the UV-vis absorbances at 220, 275, 360 and 440 nm, concentrations of four fermentation alcohols and ethyl acetate, and pH. In study 2 (27 whiskies and 2 rums), brands could be identified on the basis of the concentrations of five fermentation alcohols and ethyl acetate. Even though it was possible to distinguish brandy from whisky and rum without quantitative component analysis, whisky and rum clusters could not be clearly separated from each other or by brand on the basis of pH and absorbances at discrete wavelengths. UV spectra of whiskies, rums, and brandies were recorded and compared statistically. Whisky brands could not be differentiated but it was possible to distinguish among brands of rum and brandy.

Key words Alcoholic beverages · Principal component analysis · Whisky · Rum · Brandy

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Introduction

Chemical compounds that give a beverage its characteristic flavour and aroma can be determined and used to classify the beverage as to type and country of origin. Such analysis has important applications in product control and prevention of brand fraud. No single chemical in an alcoholic beverage is sufficient to distinguish one brand from another or to determine quality. The various components found in beverages such as whisky, rum and brandy originate from the fermentation, distillation or ageing stages. Brandy, whisky and rum contain the same volatile fermentation alcohols. The concentrations of these components depend on their substrate of origin and on the yeasts used for fermentation [1]. During the ageing process, volatile and non-volatile phenolic compounds may be extracted from oak ageing barrels. The extent of the extraction depends on the age, type and size of barrel [2]. Some of the compounds found in alcoholic beverages may react with one another, dissociate, evaporate, or be absorbed, whereby their concentrations change during the ageing process [3].

Principal component analysis

Data from quantitative measurement can be processed statistically using principal component analysis (PCA) based on clustering techniques. As a result, samples with a similar pattern of compound concentrations are grouped together [4]. A group or class, for example whisky or whisky brand, can thus be distinguished from the other groups, e.g. rum or brandy or other brands of whisky. The type groups can be broken down further to identify beverages from a particular country or region.

Herranz et al. [1], using the concentrations of fermentation alcohols and ethyl acetate, succeeded 100% in determining the country of origin of different brands of whisky from Spain and Scotland and was 80% suc-

cessful in determining the brands of samples of Scotch whiskies. The authors also used 1-propanol, found in lower concentration in Spanish brands, and 3-methyl-1-butanol, higher in Spanish brands, to differentiate between cheap Scotch whisky and Bourbon.

Grain whiskies contain smaller amounts of isoamyl alcohol than do the malt whiskies [5]. On the basis of six organic compounds of various types, Headley and Hardy [6] were able to classify correctly whiskies from five countries, with only Canadian brands overlapping other groups.

The continuous distillation process used for grain whisky tends to recover congeners up to the volatility of isobutanol and very little isoamyl alcohol or higher boiling compounds. Malt whiskies contain the same congeners plus isoamyl alcohol and a large number of higher boiling compounds. Trace congeners including alcohols, aldehydes, acids, and esters are more common in malt whiskies. Components originating in post-distillation processes are found in both types, including cask-associated components produced during maturation [5].

The concentrations of barrel-derived compounds are often directly related to the duration of ageing in the barrels. The type of oak barrel is also relevant. PCA studies indicate that whiskies and rums are more closely related whereas cognacs stand further apart [7, 8]. Analyses of samples of whisky aged for 6–48 months showed that the pH level decreased from around 5.5 to around 4.0 during the ageing process [9].

The aim of this study was to introduce into practice a method based on the determination of higher alcohols, ethyl acetate, pH and ultraviolet-visible (UV-vis) absorbance to identify the types and/or brands of samples of matured distilled beverages.

Experimental procedure

Samples

Study 1. Thirteen whiskies, seven rums and 11 brandies from nine different countries were analysed. A minimum of one brand from each type group bottled during the same year and one brand from each group bottled during consecutive years were compared to determine how consistent the components concentration between them were.

Study 2. Twenty seven whiskies from six countries and two Puerto Rico rums were analysed.

