

DETERMINING THE CONCENTRATION OF METHANOL FROM NATURAL DISTILLATE

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INTRODUCTION

Methanol **CH₃ – OH** is an aliphatic monohydric alcohol, with a molecular mass of 32.6, 0.79 density, it binds at - 97 C and it boils at 64,7 C.

It is mixable with water in any proportion, and also with ethanol, ether, chloroform and most of the organic solvents, it itself being a good solvent.

It appears as a fluid, colourless, transparent product with an intensely smell and taste similar to those of ethanol [1], [2].

Methanol is frequently found in alcoholic drinks with different concentrations, thus beer can contain between 6-27 mg/L methanol, wine between 96-321 mg/L, and ardent spirits between 10-220 mg/L [3].

The presence of methanol in natural distillates is directly proportional with the quantity of pectin that is found in the distillate material. The pectin substances that are found in the fruits' peel, in their seeds and also in grape clusters suffer a process of degradation because of the pectin methylation, resulting thus an important quantity of methanol.

The distillates that are obtained from fermented fruits have a higher concentration of methanol, in comparison with the distillates that are obtained by other techniques.

The quantity of methanol is also influenced by the age or the degradation degree of the distillate's maceration extract, the elder it is the larger is the quantity of degraded pectin and implicitly the concentration of methanol. Also, the distillates that are obtained from the black grapes marc have a larger quantity of methanol compared with the white grapes marc.

The degree of ripening of the grapes influences the concentration of methanol in the distillates, thus, ripped grapes have a lower concentration of pectin substances than the ones which are not completely ripped and implicitly more methanol [4], [5], [6].

MATERIAL AND METHODS

The determination of the methanol concentration was made using a gas-chromatographic method together with mass spectrometry.

A number of 98 samples of distillates were analyzed, respectively hand-made fruit brandy.

The samples were collected from the area of Moldavia between 2007 and 2009. The analyses were made on an Agilent Technologies 7890 A gas chromatograph fitted with an automatic Agilent Technologies 7683 B Series, injector connected with a mass spectrometer Agilent Technologies 5975C MSD inert as a system of detection. The mobile phase is represented by helium with a gas yield of 1 mL/min. For the stationary phase, a Zebron – Phenomenex, ZB-WAX plus chromatography column was used having the following parameters: 60 m long x 0.25 mm internal width and 0.25 μm thickness of the film which deposited on the internal walls of the column.

The injection volume was of 0.1 μl with a splitting proportion of 1/50, the temperature of the injector: 250°C, the temperature gradient in the column division: 50°C for 20 minutes, then the temperature rises with 10°C/min up to 250°C where is constantly maintained for 5 more minutes.

The source temperature MSD: 230°C, the quadrupole's temperature MSD: 150°C, the type of spectrum acquisition: SCAN (Checking all the lines in the mass spectrum), the mass domain: 15 – 500 atomic units of mass, approaching the results: Agilent Technologies ChemStation software.

After achieving the chromatography - gas determinations and integrating the obtained chromatograms, methanol was identified by comparing the retention times of the corresponding drops from the chromatographs

of the distillates with the chromatogram of an ethanol sample that contains methanol but also by spectral comparison.

Using the areas of the drops that corresponded to methanol, the concentration of methanol was calculated with the help of the calibration line equation obtained when studying the linearity method.

There fore, for the chromatographs in which the area of the drop is larger than 18357080 the calculated equation for the interval 2768,5 – 19775 µg/mL (Drop area = 4685,8 x Concentration + 3601973,7) was used and for smaller values of the area the calculated equation for the interval 4,9 – 2768,5 µg/mL (Drop area = 6500,4 x Concentration – 11679,5) was used [7], [8], [10], [11].

RESULTS AND DISCUSSIONS

In table 1 the obtained experimental data regarding the drop area of methanol and the calculated methanol concentration, in terms of µg/mL distillate are presented.

In table 1 data concerning methanol concentration in micrograms to mL alcoholic distillate were presented.

According to CEE Regulation Nr. 1014/90, and to Professional Standard 50-90/92, the concentration of the volatile cognates that are found in the alcoholic distillates, including methanol concentration is expressed in milligrams at 100 mL ethylic anhydrous alcohol.

The ethanol concentration of the distillates was determined by the pycnometer method, a preferred and authorized method by laws in force.

As a result, according to the volume concentration of ethanol in the alcohol distillates and to the quantity of methanol per millilitre of distillate, was obtained the concentration of methanol at 100 mL ethanol anhydrous (table 2).

The maximum rated value at 100 mL ethanol anhydrous is of 1.10 % [13], [14].

