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THE TOXIC POTENTIAL OF "CLEAN" ARTISANAL DISTILLATES OBTAINED FROM GRAPE POMACE

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***Key words**: methanol, pomace brandy, GC, congener*

INTRODUCTION

Our country is reputed for a long tradition in preparing alcoholic distillates from cereals, fruit or grape pomace. These brandy varieties are known according to the alcoholic concentration and region as "rachiu", "tuica" or "palinka". These preparations are obtained industrially, when they are analysed and controlled according to the official standards, as well as artisanally, according to the "personal recipes" and the experience of those who prepare these products. According to the EC Regulation no. 787 of April 17, 2019 on the definition, description, presentation and labelling of spirits, pomace brandy must have an alcohol level of 37.5% [1]; in this case, because it is an artisanal drink, the alcohol level is variable. Unfortunately, these distillates are not analysed and certified regarding the alcoholic concentration and, more importantly, regarding the concentration of toxic volatile congeners, especially methyl alcohol. This study aims to highlight the presence and toxic potential of methyl alcohol from artisanal distillates, a congener with a high degree of toxicity that can generate, in case of intoxication, an insidious symptomatology which is easily confused with ethanol intoxication, but with a high degree of aggression leading to blindness, metabolic acidosis and death [2,3,4,5].

MATERIAL AND METHOD

Throughout our study, a total of 49 samples of natural alcoholic distillates were analysed as products resulting from the distillation of simple grape macerates (pomace). At the organoleptic examination, the samples to be analysed are clear, without suspensions, with a specific odour of alcohol and aroma specific to the material from which they were distilled. It is clear from the data collected that they have no adjuvants or flavour enhancers and no artificial dyes. These distillates also do not contain added sugar, other sweeteners or extracts that would influence their density. The samples were taken from the area of Moldavia, most of them coming from Bacău County, respectively 42 samples, 4 samples from Buzau County, 2 samples from Vrancea County and 1 sample from Galati County. The concentration of methyl alcohol, according to the legislation in force [1,6,7,8] is compared to the anhydrous ethyl alcohol. Thus, the analysis involved two stages, respectively, determining the ethyl alcohol concentration and then comparing it to the anhydrous ethyl alcohol in the samples. The concentration of ethyl alcohol in the samples of alcoholic distillates was determined by the pycnometer method, the standardised method according to the methodological norms approved within the EEC Regulation no. 2870/2000 approved by the Ministry of Agriculture and Food, as well as according to the methods of analysis approved by the International Wine Organization, methods that correspond to the professional standards in our country [6,7,8,9]. This method is applied without other redistillation processes in the case of alcoholic distillates, without extract and without additives of other adjuvants respectively sugar, fructose, colorants, flavour and taste enhancers, suspending agents, emulsifiers, the analytical samples being appropriate to these requirements. The principle of the method was to determine the alcoholic strength by volume obtained from the density of the distillate measured by pycnometry [8,9,10]. Thus, the following equipment was used: AND HR200 analytical balance with four decimals, Pyrex glass ROTH pycnometer with a capacity of 50 mL (ISO 3570) calibrated with an accuracy of 0.001 mL, equipped with a calibrated and certified toluene thermometer and a certified INCUCEL Incubator.

The alcohol concentrations are obtained based on calculations of relative densities and actual relative densities P20/4 of distillate samples by reference to the Tables approved by the International Organization of Legal Metrology from which the values of ethyl alcohol concentration of distillates in weight percentages are obtained (TAM) [8,9]. Depending on the values of the alcoholic strength by weight taken from these tables, the values of the actual concentration by volume (% vol) are obtained on the basis of the general equation which establishes the link between the alcoholic strength by volume and the density of a water/alcohol mixture at a certain temperature. In order to determine the concentration of methyl alcohol in alcohol samples, the analyses were performed on an Agilent Technologies 7890 A

gas chromatograph equipped with an Agilent Technologies 7683 B Series automatic injector, coupled with an Agilent Technologies 5975C inert MSD mass spectrometer. The detection system - Zebron - Phenomenex chromatographic column, YB-WAXplus type was 60 m long x 0.25 mm internal diameter and 0.25 μm thick for the film deposited on the inner walls of the column. Mobile phase - helium, with a flow rate of 1 mL/minute.