UV-vis spectrophotometry

Study 1. An HP 1090 high-performance liquid chromatograph (HPLC) with a diode array detector was used to obtain UV spectra between 220 and 520 nm. No column was used, and 2 μl of each sample was injected. Samples with absorbances exceeding 1000 mAu within the spectral range were diluted 1:4 with 40% ethanol.

Study 2. An HP 9133 diode array spectrophotometer was used to measure the absorbances of samples at 380, 440 and 500 nm. One-centimetre cuvettes were used.

Comparison of UV-vis spectra

Visual comparison of spectra is usually time consuming and unsuited for automation. A correlation coefficient calculated from all the absorbances measured gives the best results [10, 11]. With the instrument used, absorbances could be measured at intervals of 2 nm. Comparison of two spectra was thus based on a match factor derived from the correlation coefficient (coefficient × 1000, range 0–1000). At the extremes, a match factor of 0 indicates no match and 1000 indicates two identical spectra. Generally, values above 990 indicate that the spectra are similar. Values between 900 and 990 indicate there is some similarity. All values below 900 mean in effect that you have two different spectra [12].

Gas chromatography

An HP 5890 gas chromatograph (GC) with a flame ionization detector was used to measure the concentrations of methanol, ethyl acetate and the following fermentation alcohols: 1-propanol, isobutanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. 2-Pentanol was used as an internal standard. A Chrompack WCOT fused silica (50 m × 0.53 mm i.d. DF 5.0) column was used.

Reagents

All reagents were of analytical grade. 1-Propanol, isobutanol, and ethyl acetate were from Merck. 2-Methyl-1-butanol and 2-pentanol were from Fluka and 3-methyl-1-butanol was from Baker.

Principal component analysis

The PRINCOMP procedure of the IBM Statistical Analysis System (SAS) was used for the classification of samples. For the PCA analysis the concentration of alcohols and ethyl acetate were calculated as milligrams in 100% alcohol. This means that, for example, if the alcohol content was 40%, the measured concentration was multiplied with a factor of 100/40 = 2.5. In this way the concentrations were comparable in beverages having different alcohol contents. The classification was carried out by testing all possible combinations of the parameters given in Tables 1 and 2. To reach some kind of separation, at least three variables had to be used. The best separation of beverages or beverage groups from each other was found by just looking at the different figures obtained.

Results and discussion

Study 1

The main variables differentiating among the three categories of beverage (whisky, rum and brandy) were the absorbances at wavelengths of 220, 275 and 360 nm, the concentrations of 1-propanol, isobutanol, 2-methyl-1-butanol and 3-methyl-1-butanol, and ethyl acetate, and pH. The absorbance values at 220 nm and 275 nm helped to separate the brandies from the rums and whiskies, whereas absorbance at 360 nm in combination with the fermentation alcohols and ethyl acetate distinguished the latter two categories. Owing to similarity of pH values and concentration of fermentation alcohols and ethyl acetate, only absorbance values could be used to subdivide the brandies by country of origin. Here, absorbances at 220 nm and 275 nm proved to be the most influential.

Table 1 (Study 1) UV-vis absorbance values at four wavelengths, pH values and concentrations of some compounds in 14 whiskies, seven rums and 11 brandies