Table 1. Determining methanol in natural distillates by gas chromatography coupled with mass spectrometry

No	The source of the sample	Characteristics	Methanol area	µg methanol / mL distillate
1	Mărgineni BC	Marc	11722365	1805,1
2	Mărgineni BC	Marc	26904721	4973,1
3	Mărgineni BC	Marc	3385459	522,6
4	Lipova BC	Marc	3254145	502,4
5	Racova BC	Marc	617505	< LD
6	Racova BC	Marc	3764349	580,9
7	Blăgești BC	Fruit mixture	12334123	1899,2
8	Blăgești BC	Marc	26944448	4981,5
9	Blăgești BC	Marc	31129926	5874,8
10	Blăgești BC	Marc	4336075	668,8
11	Buhuși BC	Fruit mixture	3675877	567,3
12	Filipești BC	Plum	42569142	8316,0
13	Racova BC	Fruit mixture	24486970	4457,1
14	Racova BC	Marc	5982738	922,2
15	Palanca BC	Fruit mixture	4914880	757,9
16	Ghimeș BC	Fruit mixture	7776283	1198,1
17	Ghimeș BC	Fruit mixture	4900717	755,7
18	Palanca BC	Plum	7223734	1113,1
19	N. Bălcescu BC	Marc	8624566	1328,6
20	N. Bălcescu BC	Marc	6745964	1039,6
21	Fărăoani BC	Marc	15875530	2444,0
22	Valea Mică BC	Fruit mixture	7062406	1088,3
23	Ghe Doja BC	Marc	6859969	1057,1
24	Oituz BC	Marc and apple 2007	13552167	2086,6
25	Soncut BC	Marc 2008	3861291	595,8
26	Pâncești BC	Apricot 2008	4225352	651,8
27	Soncut BC	Marc 2004	3928991	606,2
28	Mărgineni BC	Fruit mixture 2008	16097815	2478,2
29	Ghimeș BC	Plum	13224159	2036,2
30	Marasesti VN	Marc 2008	6255040	964,1

No	The source of the sample	Characteristics	Methanol area	µg methanol / mL distillate
31	Corbasca BC	Marc 2008	8007283	1233,6
32	L. Veche BC	Fruit mixture 2008	5660891	872,6
33	Lipova BC	Marc 2008	18132119	2791,2
34	Lipova BC	Marc 2007	463173	< LD
35	Petreşti BC	Plum 2007	24380109	4434,3
36	Petreşti BC	Fruit mixture 2008	23624481	4273,0
37	Petreşti BC	Marc 2007	17491317	2692,6
38	Petreşti BC	Marc 2007	17239227	2653,8
39	Pârjol BC	Marc 2007	6757505	1041,3
40	Pârjol BC	Marc 2007	8484056	1307,0
41	Bogdana BC	Plum 2007	13500782	2078,7
42	Șt. Cel Mare BC	Apple brandy 2008	23110377	4163,3
43	Șt. Cel Mare BC	Fruit mixture 2008	4182250	645,2
44	Șt. Cel Mare BC	Marc 2007	11451620	1763,5
45	Bogdana BC	Mere 2008	10776300	1659,6
46	Oituz BC	Plum 2008	11852512	1825,1
47	Oituz BC	Marc 2008	9637819	1484,4
48	M. Casin BC	Fruit mixture 2007	13269905	2043,2
49	M. Casin BC	Plum	23036979	4147,6
50	Cireșești BC	Plum	14373939	2213,0
51	Urechești BC	Fruit mixture 2007	8045772	1239,5
52	Câmpina BV	Plum 2007	15021533	2312,7
53	Sascut BC	Marc 2007	9522604	1466,7
54	Bihor	Plum brandy	39440517	7648,3
55	Panciu VN	Marc 2008	38520976	7452,1
56	Panciu VN	Fruit mixture 2007	20964284	3705,3
57	Straoani BC	Fruit mixture 2007	37707545	7278,5
58	Straoani BC	Fruit mixture 2007	37501876	7234,6
59	Straoani BC	Marc 2008	4571003	705,0
60	Movilita GL	Plant Decoction 2007	2650913	< LQ
61	Bacau	Marc 2008	32160824	6094,8
62	Bacau	Marc 2008	16979274	2613,8