The temperature gradient in the column compartment: 50°C for 20 minutes, then the temperature rises by 10°C/min to 250°C where it is kept constant for another 5 minutes. The injection volume of 0.1 μL; split ratio 1/50. The detection of the analytes from the alcohol distillate samples is performed by mass spectrometry, using an Agilent Technologies 5975C inert MSD mass spectrometer with a temperature of 230°C and a temperature of the quadrupole of 150°C. Spectrum acquisition mode: SCAN (tracking all lines in the mass spectrum); mass range: 15 - 500 atomic mass units; interpretation of the results obtained: Agilent Technologies ChemStation software. After performing the gas-chromatographic determinations and integrating the obtained chromatograms, the methanol was identified by comparing the retention times of the corresponding peaks in the chromatograms of the alcoholic distillates and the chromatogram of a standard sample containing methanol, as well as by spectral comparison. The concentration of methanol from the analytical samples is calculated using the areas of the peaks corresponding to methanol and the equation of the calibration curve. [11,12].

RESULTS AND DISCUSSIONS

According to the results of the ethanol volume concentration in the analysed distillate samples, compared to the concentration of methanol μg methanol/mL distilled, the concentration of methanol g / 100 mL anhydrous ethanol per distillate was obtained. Table 1 presents the data on the results of the calculations of the methanol concentration per 100 mL anhydrous ethanol depending on the ethanol concentration in volume percentages and on the methanol concentration, determined in μg methanol/mL distilled for each sample of natural alcoholic distillate analysed.

Table 1 indicates that, in the 49 distillate samples analysed, there are various ethanolic concentrations. The lowest value is 10.9% mL ethanol/100 mL distillate and is found in a sample of distillate processed from pomace in 2007 in Comăneşti – Bacău. The highest value, respectively 60.7 mL ethanol/100 mL distillate belongs to a sample processed in Oituz locality, Bacău county. Most samples were in the range of 30-40% mL ethanol /100 mL distillate, respectively 17 samples. The fewest are in the range of 10-20% mL ethanol /100 mL distillate, respectively 1 sample. 1 sample has an alcohol level higher than 60% mL ethanol /100 mL distillate. The average value of the ethanolic concentration in the 49 samples of natural alcoholic distillates analysed is 42.4% mL ethanol /100 mL distillate (Fig. 1).

Compared to methanol concentration in the 49 samples of alcoholic distillates that were processed from pomace, in two of the samples analysed, methanol was below the detection limit, respectively a sample from Racova BC from 2009 and a sample from Lipova BC from 2007. The lowest value of methanol concentration g /100mL anhydrous ethanol present in pomace distillates is 0.13 g / 100mL anhydrous ethanol, a value present in 4 samples analysed. At the same time, 6 samples registered values of methanol concentration above the legally allowed limit [1], ie 1g / 100mL representing 12.24% of the total samples of distillates analysed. The minimum value of methanol concentration (above the allowed limit g/100mL anhydrous ethanol) present in the analysed samples is 1.19 g/100mL anhydrous ethanol, at a sample from Bacău locality. The maximum value of the methanol concentration present in the distilled samples of pomace is 2.20 g/100mL anhydrous ethanol, an extremely toxic value, identified in a sample that comes from Blăgeşti locality, Bacău county and reported in Table 2.

Comparing the number of samples detected with methanol concentration above the allowed limit with the ranges/intervals of ethanol concentration found in the 49 samples analysed, two sample were found in the range of 20-30% ethanol, another two samples were in the range of 30-40% ethanol. A single sample was detected in the range of 40-50% ethanol, respectively in the range of 50-60%. At intervals of 10-20% and over 60% ethanol, no methanol sample was determined above the legal limit. (Fig. 2).

As far as the origin of the samples is concerned, five are from Bacau County, two being from the same locality – Blagesti and one from Vrancea County. Excepting one sample, all the other five samples were prepared in 2008.

Increased values of methanol concentration in distillates are obtained practically for two reasons: the quality of the grapes and the variety and the degree of ripeness. However, the most important cause is the distillation. Concerning the grape variety, from the surveys conducted when the samples were collected, it was found that most people prepared these distillates from "Capsunica" variety, a very aromatic variety, which is frequently found in households. This variety is a hybrid from America along with other hybrids, naturalized in Europe in the nineteenth century under the name of Isabella. This variety was a great success, being resistant to cold, pests and phylloxera. However, because of the poor quality of the wine, and especially the fact that, compared to other varieties, it has a much higher concentration of pectic substances with a heavy

molecule present in the grape husk, which by fermentation is transformed into methanol, in 1930, "Isabella" was banned in Italy. In 1934, it was completely eliminated from France, and in 1979, the European Commission completely banned the cultivation of hybrid varieties in vineyards.