Country	Alc. (%)	Absorbance				Alcohols (mg in 100% alcohol)				Ethyl acetate (mg in 100% alcohol)	pH
		220 nm	275 nm	360 nm	440 nm	Propanol	Isobutanol	2-Methyl-1-butanol	3-Methyl-1-butanol		
Whiskies:											
Canada	40	302	232	56	8	64	87	61	120	98	3.84
Canada	40	257	164	44	4	0	83	67	194	60	4.31
Finland	40	256	169	40	8	269	442	244	690	167	3.91
Finland	40	410	263	70	16	250	494	313	712	315	3.78
Finland	40	268	172	48	16	293	485	292	729	144	3.93
Ireland	40	340	250	70	10	565	267	198	607	139	3.93
Scotland	40	345	230	60	10	594	550	139	363	133	3.84
Scotland	40	260	76	40	10	312	634	371	991	297	3.79
Scotland	40	340	250	75	15	597	602	164	413	183	3.97
Scotland	40	430	295	80	10	799	697	203	521	290	3.88
Scotland	40	228	170	40	−5	619	556	202	453	177	3.99
Scotland	40	300	225	50	0	543	531	90	444	161	3.90
Scotland	40	280	180	50	10	518	463	78	402	165	3.90
Scotland	40	260	205	50	5	656	550	97	502	211	3.91
	Mean	310	207	56	9	501	523	199	569	199	3.89
	SD	61	56	14	6	170	104	89	176	62	0.06
Rums:											
Cuba	37.5	4	−3	−7	−8	35	58	0	108	0	4.75
Cuba	40	353	305	80	9	49	35	0	83	83	3.90
Cuba	40	54	23	1	0	115	181	77	317	76	3.63
France	54	480	840	72	0	445	518	303	1566	584	4.52
West Indies	45	370	400	110	20	48	77	52	86	131	4.10
West Indies	40	120	47	3	0	103	214	91	386	121	3.62
West Indies	45	280	312	96	24	50	78	53	87	115	4.12
	Mean	257	253	70	15	67	123	65	186	122	3.95
	SD	103	150	47	10	25	65	18	141	6	0.23
Brandies:											
France	40	1160	580	72	34	472	1307	547	2414	837	3.48
Spain	36	324	288	88	32	224	235	237	987	213	3.11
France	40	1400	800	80	6	352	1092	588	2591	397	3.66
France	36	1120	1060	80	10	273	508	364	1286	256	3.53
France	40	700	450	100	20	350	1519	691	2888	508	3.61
France	40	860	660	120	20	410	1005	712	2713	442	3.58
France	40	870	700	120	20	390	1074	605	2744	383	3.50
France	40	1528	880	120	8	344	1119	720	2677	476	3.46
France	40	1700	920	160	40	291	1057	301	2553	296	3.47
France	40	1620	880	160	20	335	1291	379	3156	335	3.52
France	40	850	900	125	25	348	993	248	2197	364	3.57
	Mean	1103	738	111	21	344	1018	490	2382	410	3.50
	SD	409	218	29	10	64	344	180	635	160	0.14

Brandies had by far the highest absorbances, regardless of wavelength (Table 1). Rums and whiskies had similar mean absorbances but the standard deviations were much higher for rums. Rums had the highest mean pH but they were also the most heterogeneous in this respect, as shown by the high standard deviation. Brandies had the lowest mean pH. The concentrations of fermentation alcohols and ethyl acetate were highest in brandies. Rums were most heterogeneous regarding these compounds. Whiskies were easily distinguished by country of origin according to the concentrations of the fermentation alcohols and ethyl acetate. The greatest differences in concentration were found for 1-propanol and 2-methyl-1-butanol.

Absorbance values at the different wavelengths and the concentrations of fermentation alcohols and ethyl acetate were used in trying to find the best variable combination to separate rums from one another. The primary distinguishing factors were found to be the concentration of 1-propanol and the absorbance at 275 nm.

Altogether, nine variables (omitting the pH values) were used in the PCA. A PCA plot is presented in Fig. 1. The beverages were well separated according to country and type of product. Whisky and rum were more closely related to each other than was either of them to the brandy. Scotch whiskies and the one Irish whiskey were clustered quite close to each other but were clearly separated from whiskies prepared in other countries. Scotch whisky and Canadian whisky were well separated. Rums were separated surprisingly well in spite of the fact that they had all been prepared more

Table 2 (Study 2) UV-Vis absorbance values at three wavelengths and concentrations of some compounds in 27 whiskies and two rums (*n.m.* not measured)