63	Tamasi BC	Marc 2008	18867353	3257,8
64	Petresti BC	Marc 2007	15679875	2413,9
65	Petresti BC	Marc 2007	18628216	3206,8
66	Hateg SV	Plum 2008	14700361	2263,3
67	Buciumeni, GL	Marc 2008	4280449	660,3
68	Hateg SV	Fruit mixture 2007	15687202	2415,1
69	Ramnicul Sarat BZ	Marc 2002	5319095	820,1
70	Râmnicu Sarat BZ	Marc 2003	4951766	763,6
71	Râmnicu Sarat BZ	Marc 2000	6638319	1023,0
72	Râmnicu Sarat BZ	Plum 2005	16424114	2528,4
73	Râmnicu Sarat BZ	Marc 2008	5278223	813,8
74	Comanesti BC	Plum 2008	25577484	4689,8
75	Comanesti BC	Plum 2008	27041216	5002,2
76	Comanesti BC	Marc 2008	8619261	1327,8
77	Comanesti BC	Marc 2008	23487930	4243,9
78	Comanesti BC	Plum 2008	20523116	3611,2
79	Comanesti BC	Fruit mixture 2007	14624263	2251,5
80	Comanesti BC	Marc 2007	8699717	1340,1
81	Comanesti BC	Marc 2007	4367547	673,7
82	Comanesti BC	Marc 2007	3234992	499,5
83	Comanesti BC	Fruit mixture 2008	27646073	5131,3
84	Comanesti BC	Fruit mixture 2008	33279508	6333,5
85	Comanesti BC	Fruit mixture 2007	24301388	4417,5
86	Comanesti BC	Fruit mixture 2008	32456402	6157,8
87	Comanesti BC	Marc 2007	4896040	755,0
88	Bacau	Marc 2007	13842927	2131,3
89	Comanesti BC	Fruit mixture 2007	12963785	1996,1
90	Hemeiusi BC	Marc 2008	15829929	2437,0
91	Câmpina BV	Plum 2007	18307491	2818,2
92	Bacau	Apricot 2007	5795628	893,4
93	Tarcau NT	Plum 2007	21114970	3737,5
94	Asau BC	Marc 2007	6894195	1062,4
95	V. Muntelui	Fruit mixture 2008	12646936	1947,4
96	Bacau	Balm and mint mixture 2007	17157405	2641,2
97	Bacau	Schintel mixture 2007	15034375	2314,6
98	Bistrita N.	Fruit brandy 2007	12404551	1910,1

Table 2. Methanol concentration at 100 mL ethanol anhydrous

No	The source of the sample	Characteristics	µg methanol / mL distillate	Percentage concentration of ethanol volume	Methanol concentration lat 100 mL ethanol anhydrous
1	Mărgineni BC	Marc	1805,1	54,6	0,33
2	Mărgineni BC	Marc	4973,1	38,6	1,28
3	Mărgineni BC	Marc	522,6	36,5	0,14
4	Lipova BC	Marc	502,4	37,4	0,13
5	Racova BC	Marc	< LD	46,8	-
6	Racova BC	Marc	580,9	24,6	0,23
7	Blăgești BC	Fruit mixture	1899,2	41,5	0,45
8	Blăgești BC	Marc	4981,5	33,02	1,5
9	Blăgești BC	Marc	5874,8	26,6	2,20
10	Blăgești BC	Marc	668,8	51,0	0,13
11	Buhuși BC	Fruit mixture	567,3	32,9	0,17
12	Filipești BC	Plum	8316,0	36,1	2,30
13	Racova BC	Fruit mixture	4457,1	32,4	1,37
14	Racova BC	Marc	922,2	26,0	0,35
15	Palanca BC	Fruit mixture	757,9	59,1	0,12
16	Ghimeș BC	Fruit mixture	1198,1	48,8	0,24
17	Ghimeș BC	Fruit mixture	755,7	38,7	0,19
18	Palanca BC	Plum	1113,1	36,4	0,30
19	N. Bălcescu BC	Marc	1328,6	53,3	0,24
20	N. Bălcescu BC	Marc	1039,6	49,5	0,21
21	Fărăoani BC	Marc	2444,0	55,3	0,44
22	Valea Mică BC	Fruit mixture	1088,3	69,8	0,15
23	Ghe Doja BC	Marc	1057,1	56,5	0,18
24	Oituz BC	Marc and apple 2007	2086,6	60,7	0,34
25	Soncut BC	Marc 2008	595,8	39,7	0,15
26	Pâncești BC	Apricot 2008	651,8	44,1	0,14
27	Soncut BC	Marc 2004	606,2	41,3	0,14
28	Mărgineni BC	Fruit mixture 2008	2478,2	42,8	0,57
29	Ghimeș BC	Plum	2036,2	39,3	0,51
30	Marasesti VN	Marc 2008	964,1	42,5	0,22
31	Corbasca BC	Marc 2008	1233,6	30,6	0,40
32	L. Veche BC	Fruit mixture 2008	872,6	34,0	0,25
33	Lipova BC	Marc 2008	2791,2	38,4	0,72
34	Lipova BC	Marc 2007	< LD	38,4	-
35	Petrești BC	Plum 2007	4434,3	50,2	0,88
36	Petrești BC	Fruit mixture 2008	4273,0	47,6	0,89
37	Petrești BC	Marc 2007	2692,6	58,6	0,45
38	Petrești BC	Marc 2007	2653,8	55,5	0,47
39	Pârjol BC	Marc 2007	1041,3	37,1	0,28
40	Pârjol BC	Marc 2007	1307,0	37,9	0,34
41	Bogdana BC	Plum 2007	2078,7	32,8	0,63
42	Șt. Cel Mare BC	Apple brandy 2008	4163,3	53,9	0,77
43	Șt. Cel Mare BC	Fruit mixture 2008	645,2	43,6	0,14
44	Șt. Cel Mare BC	Marc 2007	1763,5	36	0,48
45	Bogdana BC	Apple 2008	1659,6	28,6	0,58
46	Oituz BC	Plum 2008	1825,1	29,0	0,62
47	Oituz BC	Marc 2008	1484,4	41,2	0,36
48	M. Casin BC	Fruit mixture 2007	2043,2	25,0	0,81
49	M. Casin BC	Plum	4147,6	35,4	1,17
50	Cireșești BC	Plum	2213,0	32,9	0,67
51	Urechești BC	Fruit mixture 2007	1239,5	42,8	0,28
52	Câmpina BV	Plum 2007	2312,7	37,1	0,62
53	Sascut BC	Marc 2007	1466,7	48,9	0,29
54	Bihor	Plum brandy	7648,3	47,9	1,59
55	Panciu VN	Marc 2008	7452,1	40,7	1,83
56	Panciu VN	Fruit mixture 2007	3705,3	35,2	1,05
57	Straoani BC	Fruit mixture 2007	7278,5	37,3	1,95
58	Straoani BC	Fruit mixture 2007	7234,6	38,3	1,88
59	Straoani BC	Marc 2008	705,0	37,3	0,18
60	Movilita GL	Plant decoction 2007	< LQ	29,4	-