Table 1. Methanol concentration (per 100 mL anhydrous ethanol) in samples of natural distillates from pomace

No.	Origin of natural distillates	Alcoholic distillates analysed	Methanol concentration µg /mL	Ethanol concentration in volume percentage	Methanol concentration per 100 mL anhydrous
1.	Mărgineni(BC)	Tescovina2010	1805.1	54.6	0.33
2.	Mărgineni(BC)	Tescovina2010	4973.1	38.6	1.28
3.	Mărgineni(BC)	Tescovina2010	522.6	36.5	0.14
4.	Lipova (BC)	Tescovina2010	502.4	37.4	0.13
5.	Racova (BC)	Tescovina2010	580.9	24.6	0.23
6.	Blăgeşti (BC)	Tescovina2008	4981.5	33.2	1.5
7.	Blăgeşti (BC)	Tescovina2008	5874.8	26.6	2.20
8.	Blăgeşti (BC)	Tescovina2011	668.8	51.0	0.13
9.	Racova (BC)	Tescovina2011	922.2	26.0	0.35
10.	N.Bălcescu(BC)	Tescovina2011	1328.6	53.3	0.24
11.	N.Bălcescu(BC)	Tescovina2011	1039.6	49.5	0.21
12.	Fărăoani (BC)	Tescovina2010	2444.0	55.3	0.44
13.	Ghe Doja (BC)	Tescovina2010	1057.1	56.5	0.18
14.	Râmnicu S(BZ)	Tescovina2000	1023.0	46.9	0.21
15.	Râmnicu S(BZ)	Tescovina2002	820.1	43.6	0.18
16.	Râmnicu S(BZ)	Tescovina2003	763.6	37.9	0.20
17.	Sascut (BC)	Tescovina2004	606.2	41.3	0.14
18.	Petreşti (BC)	Tescovina2007	2692.6	58,6	0.45
19.	Petreşti (BC)	Tescovina2007	2653.8	55.5	0.47
20.	Pârjol (BC)	Tescovina2007	1041.3	37.1	0.28
21.	Pârjol (BC)	Tescovina2007	1307.0	37.9	0.34
22.	Ştefan Cel Mare (BC)	Tescovina2007	1763.5	36	0.48
23.	Sascut (BC)	Tescovina2007	1466.7	48.9	0.29
24.	Petreşti (BC)	Tescovina2007	2413.9	49.4	0.48
25.	Petreşti (BC)	Tescovina2007	3206.8	58.7	0.54
26.	Comăneşti(BC)	Tescovina2007	1340.1	58.1	0.23
27.	Comăneşti(BC)	Tescovina2007	673.7	36.4	0.18
28.	Comăneşti(BC)	Tescovina2007	499.5	38.1	0.13
29.	Comăneşti(BC)	Tescovina2007	755.0	10.9	0.69
30.	Bacău	Tescovina2007	2131.3	43.2	0.37
31.	Asău (BC)	Tescovina2007	1062.4	45.7	0.23
32.	Sascut (BC)	Tescovina2008	595.8	39.7	0.15
33.	Mărăşeşti (VN)	Tescovina2008	964.1	42.5	0.22
34.	Corbasca (BC)	Tescovina2008	1233.6	30.6	0.40
35.	Lipova (BC)	Tescovina2008	2791.2	38.4	0.72
36.	Oituz (BC)	Tescovina2008	1484.4	41.2	0.36
37.	Panciu (VN)	Tescovina2008	7452.1	40.7	1.83
38.	Străoani (BC)	Tescovina2008	705.0	37,3	0.18
39.	Bacău	Tescovina2008	6094.8	50.9	1.19
40.	Bacău	Tescovina2008	2613.8	45.3	0.57
41.	Tamaşi (BC)	Tescovina2008	3257.8	48.3	0.67
42.	Buciumeni (GL)	Tescovina2008	660.3	47.9	0.13
43.	Râmnicu S(BZ)	Tescovina2008	813.8	37.9	0.21
44.	Comăneşti (BC)	Tescovina2008	1327.8	30.2	0.43
45.	Comăneşti (BC)	Tescovina2008	4243.9	29.4	1.44
46.	Hemeiuşi (BC)	Tescovina2008	2437.0	46.8	0.52
47.	Racova BC	Tescovina2009	< LD	46.8	-
48.	Oituz BC	Tescovina2007	2086.6	60.7	0.34
49.	Lipova BC	Tescovina2007	< LD	38.4	-

