ANALYTICAL AND STATISTICAL CHARACTERIZATION OF GRAPPA FROM DIFFERENT ITALIAN REGIONS

VERSINI G., MONETTI A., DALLA SERRA A., INAMA S.
ISTITUTO AGRARIO PROVINCIALE
S. Michele all'Adige, Trento - Italie

INTRODUCTION

Volatile compounds or "impurities" of distillates fermerted grape products have been examined in several researches (ter Heide, 1986). At the same time, interesting quantitative differences among the compounds derived from both different raw materials and different distillation processes were pointed out, (Reinhard, 1969, Schreier *et al.*, 1979, Postel *et al.*, 1980). It is therefore possible, also through the application of discriminant data analysis, to distinguish between the various typologies of such products for example, wine distillates according to their geographical origin).

As for the Italian pomace distillate, grappa, considerable differences may arise from the varietal origin of the grapemarc, from storage times and methods, and from the distillation technology employed.

A number of quantitative analysis on the volatile compounds Composition of grappa have already been carried out (Usseglio Tomasset, 1970, Migli 1972, Versini et Margheri, 1979, Incitti *et al.*, 1982). In other cases, the behavior during distillation of certain substances or of groups of them was studied with respect to the traditional batch distillation methods used in Trentino (North Italy), i.e. by blowing steam through baskets containing pomace or by heating a mixture of pomace and water in a pot still ("bagnomaria") (Avancini et Versini, 1977, Versini, 1978). In this region, during the last years, marc has been ensiled more and more by using marc acidification techniques with strong acids to lower its original pH value especially when marc is not or only partially fermented. Following this procedure, it is possible both to limit bacterial spoilage and improve the organoleptic quality of the distillate (Versini et Inama, 1981).

In spite of the variability deriving from varietal and technological parameters, a differentiation between the various regional grappas was tried by talking into account dozens of commercial samples and their contents of volatile coumpounds. Such a research can be a first step towards the objective definition of the geographical Appellation in accordance with the recent E.E.C. dispositítions on distilled spirits and, in particular, on grappa (E.E.C., 1989).

MATERIELS AND METHODS

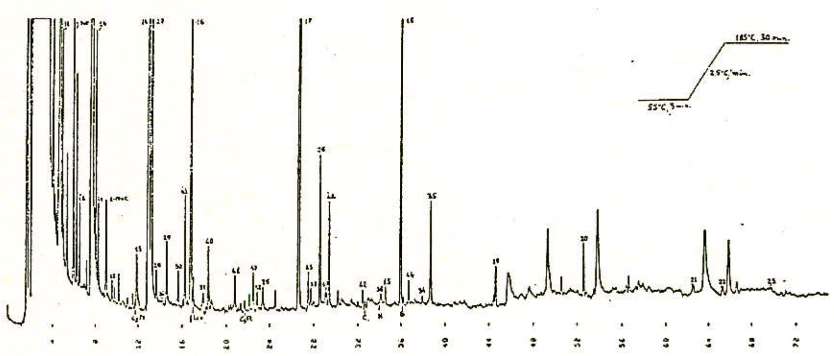
51 commercial samples of grappa were chosen, produced with autochthonous non-aromatic pomace in six Italian regions in 1988 and 1989 and not aged in wooden barrels. These samples underwent a gaschromatographic analysis performed by direct injection of the distillate in :

— a glass column (2m x 2mm i.d.) packed with 0,2% CW 1500 on Carbopack C. 60-80 mesh (Supelco Inc.), which was used above all in the dosage of methanol, acetaldehyde, ethyl acetate, and the individual "fusel" alcohols (Gabri et Salvagiotto, 1980).

— a fused silica capillary column (Supelcowax-30 m x. 0,32 mm x O.,2 um) usel in the quantification of the remaining compounds (Versini *et.al.*, 1979).

Fig. 1 shows a typical example of such chromatogram.

The statistical data analysis was carried out at the Computer Center of our Institute by means of SAS 5.18 and Genstat 5 softwares on a computer DEC VAX 8250 with o.s. VMS 5.



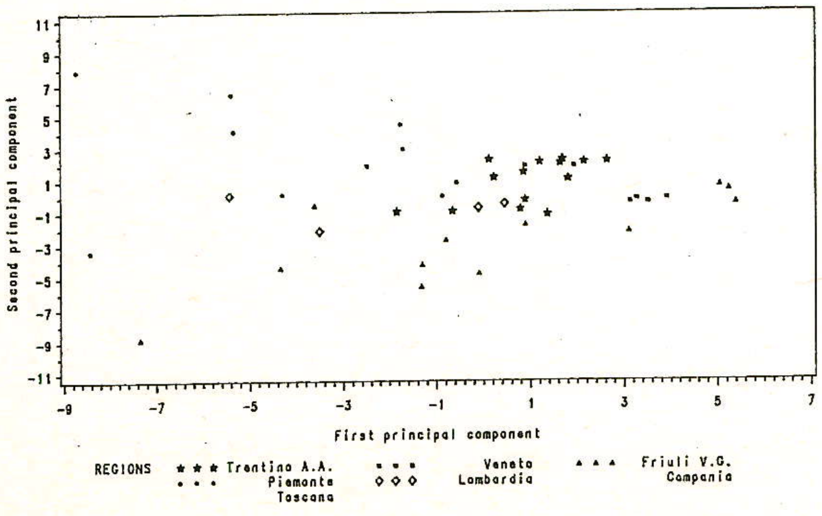


Fig. 1 : Scores of the 51 samples of Grappa on the first and second principal components

RESULTS AND DISCUSSION

The univariate analysis of the data in ***table 1*** underlines interesting linear correlations ***(table 2)*** between certain variables which can be grouped according to their similar phygico-chemical properties, among which specific distillatory behaviors (Barbet, 1895, Versini, 1978), or according to their being potentially influenced by particular microbiological situations of pomace.