Country	Alc. (%)	Absorbances			Alcohols (mg in 100% alcohol)					Ethyl acetate (mg in 100% alcohol)
		380 nm	440 nm	500 nm	Methanol	Propanol	Isobutanol	2-Methyl-1-butanol	3-Methyl-1-butanol	
Whiskies:										
Canada	40	1116	335	135	68	139	193	80	245	95
Canada	40	932	264	108	60	25	97	67	217	110
Ireland	40	1831	577	203	86	462	242	177	532	140
Ireland	40	1707	511	175	83	493	255	186	554	104
Ireland	40	1722	567	206	90	440	217	160	500	149
Ireland	40	1619	493	181	80	470	237	169	503	129
Ireland	40	1577	464	165	78	453	250	177	528	109
Ireland	40	1656	499	176	77	460	235	170	508	126
Ireland	40	1687	514	180	79	464	238	170	509	133
Ireland	40	1637	504	189	80	467	238	172	513	141
Ireland	40	1660	504	183	78	465	239	171	505	138
Ireland	40	1727	542	189	89	476	232	176	557	123
Scotland	40	1040	349	132	62	519	667	206	539	198
Scotland	40	1070	349	128	56	597	666	195	517	202
Scotland	40	1165	397	147	52	669	627	196	528	238
Scotland	40	1089	358	132	59	718	635	211	570	220
Scotland	40	1127	389	146	56	605	646	197	531	191
Scotland	40	1919	656	232	96	779	584	132	378	200
Scotland	40	1427	467	170	51	487	693	201	547	134
Scotland	40	1608	505	192	141	599	558	131	383	170
Scotland	40	1600	512	193	67	774	606	215	578	210
Scotland	40	2063	705	256	77	738	648	170	496	294
Scotland	43	n.m.	n.m.	n.m.	78	716	636	168	491	263
Scotland	40	n.m.	n.m.	n.m.	85	705	653	191	538	208
Scotland	40	n.m.	n.m.	n.m.	89	440	788	462	1449	350
Scotland	40	n.m.	n.m.	n.m.	86	435	783	455	1426	350
Scotland	40	n.m.	n.m.	n.m.	85	526	860	496	1436	429
	Mean	1499	476	174	77	523	471	204	595	191
	SD	315	104	35	18	169	231	100	310	83
Rums:										
Puerto Rico	40	n.m.	n.m.	n.m.	23	151	59	31	281	57
Puerto Rico	40	n.m.	n.m.	n.m.	25	159	58	31	278	56

or less in the same region. The only available explanation is the different production procedures in each country.

Study 2

The absorbance values and the concentrations of methanol, ethyl acetate, and the fermentation alcohols are presented in Table 2. The absorbance values were not in the same level in studies 1 and 2 because of the different methods used in the measurements. The best separation power, using PCA, was achieved by omitting the absorbance values (Fig. 2), thereby using six variables in the analysis. Scotch, Irish and Canadian whiskies were clearly separated. The two Puerto Rican rums were also clearly separated from the whiskies.

Comparison of UV-vis spectra

Each spectrum was compared with each of the other 28 sample spectra. Match factors within product categories (whiskies, rums or brandies) as well as between different categories of products are presented in Fig. 3. UV-vis spectra of whiskies were quite close to each other. Rums made up the most heterogeneous group, having a mean match factor of only 857 and a standard deviation of 143. Brandies were between whiskies and rums in heterogeneity. Rum and brandy could be most easily distinguished from each other, followed by rum and whisky. Of the three categories, whisky and brandy resembled each other most in terms of UV-vis spectra.

Based on the correlation of UV-vis spectra, it appeared that whiskies could not be separated from one another by spectrophotometry. The ability to distinguish among brands of rum was already apparent from the large standard deviation of values within this product category (Fig. 3). The same was true for brandies.

Consistency of findings within brands

Samples were taken of a whisky and brandy bottled over 3 consecutive years, 1993–1995. Samples of rum were taken from bottles filled 4 years apart, 1990 and