No	The source of the sample	Characteristics	μg methanol / mL distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
61	Bacau	Marc 2008	6094,8	50,9	1,19
62	Bacau	Marc 2008	2613,8	45,3	0,57
63	Tamasi BC	Marc 2008	3257,8	48,3	0,67
64	Petresti BC	Marc 2007	2413,9	49,4	0,48
65	Petresti BC	Marc 2007	3206,8	58,7	0,54
66	Hateg SV	Plum 2008	2263,3	42,0	0,53
67	Buciumeni, GL	Marc 2008	660,3	47,9	0,13
68	Hateg SV	Fruit mixture 2007	2415,1	30,6	0,78
69	Râmnicu Sarat BZ	Marc 2002	820,1	43,6	0,18
70	Râmnicu Sarat BZ	Marc 2003	763,6	37,9	0,20
71	Râmnicu Sarat BZ	Marc 2000	1023,0	46,9	0,21
72	Râmnicu Sarat BZ	Plum 2005	2528,4	53,9	0,46
73	Râmnicu Sarat BZ	Marc 2008	813,8	37,9	0,21
74	Comanesti BC	Plum 2008	4689,8	28,9	1,62
75	Comanesti BC	Plum 2008	5002,2	30,2	1,65
76	Comanesti BC	Marc 2008	1327,8	30,2	0,43
77	Comanesti BC	Marc 2008	4243,9	29,4	1,44
78	Comanesti BC	Plum 2008	3611,2	29,3	1,23
79	Comanesti BC	Fruit mixture 2007	2251,5	28,8	0,78
80	Comanesti BC	Marc 2007	1340,1	58,1	0,23
81	Comanesti BC	Marc 2007	673,7	36,4	0,18
82	Comanesti BC	Marc 2007	499,5	38,1	0,13
83	Comanesti BC	Fruit mixture 2008	5131,3	49,2	1,04
84	Comanesti BC	Fruit mixture 2008	6333,5	46,3	1,36
85	Comanesti BC	Fruit mixture 2007	4417,5	38,4	1,15
86	Comanesti BC	Fruit mixture 2008	6157,8	50,3	1,22
87	Comanesti BC	Marc 2007	755,0	10,9	0,69
88	Bacau	Marc 2007	2131,3	43,2	0,37
89	Comanesti BC	Fruit mixture 2007	1996,1	56,9	0,46
90	Hemeiusi BC	Marc 2008	2437,0	46,8	0,52
91	Câmpina BV	Plum 2007	2818,2	42,9	0,65
92	Bacau	Apricot 2007	893,4	41,4	0,21
93	Tarcau NT	Plum 2007	3737,5	40,0	0,93
94	Asau BC	Marc 2007	1062,4	45,7	0,23
95	V. Muntelui	Fruit mixture 2008	1947,4	54,0	0,36
96	Bacau	Balm and mint mixture 2007	2641,2	39,3	0,67
97	Bacau	Schintel mixture 2007	2314,6	46,2	0,50
98	Bistrita N.	Fruit brandy 2007	1910,1	46,4	0,41