Here follows a list of such correlations:

— between 2- and 3-methyl-1-butanol, and between these two compounds and 2-methyl-1-propanol, ethyl and isoamyl octanoate and decanoate. The correlation with ethyl dodecanoate is less relevant than the others. These relations can be explained by analogous distillation properties characteristic of the "hybrid" (sometimes called "heart") impurities;

— between 1-propanol, 2-butanol, isoamyl and hexyl acetate. These compounds distill with intermediate behavior between heads and hybrid products (furthermore, ethyl hexanoate is correlated with isoamyl acetate). The amount of both alcohols can increase by means of bacterial spoilage in the ensiled pomace when pomace pH value is quite high; in this situation the chemical hydrolysis of acetates is reduced (Versini et Inama, 1981);

— between long chain fatty acids ethyl esters (from myristate to linolenate), and between these and proof. Such compounds are not found in trace levels in a few samples only. Due to their poor solubility, their content is in relation to a missing or to a partial refrigeration process after the proof reduction of the raw distillate by dilution with water;

— between all the individual long chain (from C7 to C10) quantified aliphatic alcohols, between l-hexanol and some hexenols, between linalool and nerol, but not with terpineol;

— between aldehydes furfural and benzaldehyde and certain tails compounds such as lactates and diethylsuccinate.

It is worth noticing that benzaldehyde level is low both in some samples such as those from Trentino (from 0.05 to 0.7 mg% ml.a.a.) and in others characterised by smaller methanol and 1-hexanol contents that is, in vinous pomace distillates with likely a lower pH level. A higher content, reaching up to 3.3 mg/100 ml.a.a., was found in samples characterized by a relatively high level of 3-methylbutanal. It is known that benzaldehyde may be formed by enzymatic oxidation of benzyl alcohol (Blaise et Brun, 1986) and that the content of 3-methylbutanal may be improved by malolactic fermentation (Sponholz, 1982), both processes being favored by a high environmental pH level. An interesting amount of benzaldehyde together with traces of unsatured aliphatic aldehydes were also detected in high proof pomace alcohols characterized by rancid off-flavour (Williams et Strauss, 1978).

It is also interesting that there is no correlation between acetaldehyde and ethyl acetate contents, both heads products. Therefore, in most cases, the acetaldehyde level depends more on the glucidic fermentation than on the spoiling oxidation of ethanol to acetic acid (Usseglio Tomasset, 1971).

PRINCIPAL COMPONENT ANALYSIS (PCA)

The main aim of PCA is that of reducing the number of dimensions in a given sample space described by large set of correlated variables. The simplification of the sample space takes place through the identification of new and not correlated variables. These are ordered in such a way as to allow the description of most of the variation found in the initial variables (Jolliffe, 1986). It is thus possible to isolate the relations between groups of variables on one hand, and on the other those between objects (Piggott, 1986).

Considering the intrinsic difference between some variables, and, above all, between variance, PCA was carried out on standardized variables.

Four of the resulting eigenvectors accounted for 65% of the whole variance (see analysis results in ***table 3***).

In examining the single components, the most important variables or groups of them were selected. Such groupings were interpreted from three standpoints, i.e. biochemical, distillatory and other technolgical considerations (see the first four eigenvectors in ***table 4***).

Some variables sharing the same distillatory behavior prevail in the first component: heads substances 1 (such as acetaldehyde and ethyl acetate); tails substances (such as lactates, diethylsuccinate, and 2-phenylethanol); and hybrid substances (such as isoamyl alcohols, medium chain fatty acids ethyl and isoamyl esters, and already cited linear aliphatic primary alcohols). This eigenvector draws a first rough distinction between Trentinian grappas and those from other regions, and between the products of certain distilleries and the remaining majority of products.

In the second component some parameters, affected by microbiological processes typical of the ensilage period such as l-propanol, l-butanol, benzaldehyde, methanol (Postel et Adam, 1980), etc., and depending on the characteristics of the raw material of distillation (again methanol, 1-hexanol, and hexenols), shows a tendency opposite to that of isoamyl alcohols and Medium chain fatty acids ethyl esters.

This eigenvector helps in discriminating the majority of the grappa samples produced in Piemonte from those produced in Friuli (***table 2***).

The third component is characterized by compounds with an intermediate distillatory behavior, between that of heads and hybrid impurities, all in particular:

— some acetates and ethyl hexanoate (with their pleasant apple-banana aroma);

— some shorter chain higher alcohols such as l-propanol, 2-butanol, and 2-methyl-1-propanol. The presence in this component of 2-butanol is emphasized: this bacterial compound is sometimes relevant in grappa.

In the fourth eigenvector, compounds slightly soluble in hydroalcoholic solutions such as ethyl esters from myristate to linolenate prevail. Their content depends on the final proof and on refrigeration and filtration of the raw diluted distillate.

CANONICAL VARIATES ANALYSIS

A canonical discriminant analysis was carried out to determine whether and in what measure samples could be characterized and thus distinguished according to their origin.

The first problem was that of selecting a combination of variables, among the 43 taken into account, which would result in the almost discrimination among groups. Ethanol was not included in the next analyses because its content is fixed during its reduction with water to the normal drinking proof. Since it was difficult to recognize in advance which variables were actually relevant to a characterization of the grappas under consideration, there were certain risks:

— some variables might be completely irrilevant and might disguise the effects of some other ones;

— the sample numeric dimension might be insufficent with respect to the number of variables being considered;

— the large number of parameters under estimation might entangle the situation because of the variability of the sample itself (Krzanowski, 1988). Through a stepwise discriminant analysis it was possible to select the following variables: methanol, 1-propanol, 1-butanol, 2-methyl-1-butanol, ethyl acetate, hexyl acetate, ethyl hexanoate, unidentified compound, diethyl succinate, trans3-hexen-1-ol, 1-eptanol, 1-octanol, 3-ethoxy-1-propanol, benzaldehyde (***table 5***).