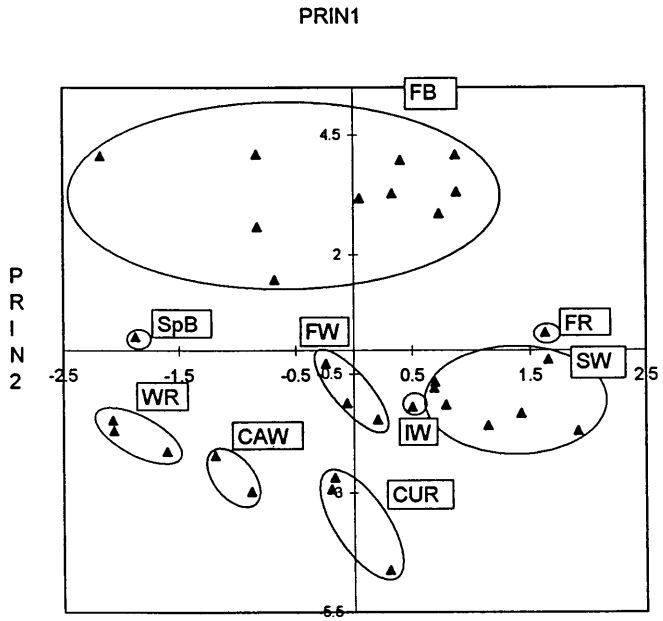

Fig. 1 (Study 1) Principal component analysis (PCA) of 14 whiskies, seven rums and 11 brandies. *FB* French brandies, *SpB* Spanish brandy, *WR* West Indian rums, *CAW* Canadian whiskies, *FW* Finnish whiskies, *IW* Irish whisky, *CUR* Cuban rums, *FR* French rum, *SW* Scotch whiskies

1994. UV-vis spectral analysis, GC analysis, and pH determination were used to assess the degree of variation among batches from different years. Further, duplicate samples bottled during the same year were available for many of the brands analysed in the study reported above.

Although the concentrations of the components and the wavelengths of different samples of a brand were not always exactly the same, they were within a narrow range of values. When analysed by PCA, each duplicate acquired almost the same location as the original same-

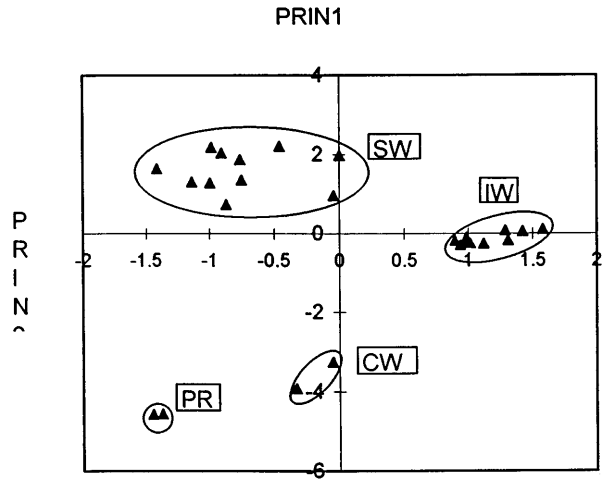

Fig. 2 (Study 2) PCA of 27 whiskies and two rums. *SW* Scotch whiskies, *CW* Canadian whiskies, *IW* Irish whiskies, *PR* Puerto Rican rums

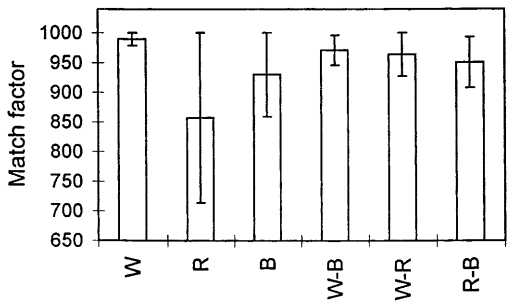

Fig. 3 (Study 1) UV-vis spectral comparison of whiskies, rums, and brandies. *W* Whiskies ($n = 14$), *R* rums ($n = 7$), *B* brandies ($n = 11$), *W-B* comparison between whiskies and brandies, *W-R* comparison between whiskies and rums, *R -B* comparison between rums and brandies

year sample of the brand. Even batches from different years proved to have similar component concentrations and UV-vis spectra, acquiring locations close to one another on the PCA diagram. Match factors for samples within brands ranged from 990 to 999.9.

Conclusion

PCA was an effective way to differentiate various distilled alcoholic beverages from one another. The type and number of variables required depended on the type of product. Generally, the fermentation alcohols and ethyl acetate are powerful in classifying matured distilled alcoholic beverages. In some cases, simply the UV-vis spectrum sufficed to identify the product.

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