From the resulting data we observe that out of the 98 samples of natural alcoholic distillates, 19 samples have an overrunning concentration of methanol

Table 3. Methanol concentration (at 100 mL ethanol anhydrous) in samples of natural distillates of fruit mixture

No	The source of natural distillates	Analysed natural distillates	Methanol concentration μg / mL distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
1.	Blăgești (BC)	Fruit mixture	1899,2	41,5	0,45
2.	Buhuși (BC)	Fruit mixture	567,3	32,9	0,17
3.	Racova (BC)	Fruit mixture	4457,1	32,4	1,37
4.	Palanca (BC)	Fruit mixture	757,9	59,1	0,12
5.	Ghimeș (BC)	Fruit mixture	1198,1	48,8	0,24
6.	Ghimeș (BC)	Fruit mixture	755,7	38,7	0,19
7.	Valea Mică (BC)	Fruit mixture	1088,3	69,8	0,15
8.	M. Casin (BC)	Fruit mixture	2043,2	25,0	0,81
9.	Urechești (BC)	Fruit mixture	1239,5	42,8	0,28
10.	Panciu (VN)	Fruit mixture	3705,3	35,2	1,05
11.	Straoani (BC)	Fruit mixture	7278,5	37,3	1,95
12.	Straoani (BC)	Fruit mixture	7234,6	38,3	1,88

No	The source of natural distillates	Analysed natural distillates	Methanol concentration $\mu\text{g/mL}$ distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
13.	Hateg (SV)	Fruit mixture	2415,1	30,6	0,78
14.	Comanesti (BC)	Fruit mixture	2251,5	28,8	0,78
15.	Comanesti (BC)	Fruit mixture	4417,5	38,4	1,15
16.	Comanesti (BC)	Fruit mixture	1996,1	56,9	0,46
17.	Mărgineni (BC)	Fruit mixture	2478,2	42,8	0,57
18.	L. Veche (BC)	Fruit mixture	872,6	34,0	0,25
19.	Petrești (BC)	Fruit mixture	4273,0	47,6	0,89
20.	Șt. Cel Mare (BC)	Fruit mixture	645,2	43,6	0,14
21.	Comanesti (BC)	Fruit mixture	5131,3	49,2	1,04
22.	Comanesti (BC)	Fruit mixture	6333,5	46,3	1,36
23.	Comanesti (BC)	Fruit mixture	6157,8	50,3	1,22
24.	V. Muntelui	Fruit mixture	1947,4	54,0	0,36

In the 24 samples of fruit mixture distillate, 8 samples of brandy with a methanol concentration in the limits or beyond the limit accepted by the laws in force were determined (table 3).

Table 4. Methanol concentration (at 100 mL ethanol anhydrous) in samples of natural distillates of plums

No	The source of natural distillates	Analysed natural distillates	Methanol concentration $\mu\text{g/mL}$ distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
1.	Filipești (BC)	Plums	8316,0	36,1	2,30
2.	Palanca (BC)	Plums	1113,1	36,4	0,30
3.	Ghimeș (BC)	Plums	2036,2	39,3	0,51
4.	M. Casin (BC)	Plums	4147,6	35,4	1,17
5.	Cireșești (BC)	Plums	2213,0	32,9	0,67
6.	Râmnicu Sarat (BZ)	Plums	2528,4	53,9	0,46
7.	Petrești (BC)	Plums	4434,3	50,2	0,88
8.	Bogdana (BC)	Plums	2078,7	32,8	0,63
9.	Câmpina (BV)	Plums	2312,7	37,1	0,62
10.	Câmpina (BV)	Plums	2818,2	42,9	0,65
11.	Tarcau (NT)	Plums	3737,5	40,0	0,93
12.	Oituz (BC)	Plums	1825,1	29,0	0,62
13.	Hateg (SV)	Plums	2263,3	42,0	0,53
14.	Comanesti (BC)	Plums	4689,8	28,9	1,62
15.	Comanesti (BC)	Plums	5002,2	30,2	1,65
16.	Comanesti (BC)	Plums	3611,2	29,3	1,23

In the samples of plum brandy, 4 samples with an overrunning methanol concentration were found (table 4).