On their turn, these variables were used in the canonical variables analysis.

In some respect, the canonical variates analysis is similar to the PCA in that successive axes are derived that are mutually perpendicular (Mac Fie, 1983): Such new axes present a ratio of variation between groups with respect to that within groups which is maximized in all directions (see the analysis results in ***table 6***). In ***table 3*** the group mean values are represented together with their corresponding confidence limits in the space enclosed by the first three canonical variables. These graphics show 92% of the whole variance and point out a good characterization of the various groups.

Similarly, from the analysis of the Mahalanobis' distances (***table 7***), that is the distances between the group mean values in the space enclosed by canonical variables, it is possible to see the degree of characterization of the grappas produced in different regions Powers et Were, 1986).

CONCLUSIONS

This study allowed us to focus some aspects useful in both the characterization of grappa and an objective definition of the Geographic Appellation of this distillates. Taking into account the compounds measurable by direct gaschromatographic injection of the sample, it is difficult to point out specific varietal environmental parameters for the regional characterization of grappa. Marc ensilage, distillatory and proof reduction technology are very important in determining the final analytic characteristics of the distillate under examination. The same considerations apply to the variables selected for discriminatory purposes. Such variables allowed us to group the various sampled grappas with a probability level which is always significant. In spite of these encouraging results, an improvement of our knowledge about the factors influencing the chemical composition of pomace and of the physico-chemical phenomena related to the different distillation processes is necessary.

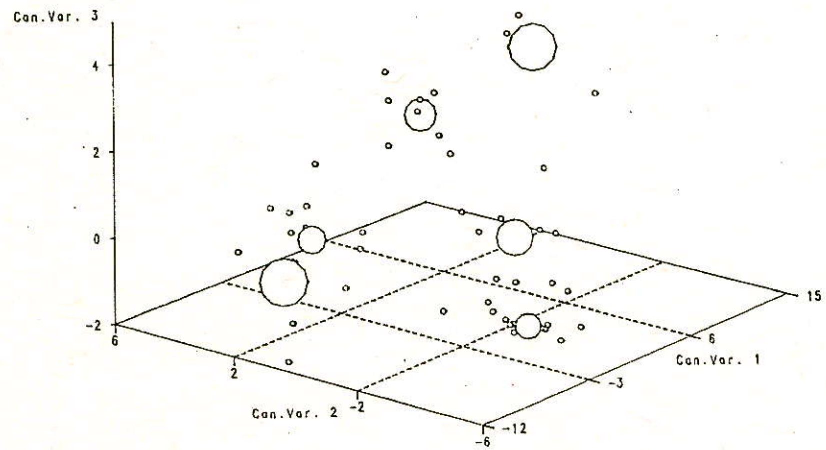
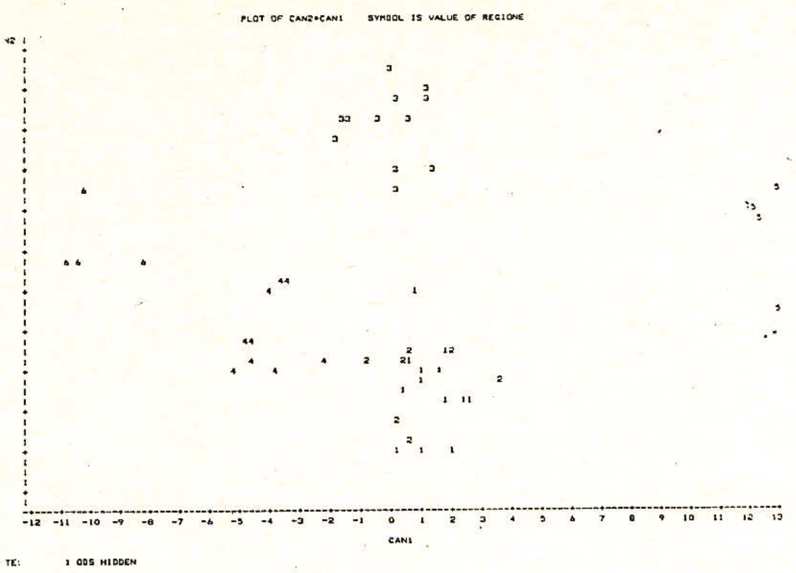


Fig. 3 Geometric representation of the 51 samples and confidence limits (95%) for the 6 regions based on canonical discriminant analysis