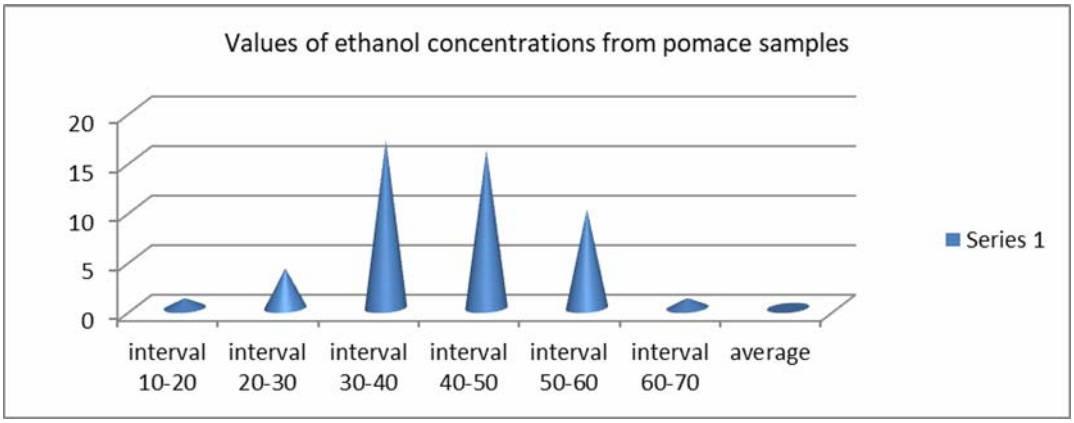

Fig. 1 Ethanol concentration values according to reference intervals

Table 2. Methanol concentration (per 100 mL anhydrous ethanol) over 1 g/100 Ml anhydrous ethanol in natural distillate samples from pomace analysed

No.	Origin of natural distillates	Alcoholic distillates analysed	Methanol concentration µg /mL distillated	Ethanol concentration in volume percentage	Methanol concentration per 100 mL anhydrous ethanol
1.	Bacău	Tescovina2008	6094.8	50.9	1.19
2.	Mărgineni (BC)	Tescovina 2010	4973.1	38.6	1.28
3.	Comăneşti (BC)	Tescovina2008	4243.9	29.4	1.44
4.	Blăgeşti (BC)	Tescovina2008	4981,5	33.2	1.50
5.	Panciu (VN)	Tescovina2008	7452.1	40.7	1.83
6.	Blăgeşti (BC)	Tescovina2008	5874.8	26.6	2.20

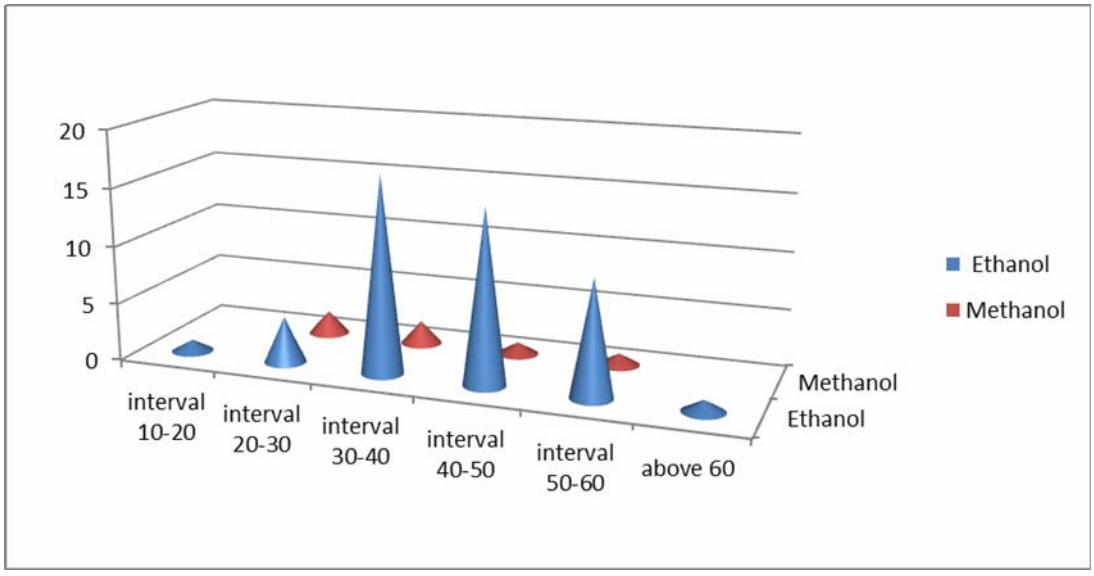

Fig. 2 Distribution of methanol samples above the legal limit according to ethanol intervals