Table 5. Methanol concentration (at 100 mL ethanol anhydrous) in samples of natural distillates of marc

No	The source of natural distillates	Analysed natural distillates	Methanol concentration $\mu\text{g/mL}$ distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
1.	Mărgineni (BC)	Marc	1805,1	54,6	0,33
2.	Mărgineni (BC)	Marc	4973,1	38,6	1,28
3.	Mărgineni (BC)	Marc	522,6	36,5	0,14
4.	Lipova (BC)	Marc	502,4	37,4	0,13
5.	Racova (BC)	Marc	580,9	24,6	0,23
6.	Blăgești (BC)	Marc	4981,5	33,02	1,5
7.	Blăgești (BC)	Marc	5874,8	26,6	2,20
8.	Blăgești (BC)	Marc	668,8	51,0	0,13
9.	Racova (BC)	Marc	922,2	26,0	0,35
10.	N. Bălcescu (BC)	Marc	1328,6	53,3	0,24
11.	N. Bălcescu (BC)	Marc	1039,6	49,5	0,21
12.	Fărăoani (BC)	Marc	2444,0	55,3	0,44
13.	Ghe Doja (BC)	Marc	1057,1	56,5	0,18
14.	Râmnicu Sarat (BZ)	Marc	1023,0	46,9	0,21

No	The source of natural distillates	Analysed natural distillates	Methanol concentration $\mu\text{g}/\text{mL}$ distillate	Percentage concentration of ethanol volume	Methanol concentration at 100 mL ethanol anhydrous
15.	Râmnicu Sarat (BZ)	Marc	820,1	43,6	0,18
16.	Râmnicu Sarat (BZ)	Marc	763,6	37,9	0,20
17.	Soncut (BC)	Marc	606,2	41,3	0,14
18.	Petrești (BC)	Marc	2692,6	58,6	0,45
19.	Petrești (BC)	Marc	2653,8	55,5	0,47
20.	Pârjol (BC)	Marc	1041,3	37,1	0,28
21.	Pârjol (BC)	Marc	1307,0	37,9	0,34
22.	Șt. Cel Mare (BC)	Marc	1763,5	36	0,48
23.	Sascut (BC)	Marc	1466,7	48,9	0,29
24.	Petresti (BC)	Marc	2413,9	49,4	0,48
25.	Petresti (BC)	Marc	3206,8	58,7	0,54
26.	Comanesti (BC)	Marc	1340,1	58,1	0,23
27.	Comanesti (BC)	Marc	673,7	36,4	0,18
28.	Comanesti (BC)	Marc	499,5	38,1	0,13
29.	Comanesti (BC)	Marc	755,0	10,9	0,69
30.	Bacau	Marc	2131,3	43,2	0,37
31.	Asau (BC)	Marc	1062,4	45,7	0,23
32.	Soncut (BC)	Marc	595,8	39,7	0,15
33.	Marasessti (VN)	Marc	964,1	42,5	0,22
34.	Corbasca (BC)	Marc	1233,6	30,6	0,40
35.	Lipova B(BC)	Marc	2791,2	38,4	0,72
36.	Oituz (BC)	Marc	1484,4	41,2	0,36
37.	Panciu (VN)	Marc	7452,1	40,7	1,83
38.	Straoani (BC)	Marc	705,0	37,3	0,18
39.	Bacau	Marc	6094,8	50,9	1,19
40.	Bacau	Marc	2613,8	45,3	0,57
41.	Tamasi (BC)	Marc	3257,8	48,3	0,67
42.	Buciumeni, (GL)	Marc	660,3	47,9	0,13
43.	Râmnicu Sarat (BZ)	Marc	813,8	37,9	0,21
44.	Comanesti (BC)	Marc	1327,8	30,2	0,43
45.	Comanesti (BC)	Marc	4243,9	29,4	1,44
46.	Hemeiusti (BC)	Marc	2437,0	46,8	0,52

Out of the 46 samples of marc only 6 have an overrunning concentration of methanol, two of these having almost double values (table 5).