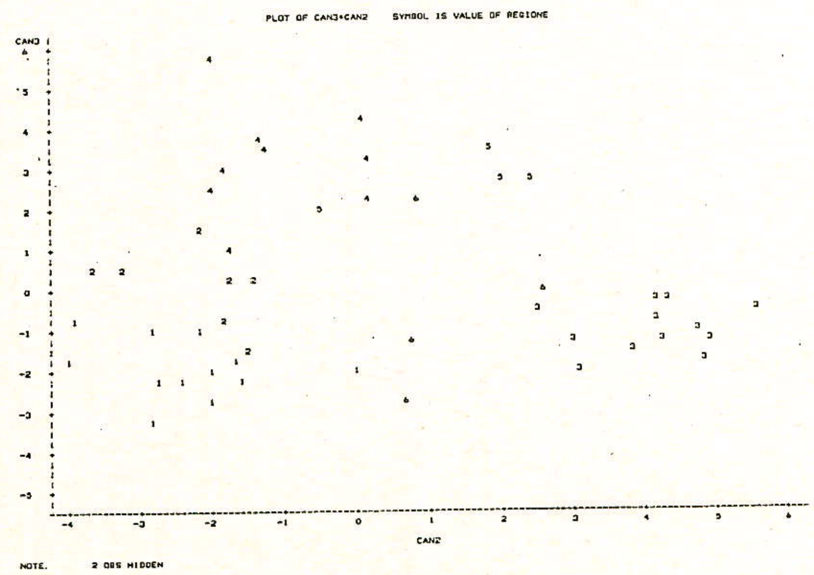


Fig. 2

	Compounds	mean	st.dev.	c.v.	max	min
1	ethanol (*)	45.04	3.6985	8.21	60.00	39.44
2	methanol (**)	0.51	0.2244	43.66	0.92	0.12
3	1-propanol	50.02	22.3040	44.59	117.50	18.50
4	2-butanol	30.22	52.9223	175.13	212.00	1.00
5	2-methyl-1-propanol	69.98	18.6580	26.66	119.00	25.50
6	1-butanol	2.55	1.3002	51.00	7.50	0.90
7	2-methyl-1-butanol	48.04	14.4020	29.98	95.00	19.00
8	3-methyl-1-butanol	181.52	60.0078	33.06	377.00	65.00
9	acetaldehyde	114.91	128.3713	111.71	540.00	2.00
10	ethyl acetate	162.99	133.4181	81.86	529.00	4.50
11	isoamyl acetate	2.54	1.9418	76.34	9.20	0.39
12	hexyl acetate	0.20	0.1693	85.41	0.72	0.01
13	2-phenylethylacetate	0.18	0.1613	90.72	0.69	0.01
14	ethyl hexanoate	1.85	0.9449	50.94	4.14	0.10
15	* unidentified *	0.40	0.2190	54.29	1.07	0.06
16	ethyl octanoate	7.08	4.7826	67.51	23.00	0.86
17	ethyl decanoate	11.97	9.2318	77.12	42.90	1.35
18	ethyl dodecanoate	3.42	3.2513	95.13	15.30	0.09
19	ethyl myristate	0.30	0.4972	168.17	2.40	0.01
20	ethyl palmitate	0.69	1.3010	188.71	7.73	0.01
21	ethyl oleate	0.08	0.2130	264.29	1.33	0.01
22	ethyl linoleate	0.35	0.7130	204.30	3.70	0.01
23	ethyl linolenate	0.08	0.1837	232.53	0.96	0.01
24	ethyl lactate	32.16	7.7991	86.43	98.80	0.01
25	isoamyl lactate	0.30	0.3276	108.16	1.24	0.01
26	diethyl succinate	2.98	2.8238	94.75	11.80	0.01
27	1-hexanol	8.97	3.4959	38.98	17.00	3.69
28	tr.-3-hexen-1-ol	0.18	0.1223	68.62	0.44	0.01
29	cis-3-hexen-1-ol	0.38	0.2325	61.72	1.21	0.06
30	tr.-2-hexen-1-ol	0.19	0.1591	82.03	0.63	0.01
31	1-eptanol	0.14	0.0951	69.16	0.45	0.01
32	1-octanol	0.12	0.0667	55.26	0.25	0.01
33	1-nonanol	0.12	0.0817	68.51	0.37	0.01
34	benzyl alcohol	0.07	0.0789	117.27	0.40	0.01
35	2-phenylethanol	2.30	2.1702	94.20	7.20	0.01
36	3-ethoxy-1-propanol	0.12	0.2111	172.26	0.88	0.01
37	linalool	0.07	0.0847	115.23	0.52	0.01
38	nerol	0.06	0.2082	321.70	1.50	0.01
39	α-terpineol	0.08	0.1586	194.39	0.70	0.01
40	furfural	0.45	0.2944	64.91	1.20	0.01
41	benzaldehyde	0.81	0.8460	104.70	3.28	0.04
42	1-decanol	0.10	0.0586	61.49	0.25	0.01
43	isoamyl octanoate	0.14	0.1872	135.07	1.10	0.01
44	isoamyl decanoate	0.15	0.1629	110.62	0.88	0.01

* % vol.
** ml/100 a.a.

Table 1 : Data of the volatile compounds (mg/100 ml a.a.) in the 51 analysed samples of Grappa.

Correlations:

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 ethanol	1.000														
2 methanol	0.078	1.000													
3 1-propanol	0.019	0.189	1.000												
4 2-butanol	0.073	-0.091	0.691	1.000											
5 2-methyl-1-propanol	0.161	0.174	0.186	0.136	1.000										
6 1-butanol	0.096	-0.060	0.437	0.176	-0.110	1.000									
7 2-methyl-1-butanol	0.058	0.072	-0.237	-0.311	0.711	-0.080	1.000								
8 3-methyl-1-butanol	0.062	-0.069	-0.262	-0.306	0.709	-0.130	0.963	1.000							
9 acetaldehyde	0.135	0.113	-0.307	-0.339	0.409	-0.020	0.690	0.688	1.000						
10 ethyl acetate	0.247	0.631	0.132	-0.142	0.236	0.233	0.288	0.192	0.482	1.000					
11 isoamyl acetate	0.046	-0.019	0.728	0.508	0.233	0.479	0.062	0.024	-0.027	0.213	1.000				
12 hexyl acetate	0.069	0.088	0.821	0.587	0.122	0.386	-0.136	-0.167	-0.126	0.120	0.320	1.000			
13 2-phenylethylacetate	0.285	0.533	0.457	0.165	0.221	0.326	0.193	0.091	0.232	0.791	0.549	0.534	1.000		
14 ethyl hexanoate	0.273	-0.056	0.360	0.353	0.336	0.341	0.301	0.300	0.391	0.172	0.611	0.562	0.337	1.000	
15 * unidentified *	0.202	0.362	-0.077	-0.287	0.034	0.212	0.272	0.206	0.244	0.474	0.044	-0.017	0.552	0.175	1.000
16 ethyl octanoate	0.232	-0.197	-0.385	-0.282	0.500	-0.013	0.745	0.775	0.681	0.068	-0.099	-0.254	-0.028	0.391	0.275
17 ethyl decanoate	0.363	-0.011	-0.346	-0.259	0.381	-0.035	0.652	0.673	0.641	0.193	-0.167	-0.231	0.103	0.389	0.389
18 ethyl dodecanoate	0.522	0.034	-0.320	-0.242	0.287	0.020	0.540	0.576	0.608	0.263	-0.179	-0.212	0.155	0.354	0.394
19 ethyl myristate	0.562	-0.183	-0.242	-0.050	0.227	-0.032	0.294	0.385	0.384	0.067	-0.109	-0.224	-0.075	0.208	0.006
20 ethyl palmitate	0.520	0.257	-0.035	-0.035	0.098	-0.005	0.018	0.015	0.071	0.281	0.029	0.000	0.274	0.000	0.355
21 ethyl oleate	0.631	0.189	0.190	0.159	0.247	0.109	0.061	0.050	0.008	0.336	0.165	0.036	0.370	0.072	0.257
22 ethyl linoleate	0.712	0.212	0.023	0.033	0.250	0.121	0.194	0.185	0.197	0.409	0.112	0.012	0.333	0.190	0.322
23 ethyl linolenate	0.566	0.288	0.076	0.042	0.226	0.074	0.091	0.062	0.091	0.415	0.121	0.090	0.376	0.070	0.325
24 ethyl lactate	0.275	0.568	0.005	-0.186	-0.097	0.133	-0.028	-0.117	-0.040	0.593	-0.143	-0.134	0.503	-0.199	0.499
25 isoamyl lactate	0.236	0.532	0.180	-0.076	0.027	0.225	0.081	-0.009	-0.019	0.639	0.105	0.063	0.670	-0.073	0.577
26 diethyl succinate	0.387	0.372	-0.079	-0.162	0.109	0.164	0.222	0.149	0.145	0.555	-0.102	-0.103	0.487	0.055	0.453
27 1-hexanol	0.107	0.499	0.327	0.031	0.123	0.248	0.164	0.062	0.184	0.391	0.265	0.517	0.514	0.333	0.359
28 tr.-3-hexen-1-ol	-0.106	0.161	0.456	0.236	-0.360	0.432	-0.352	-0.428	-0.218	0.048	0.386	0.512	0.248	0.165	0.136
29 cis-3-hexen-1-ol	0.004	0.243	0.141	-0.025	-0.032	0.263	-0.016	-0.096	-0.092	0.111	-0.112	0.119	0.138	0.096	0.235
30 tr.-2-hexen-1-ol	0.047	0.456	0.339	0.173	0.111	-0.067	-0.045	-0.132	-0.161	0.192	0.193	0.329	0.332	0.140	0.184
31 1-eptanol	0.384	0.093	-0.187	-0.153	0.520	0.102	0.669	0.638	0.770	0.416	0.086	-0.063	0.308	0.484	0.406
32 1-octanol	0.401	0.304	-0.097	-0.180	0.432	0.108	0.536	0.489	0.623	0.528	0.014	-0.010	0.471	0.374	0.571
33 1-nonanol	0.392	-0.050	-0.305	-0.139	0.285	-0.115	0.555	0.567	0.638	0.135	-0.112	-0.127	0.140	0.411	0.358
34 benzyl alcohol	0.321	0.560	-0.081	-0.183	-0.133	-0.016	-0.051	-0.176	0.059	0.467	-0.131	-0.063	0.398	-0.071	0.508
35 2-phenylethanol	0.358	0.081	-0.438	-0.340	0.188	-0.148	0.510	0.512	0.604	0.352	-0.240	-0.309	0.177	0.220	0.442
36 3-ethoxy-1-propanol	0.336	0.346	0.072	-0.069	-0.077	0.194	-0.020	-0.110	0.020	0.495	0.079	0.025	0.486	-0.008	0.544
37 linalool	0.062	0.180	0.066	0.060	0.161	-0.025	0.117	0.067	0.128	0.031	-0.004	0.141	0.118	0.096	0.008
38 nerol	0.129	0.103	-0.077	-0.046	0.024	-0.039	0.019	0.027	0.079	0.037	-0.022	-0.048	0.019	0.075	0.017
39 α-terpineol	0.425	0.307	0.224	0.204	0.214	0.233	0.038	-0.021	0.032	0.433	0.232	0.272	0.441	0.189	0.252
40 furfural	0.243	0.454	0.104	-0.004	0.046	0.139	0.013	-0.099	-0.118	0.334	0.039	0.145	0.403	-0.009	0.424
41 benzaldehyde	0.315	0.502	0.255	0.021	-0.061	0.397	-0.077	-0.188	0.036	0.572	0.236	0.261	0.597	0.275	0.557
42 1-decanol	0.362	0.215	-0.253	-0.249	0.342	0.133	0.490	0.477	0.684	0.378	-0.179	-0.229	0.206	0.258	0.414
43 isoamyl octanoate	0.516	-0.112	-0.320	-0.216	0.245	0.031	0.547	0.602	0.605	0.179	-0.113	-0.193	0.099	0.353	0.267
44 isoamyl decanoate	0.322	-0.193	-0.385	-0.245	0.364	-0.095	0.651	0.717	0.654	0.067	-0.153	-0.233	-0.009	0.351	0.215