Unfortunately, according to the 2016 data of the National Institute of Statistics, half of the Romanian vineyards still largely contain hybrid varieties, especially the Isabella variety which is highly valued by private owners for its olfactory qualities and productivity. Considering that most of the contaminated samples come from distillates processed in 2008, we can also mention the fact that pectin is much higher in less ripe grapes, their collection and processing before full maturation increasing the risk of methanol contamination [13,14, 15,16]. In addition to grape quality and origin,

another essential factor regarding methanol origin in the samples must be mentioned, namely the method of processing or distillation. Methanol is known to have a boiling point of 65° compared to ethyl alcohol which boils at 78° [17,18]. In the correct process of distilling pomace, it is correct that the first part of the distillate should not be collected, this being the fraction which contains methanol [19,20]. In the case of the analysed samples, these two possibilities can coexist, leading to toxic finished products. If a correct distillation is performed, the percentage of methanol in the distillates may range within legal limits or even be absent.

CONCLUSIONS

Throughout our study, a total of 49 samples of grape pomace distillates were analysed in order to estimate the ethanol concentration with which the methanol concentration found in the samples was compared. According to the European Regulation EEC no. 2870/2000, the maximum concentration of methanol which is allowed in pomace distillates is 1g /100mL anhydrous ethanol. Of the samples analysed, two had a methanol concentration below the detection limit, the lowest value detected was 0.13 g /100 mL, the highest value detected was 2.20 g /100 mL. 6 samples of the ones analysed had values above the limit, meaning a significant percentage of 12.24%, with values between 1.19 g /100mL - 2.20 g /100mL. These values could be obtained, to some extent, because of the grape varieties present in the pomace. However, if the distillation technology is strictly respected, the methanol percentage in the distillates would not exceed the legal limit. Many people do not meet these requirements given that they are ignorant of the aspects referring to both the grape variety and the pomace distilling technique and they are eager to obtain as much distillate with a high alcohol concentration as possible. Hence, they obtain distillates contaminated with methanol, sometimes in lethal concentrations, as highlighted in this study. For this reason, it is important that the population be informed about the correct techniques of distilling natural fruit macerates, or when buying them from someone else, they should receive information about the experience of the one who prepared them, the grape variety present in the pomace, the degree of ripening and the maceration time. Otherwise, a product that has the attribute of being a natural, "clean" product can be more toxic than an industrial one, the former having the potential of being even lethal.

ABSTRACT

This study aims to highlight the presence and toxic potential of methyl alcohol from artisanal distillates, a congener with a high degree of toxicity that can generate, in case of intoxication, an insidious symptomatology which is easily confused with ethanol intoxication, but with a high degree of aggression leading to blindness, metabolic acidosis and death.Throughout our study, a total of 49 samples of natural alcoholic distillates were analysed as products resulting from the distillation of simple grape macerates (pomace). The samples were taken from the area of Moldavia, most of them coming from Bacău County, respectively 42 samples, 4 samples from Buzau County, 2 samples from Vrancea County and 1 sample from Galati County. The concentration of methyl alcohol, according to the legislation in forceis compared to the anhydrous ethyl alcohol. Thus, the analysis involved two stages, respectively, determining the ethyl alcohol concentration and then comparing it to the anhydrous ethyl alcohol in the samples. To determine the concentration of methyl alcohol in alcohol samples, the analyses were performed on an Agilent Technologies 7890 A gas chromatograph equipped with an Agilent Technologies 7683 B Series automatic injector, coupled with an Agilent Technologies 5975C inert MSD mass spectrometer. Of the samples analysed, two had a methanol concentration below the detection limit, the lowest value detected was 0.13 g /100 mL, the highest value detected was 2.20 g /100 mL. 6 samples of the ones analysed had values above the limit, meaning a significant percentage of 12.24%, with values between 1.19 g /100mL - 2.20 g /100mL. These values could be obtained, to some extent, because of the grape varieties present in the pomace. However, if the distillation technology is strictly respected, the methanol percentage in the distillates would not exceed the legal limit. Many people do not meet these requirements given that they are ignorant of the aspects referring to both the grape variety and the pomace distilling technique and they are eager to obtain as much distillate with a high alcohol concentration as possible. Hence, they obtain distillates contaminated with methanol, sometimes in lethal concentrations, as highlighted in this study.

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