Average concentration of methanol
at 100 mL ethanol anhydrous

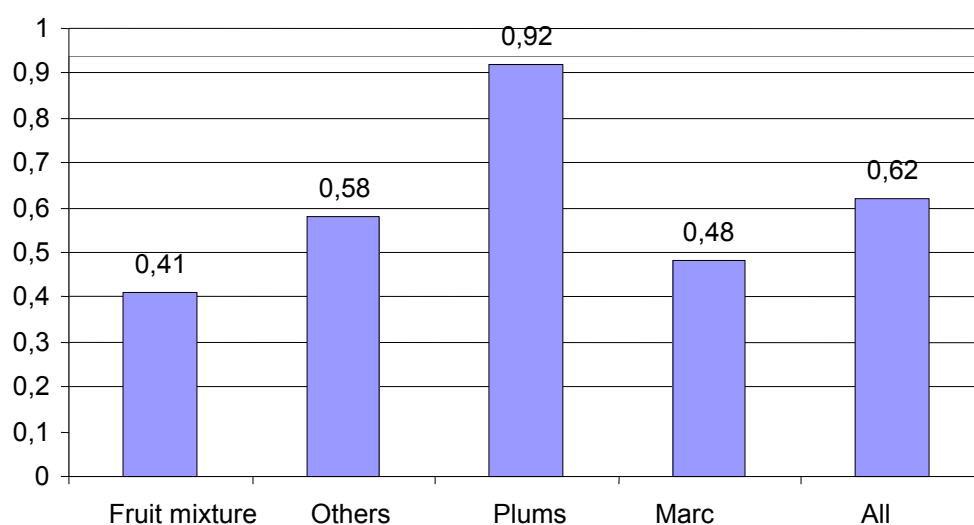


Diagram 1. The variation of the average value of the methanol concentration (100 mL ethanol anhydrous) depending on the nature of the distillates

Table 6. Summarizing table according to the nature of the distillates

Natural distillates	Number of samples	Average concentration of methanol $\mu\text{g} / \text{mL}$ distillate	Average concentration of methanol at 100 mL ethanol anhydrous
Marc	6	5603,37	1,57
Fruit mixture	8	5589,45	1,38
Plums	5	5960,78	1,67
Total	19	5691,56	1,51

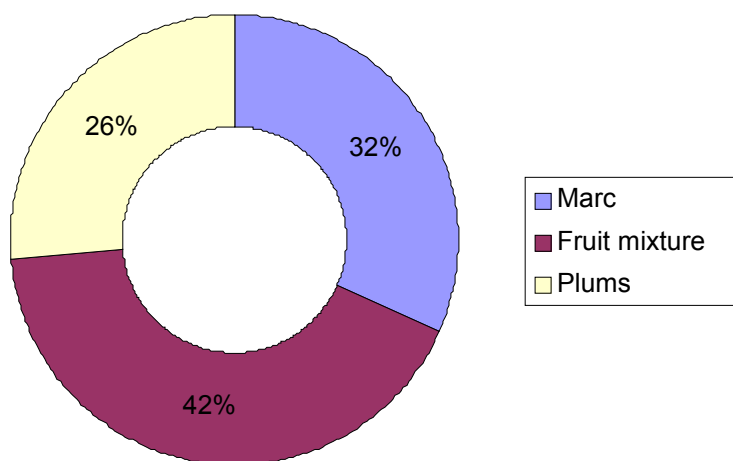


Diagram 2. Statistical weight of the analyzed samples with values over the accepted limits by the State Norms

Table 7. Summarizing table according to the place

The place source of the natural distillates	Number of samples	Average concentration of methanol $\mu\text{g} / \text{mL}$ distillate	Average concentration of methanol at 100 mL ethanol anhydrous
Comanesti (BC)	7	5139,43	1,35
Blăgești (BC)	2	5428,15	1,85
Straoani (BC)	2	7256,55	1,92
Panciu (VN)	2	5578,7	1,44
Others	6	5939,48	1,48
Total	19	5691,56	1,51

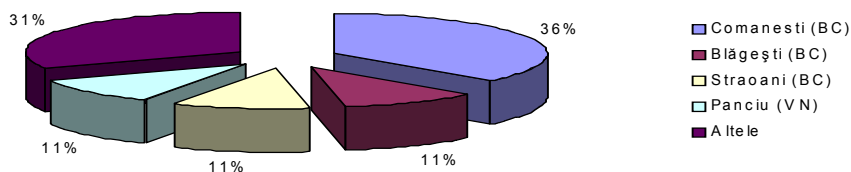


Diagram 3. Statistical weight of the source places of the analyzed distillates with values of methanol over the accepted limits by the State Norms