	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
16 ethyl octanoate	1.000														
17 ethyl decanoate	0.706	1.000													
18 ethyl dodecanoate	0.779	0.938	1.000												
19 ethyl myristate	0.496	0.510	0.646	1.000											
20 ethyl palmitate	-0.023	0.094	0.266	0.368	1.000										
21 ethyl oleate	0.016	0.079	0.223	0.540	0.678	1.000									
22 ethyl linoleate	0.173	0.281	0.470	0.598	0.860	0.819	1.000								
23 ethyl linolenate	-0.032	0.058	0.234	0.392	0.895	0.783	0.905	1.000							
24 ethyl lactate	-0.102	0.077	0.120	-0.077	0.213	0.301	0.254	0.250	1.000						
25 isoamyl lactate	-0.064	0.092	0.125	-0.122	0.312	0.378	0.330	0.347	0.897	1.000					
26 diethyl succinate	0.193	0.363	0.398	0.100	0.259	0.318	0.363	0.343	0.736	0.666	1.000				
27 1-hexanol	0.016	0.110	0.085	-0.146	0.112	0.022	0.108	0.191	0.225	0.326	0.212	1.000			
28 tr.-3-hexen-1-ol	-0.397	-0.312	-0.266	-0.268	0.031	-0.031	-0.060	0.047	0.020	0.125	-0.097	0.590	1.000		
29 cis-3-hexen-1-ol	0.050	0.176	0.109	-0.179	-0.196	-0.158	-0.168	-0.182	0.283	0.251	0.312	0.628	0.414	1.000	
30 tr.-2-hexen-1-ol	-0.261	-0.160	-0.189	-0.261	0.193	0.094	0.108	0.251	0.224	0.289	0.161	0.650	0.457	0.385	1.000
31 1-eptanol	0.766	0.689	0.634	0.437	0.159	0.257	0.395	0.223	0.131	0.148	0.319	0.154	-0.249	-0.026	-0.184
32 1-octanol	0.613	0.653	0.612	0.311	0.257	0.332	0.432	0.349	0.355	0.396	0.479	0.422	-0.110	0.137	0.138
33 1-nonanol	0.769	0.771	0.727	0.530	0.007	0.093	0.240	0.032	0.006	-0.009	0.205	0.198	-0.170	0.115	-0.092
34 benzyl alcohol	-0.142	0.084	0.166	-0.064	0.524	0.253	0.422	0.540	0.589	0.560	0.447	0.390	0.294	0.166	0.530
35 2-phenylethanol	0.591	0.630	0.718	0.477	0.325	0.190	0.422	0.350	0.289	0.239	0.501	0.058	-0.215	-0.050	0.027
36 3-ethoxy-1-propanol	-0.144	-0.008	0.086	0.039	0.405	0.363	0.431	0.554	0.499	0.523	0.338	0.302	0.259	0.015	0.374
37 linalool	0.171	0.130	0.080	0.074	-0.035	0.001	-0.008	0.059	0.086	-0.010	0.272	0.305	0.099	0.172	0.229
38 nerol	0.138	0.132	0.143	0.186	0.092	0.105	0.122	0.120	0.167	0.009	0.414	-0.025	-0.067	0.007	0.008
39 α-terpineol	-0.068	-0.037	0.080	0.260	0.630	0.639	0.676	0.765	0.294	0.339	0.455	0.375	0.190	0.056	0.319
40 furfural	-0.058	0.129	0.171	-0.179	0.286	0.169	0.259	0.313	0.668	0.657	0.590	0.256	0.154	0.254	0.306
41 benzaldehyde	-0.150	0.072	0.173	-0.161	0.300	0.238	0.340	0.330	0.594	0.630	0.511	0.337	0.281	0.308	0.251
42 1-decanol	0.660	0.700	0.676	0.431	0.228	0.206	0.349	0.270	0.234	0.227	0.417	0.226	-0.082	0.134	-0.029
43 isoamyl octanoate	0.749	0.653	0.928	0.757	0.282	0.245	0.493	0.226	-0.031	0.018	0.276	0.072	-0.218	0.035	-0.198
44 isoamyl decanoate	0.889	0.911	0.863	0.650	0.073	0.060	0.247	0.028	-0.155	-0.102	0.124	0.067	-0.311	0.063	-0.209

	31	32	33	34	35	36	37	38	39	40	41	42	43	44
31 1-eptanol	1.000													
32 1-octanol	0.813	1.000												
33 1-nonanol	0.756	0.671	1.000											
34 benzyl alcohol	0.055	0.324	0.041	1.000										
35 2-phenylethanol	0.559	0.488	0.635	0.431	1.000									
36 3-ethoxy-1-propanol	0.113	0.341	0.053	0.760	0.330	1.000								
37 linalool	0.210	0.226	0.205	0.052	0.180	0.047	1.000							
38 nerol	0.169	0.099	0.122	0.034	0.289	-0.063	0.805	1.000						
39 α-terpineol	0.254	0.303	0.029	0.407	0.261	0.419	0.375	0.394	1.000					
40 furfural	0.071	0.255	-0.086	0.565	0.269	0.362	0.134	0.113	0.307	1.000				
41 benzaldehyde	0.182	0.325	-0.058	0.567	0.157	0.477	-0.126	-0.047	0.272	0.632	1.000			
42 1-decanol	0.704	0.776	0.652	0.300	0.639	0.233	0.264	0.266	0.192	0.181	0.147	1.000		
43 isoamyl octanoate	0.582	0.518	0.725	0.059	0.642	0.044	0.041	0.089	0.070	-0.043	0.030	0.587	1.000	
44 isoamyl decanoate	0.608	0.538	0.774	-0.075	0.617	-0.064	0.087	0.048	-0.092	-0.157	-0.185	0.613	0.908	1.000

Table 2 : Coefficient of correlations between Grappa variables

Latent root	% var.	cum. %	
12.180	27.68	27.68	***)
8.394	19.08	46.76	**********************************
4.343	9.87	56.63	*****************
3.678	8.36	64.99	***************
2.230	5.07	70.06	*********
2.072	4.71	74.77	*******
1.762	4.00	78.77	*******
1.299	2.95	81.72	*****
1.029	2.34	84.06	****
0.916	2.08	86.14	****
0.773	1.76	87.90	***
0.737	1.68	89.58	***
0.591	1.34	90.92	**
0.535	1.22	92.14	**
0.446	1.01	93.15	**
0.431	0.98	94.13	**
0.359	0.82	94.95	*
0.334	0.76	95.71	*
0.231	0.53	96.23	*
0.207	0.47	96.70	*
0.201	0.46	97.16	*
0.182	0.41	97.57	*
0.158	0.36	97.93	*
0.147	0.33	98.26	*
0.127	0.29	98.55	
0.112	0.25	98.80	
0.092	0.21	99.01	
0.076	0.17	99.18	
0.069	0.16	99.34	
0.059	0.13	99.47	
0.050	0.11	99.58	
0.041	0.09	99.67	
0.038	0.09	99.76	
0.027	0.06	99.82	
0.020	0.05	99.87	
0.015	0.03	99.90	
0.013	0.03	99.93	
0.010	0.02	99.95	
0.006	0.01	99.96	
0.004	0.01	99.97	
0.003	0.01	99.98	
0.001	0.00	99.99	
0.001	0.00	99.99	
0.000	0.00	100.00	

Table 3 : Scree diagram of principal components analysis

Eigenvectors:	1	2	3	4
Variables:				
ethanol	-0.16706	-0.05966	0.01911	0.24205
methanol	-0.08613	-0.19922	0.07427	-0.16187
1-propanol	0.05651	-0.19671	-0.32113	0.05522
2-butanol	0.06895	-0.09882	-0.27050	0.17213
2-methyl-1-propanol	-0.13094	0.05786	0.19232	0.03854
1-butanol	-0.02624	-0.12226	-0.18901	-0.02084
2-methyl-1-butanol	-0.18624	0.13644	-0.10218	-0.10089
3-methyl-1-butanol	-0.17630	0.17867	-0.10462	-0.05487
acetaldehyde	-0.19620	0.13079	-0.08153	-0.09359
ethyl acetate	-0.16892	-0.16402	0.00601	-0.08312
isoamyl acetate	0.00204	-0.13121	-0.37652	0.08453
hexyl acetate	0.02737	-0.16953	-0.37704	0.02637
2-phenylethylacetate	-0.13758	-0.21956	-0.14056	-0.06802
ethyl hexanoate	-0.11285	-0.00377	-0.35735	0.01108
* unidentified *	-0.17246	-0.11519	0.06459	-0.14475
ethyl octanoate	-0.19952	0.21097	-0.08222	-0.07360
ethyl decanoate	-0.22786	0.15301	-0.02979	-0.09377
ethyl dodecanoate	-0.23793	0.11651	0.00776	0.00179
ethyl myristate	-0.15994	0.12400	0.00623	0.28449
ethyl palmitate	-0.13184	-0.12813	0.12120	0.30858
ethyl oleate	-0.13296	-0.12321	0.03420	0.34177
ethyl linoleate	-0.18711	-0.09875	0.05084	0.33273
ethyl linolenate	-0.14910	-0.15784	0.07538	0.31702
ethyl lactate	-0.11050	-0.19879	0.21689	-0.14969
isoamyl lactate	-0.12273	-0.22269	0.11613	-0.12213
diethyl succinate	-0.17185	-0.12408	0.13266	-0.09880
1-hexanol	-0.09220	-0.16817	-0.17684	-0.20432
tr.-3-hexen-1-ol	0.04829	-0.19318	-0.14977	-0.08869
cis-3-hexen-1-ol	-0.03356	-0.09114	-0.05100	-0.30056
tr.-2-hexen-1-ol	-0.02151	-0.19901	-0.05869	-0.09789
1-eptanol	-0.23016	0.08359	-0.10481	-0.02591
1-octanol	-0.24121	-0.01306	-0.05028	-0.09518
1-nonanol	-0.20326	0.14334	-0.07652	-0.06463
benzyl alcohol	-0.11898	-0.20650	0.20180	-0.05148
2-phenylethanol	-0.22255	0.06045	0.12159	-0.01781
3-ethoxy-1-propanol	-0.11020	-0.19830	0.11565	0.02393
linalool	-0.06219	-0.02207	-0.06269	-0.06582
nerol	-0.06319	-0.00359	0.04044	0.02639
α-terpineol	-0.12295	-0.18681	-0.02533	0.21658
furfural	-0.09318	-0.19550	0.10823	-0.11340
benzaldehyde	-0.10182	-0.23122	0.01795	-0.09819
1-decanol	-0.22698	0.05426	0.01482	-0.07781
isoamyl octanoate	-0.21792	0.14300	-0.02866	0.07069
isoamyl decanoate	-0.19787	0.20751	-0.06485	-0.01675

Table 4 : Principal components coefficients

Variables:	Partial R square	F	Prob. F
methanol	0.5802	8.570	0.0001
1-propanol	0.5264	6.891	0.0002
1-butanol	0.7042	14.758	0.0001
2-methyl-1-butanol	0.3857	3.893	0.0075
ethyl acetate	0.7017	14.583	0.0001
hexyl acetate	0.5262	6.884	0.0002
ethyl hexanoate	0.3086	2.767	0.0352
* unidentified *	0.4768	5.650	0.0008
diethyl succinate	0.4413	4.897	0.0020
tr.-3-hexen-1-ol	0.7135	15.440	0.0001
1-eptanol	0.7412	17.761	0.0001
1-octanol	0.5486	7.536	0.0001
3-ethoxy-1-propanol	0.7011	14.543	0.0001
benzaldehyde	0.5347	7.126	0.0002