micrograms/ mL distillate

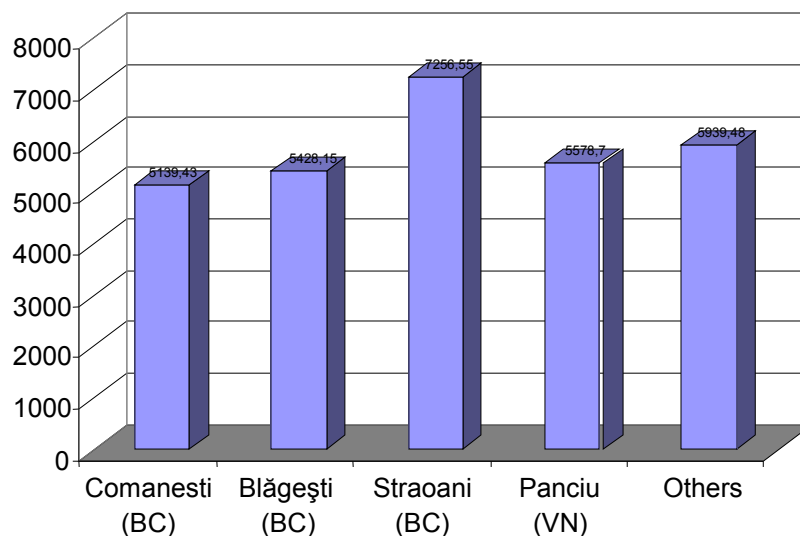


Diagram 4. Average concentration for the source places of the analyzed distillates with values of methanol over the accepted limits by the State Norms

CONCLUSIONS

A number of 98 samples of brandy mostly from Moldavia were analyzed. The method used was the gas-chromatograph method coupled with mass spectrometry. The analyses were made on an Agilent Technologies 7890 A gas chromatograph provided with an automatic Agilent Technologies 7683 B Series injector, coupled with an Agilent Technologies 5975C inert MSD mass spectrometer as a system of detection. The mobile phase is represented by helium, with a 1 mL/minute debit. For the stationary phase a Zebron – Phenomenex, type ZB-WAX plus chromatograph column was used, having the following characteristics: 60 m long x 0.25 mm internal width and 0.25 μ m thickness of the film which deposited on the internal walls of the column. As a result to the analyses, it was observed that 19 out of the 98 samples had a methanol concentration over the accepted limits (table 2). According to the material, out of 24 samples from fruit mixture, 8 had methanol over the limits (table 2) with a statistical weight of 42% (diagram 2); out of 16 plum samples, 4 had methanol concentration beyond limits (table 4) with a weight of 26% (diagram 2), and out of 46 marc samples only 6 (table 5) with 32 % (diagram 2).

The average value according to the nature of the distillates is expressed in Diagram 1 and is

observed that the plum distillates have an average value of methanol concentration of 0.92%, followed by those of marc with 0.48% and the fruit mixture with 0.41%. The highest average concentration of methanol is in the plum distillates with 1.67 mL at 100 mL ethanol anhydrous (table 6).

According to the source place of the samples with an overrunning methanol concentration, the most samples are from Comanesti – Bacau: 36%, 11% from Straoani – Bacau, 11% Panciu – Vrancea and 31% from other places (diagram 3).

When it comes to the average concentration for the source places of the distillates with values of methanol (μ g/mL distillate) over the accepted limits by the State Norms, on the first place there is Straoani – Bacau followed by Panciu – Vrancea and Blagești – Bacau (tabel 7, diagram 4). From the analyzed data it is determined that 19.38% of the samples contain methanol over the accepted limit and this represents a source of intoxication with methanol with serious consequences, such as blindness or movable dysfunctions. Due to the fact that it starts in an insidious manner and taking into consideration that methanol is disguised by the quantity of ethanol in the brandy and the plum brandy, intoxication with methanol is very hard to discover, many times leading to death.

ABSTRACT

The study was done on 98 samples of brandy and plum brandy taken from Moldavia between 2007 and 2009, to determine the methanol concentration from the natural distillates. The samples were analyzed using an Agilent Technologies 7890 chromatography gas coupled with an Agilent Technologies 5975 C mass spectrometer, the mobile phase being represented by helium and the stationary phase by a Zebron – Phenomenex ZB-WAX plus chromatography column. Out of the 98 samples of brandy, 19 had a higher concentration of methanol than the working standards. The methanol concentration was related to 100 ml anhydrous ethanol. Depending on the material from which it was treated, the fruit mixture brandy represents 42% from the share of the samples with an exceeded methanol concentration, the marc 32% and the plum brandy 26%. The place where the most samples with an exceeded methanol concentration can be found is Comanesti- Bacau, followed by Blagesti - Bacau and Straoanu - Bacau.

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