Wilks' = 0.00013904
F(70,152) = 11.827 Prob. > F = 0.0001

Average squared canonical correlation = 0.7284

Table 5 : Selected variables from stepwise discriminant analysis

	1	2	3	4	5
Latent roots	27.4534	7.9618	4.2968	3.1661	0.2782
Proportion var.	0.6361	0.1845	0.0996	0.0734	0.0064
Cumulative var.	0.6361	0.8206	0.9202	0.9936	1.0000
Variables	**Standardised canonical coefficients of canonical variates**				
methanol	-0.8495	-1.5049	-0.7043	-0.5004	-0.3648
1-propanol	1.9728	0.5507	0.1969	0.3703	0.7042
1-butanol	-2.1769	0.0077	-0.0839	0.2054	-0.3186
2-methyl-1-butanol	0.5701	-0.0405	-0.2314	1.0100	1.1560
ethyl acetate	-2.0261	1.5578	-0.5096	-0.6232	0.2126
hexyl acetate	1.3781	-0.6193	1.4502	-1.1978	-0.3293
ethyl hexanoate	0.9789	0.1425	-0.4348	0.2286	0.1954
* unidentified *	-1.2664	0.6384	-0.0062	0.3842	0.5339
diethyl succinate	0.3454	0.1874	0.8091	0.9637	-0.0351
tr.-3-hexen-1-ol	1.0918	1.7741	-0.1805	1.0286	-0.1839
1-eptanol	-2.5379	-0.0255	3.0447	-0.2486	-1.0310
1-octanol	1.4798	-0.9406	-1.4571	-0.3598	0.0575
3-ethoxy-1-propanol	1.7912	-0.4053	0.1725	1.0268	-0.4437
benzaldehyde	-0.6531	1.3688	-0.3224	-1.1184	0.4321

Regions	Class means on canonical variables 1	2	3	4	5
Trentino A.Adige	1.3649	-2.4899	-1.9443	0.8018	0.3046
Veneto	0.9589	-2.2288	0.0966	-1.9464	-0.9937
Friuli V.Giulia	-0.0330	4.1289	-0.9940	0.8463	-0.2295
Piemonte	-4.0490	-1.0668	3.2236	1.6379	0.0288
Campania	12.6282	1.4345	2.7439	-1.8263	0.5890
Lombardia	-9.8741	1.1942	-0.3792	-3.7982	0.7075

Table 6 : Results from canonical variate analysis : canonical cœfficients and group means

Mahalanobis distances (upper triangle) and relative probabilities (lower triangle) between regions

Regions	Trentino	Veneto	Friuli	Piemonte	Campania	Lombardia
Trentino A.Adige	.	3.6928	6.8522	7.6692	13.0855	12.7929
Veneto	0.0034	.	7.1398	7.0781	12.6142	11.6456
Friuli V.Giulia	0.0001	0.0001	.	7.8489	13.7604	11.3264
Piemonte	0.0001	0.0001	0.0001	.	17.2316	9.0574
Campania	0.0001	0.0001	0.0001	0.0001	.	22.8050
Lombardia	0.0001	0.0001	0.0001	0.0001	0.0001	.

Table 7 : Mahalanobis distances between regions

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ETUDE D'UNE METHODE POUR LA CARACTERISATION DE LA GRAPPA

SENSIDONI A., BORTOLOMEAZZI R., DA PORTO C.
DOMENIS C., AMATI A.

Universita' Degli Studi di Udine, Istituto di Tecnologie Alimentari
Via Marangoni 97, 33100 Udine, Italie

RESUME

La Grappa est un produit typiquement italien, obtenu par distillation directe du marc avec une installation continue ou discontinue (1-12).

Il est permis d'ajouter une certaine quantité de lie de vin entre les limites consenties par la loi italienne (13). Dans une distillerie traditionnelle équipée d'une installation discontinue, des échantillons ont été distillés dans des conditions bien définies et contrôlées, soit pour ce qui concerne les matières premières utilisées soit pour les différentes phases technologiques.

Certaines substances ont été choisies (14) car elles sont les plus caractéristiques sur la base des expériences précédentes.

Sur certains échantillons et sur une série de grappa commercialisées, provenant de régions typiques de l'Italie du Nord, des analyses chromatographiques ont été effectuées avec une colonne capillaire (HRGC) pour quantifier les composants suivants: acétaldéhyde, acétate d'éthyle, méthanol, butanol-2, alcools amyliques, caproate d'éthyle, lactate d'éthyle, caprylate d'éthyle, caprate d'éthyle, myristate d'éthyle. Les résultats obtenus ont été soumis à une analyse statistique en utilisant le procédé Cluster et Factor du SPSSX VS 3.1 (1989)[120].

L'analyse statistique a mis en évidence une possible corrélation des données analytiques soit avec certaines phases technologiques (déméthanolisation, distillation avec ou sans recyclage des têtes ou des queues), soit avec les matières utilisées (seulement marc ou marc avec lie).

INTRODUCTION

Depuis quelques années déjà, la consommation des spiritueux a subi une sensible diminution en Italie ainsi que dans les principaux pays occidentaux évolués.

La grappa, eau-de-vie typiquement italienne, récemment reconnue par la CEE, présente également les problèmes du secteur, auxquels viennent s'en ajouter d'autres liés à ses caractéristiques.