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Quality and Safety Analysis for some Traditional Homemade Fruit Distillates from Transylvania (North West Romania)

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Abstract. There were analyzed nine homemade samples of plum and apple distillates (brandies) originating from different areas of Romania- Transylvania (Maramureş, Cluj, Bistriţa-Năsăud counties). There were investigated some quality parameters (alcohol concentration, relative density, total dry extract, pH and total acidity) as well two safety markers (organo chlorinated pesticides and heavy metals - lead and copper). The methods used were routine determinations for quality analysis while, gas-chromatographic (GC-FID) quantitative evaluation of organo chlorinated pesticides and atomic absorption analysis for heavy metals. We found generally acceptable quality parameters, included in the standardized limits, while for safety, three samples were found to contain pesticides and two samples to contain higher concentrations of lead or copper. Further investigations will be focused more on safety parameters of a larger number of samples from Transylvania.

INTRODUCTION

The natural fruit brandies (distillates) are produced by distillation of fruit pulp and/or juices in copper stills with open fire (woods). The maturing and conditioning of these drinks are made especially in oak barrels (Pomohaci, 2002) or in stainless steel recipients.

One can distinguish several types of fruit brandies such as plum brandy (called also *ţuica*), apricot brandy, apple or pear brandies. The plum brandy can also be classified: *ţuica curentă* (made from a mixture of plum pulp with a minimum 24% alcohol concentration, *ţuica cu denumire de origine* (eg. Piteşti ţuica, Horezu, Văleni) with a minimum 28 % alcohol concentration, *ţuica bătrână* (maturated in barrels at least one year) with an alcoholic concentration between 28-32%; *ţuica superioară* (şliboviţa, ţuică de Turţ, ţuică de Zalău) with an alcohol concentration between 40-50% (double distillation of *ţuica* and maturing in barrels for a few years).

Plum distillate is well known in many countries with different names such as slivovitz of Yugoslavia, raki in balkanical countries, palinka in Hungary. The name of *ţuica* is specific only for Romania. For the area of Transylvania are common also the apple and pear brandies. For Romania, the international recognized names for fruit brandies are: *pălincă*, *ţuică Zetea de Medieşu Aurit*, *ţuică de Valea Milcovului*, *Ţuică de Buzău*, *Ţuică de Argeş*, *Ţuică de Zalău*, *Ţuică Ardelenească de Bistriţa*, *Horincă de Maramureş*, *Horincă de Cămârzana*, *Horincă de Seini*, *Horincă de Chioar*, *Horincă de Lăpuş*, *Turţ de Oaş*, *Turţ de Maramureş* (REGULATION (EC) No 110/2008**)**. In Romania - Transylvania areals - the distillation is applied more than in the rest of the country (Pomohaci, 2002), being produced plum and apple

distillates with an higher alcohol concentration (around 50 % vol. alc.) by double distillation and fraction separation.

According to Romanian legislation, *ţuica* is a traditional alcoholic drink obtained exclusivelly by alcoholic fermentation and distillation of plums. The fermentation of plums is made wood barrels or other stainless steel recipients. Distillation must be made in copper stills with open fire or in distillation installation, at an alcoholic concentration of maximum 86% volume, with flavor and taste of the distilled product being the same with the fruit. Double distillation it is permitted at the same 86% vol. alcohol concentration. The minimum alcoholic concentration it is 24% vol. *Pălinca* it is the traditional Romanian alcoholic beverage obtained exclusively by alcoholic fermentation and distillation of a fruit or of a mixture of fruits, a fruit marc or a fruit juice or a mixture of juices. Distillation takes place in copper stills with open fire or in distillation installation, at an alcoholic concentration of maximum 70% volume, with flavor and taste of the distilled product being the same with the fruit. The minimum alcoholic concentration it is 40%. The usage of caramel for adjusting the beverage color it is forbidden. The yellow or gold-yellow color can be obtained by maturing in wood barrels. It is forbidden the use of pure alcohol of industrial origin, the storage and maturing are made in recipients made of wood, stainless steel or glass.

The soil treatments done in agricultural sector (pesticides, fungicides, insecticides) have a lot of influence to the human health, by pollution of the ground and surface water. The pesticides persist in water transferred to soil and plants synthesize those chemicals even after many years (Wauchope, 1994). Even though only a small amount of pesticides residues present in the raw material can be transfered to the distilled spirit (Cabras, 1997), there still is a risk for human health if the consuming amount is high.

Recently, there were compared different Romanian commercial and traditional fruit brandies regarding the chemical properties (Beceanu, 2009).

In India an analysis of pesticides residues (Johnson, 2006) showed soft drinks from the market contain 24 times higher concentration of total pesticides residues comparing with the standard followed (0.5 ppb for the total pesticides residues).

Another contaminant of fruit distillates is lead with effects to human health. As with most environmental pollutants, lead occurs in air, water, land and biota. The human body is exposed to and accumulates lead over a lifetime and releases it slowly, so that even small amounts, over time, can cause lead poisoning (Juberg, 2000).

The provenience of copper in fruit distillates is from the distillation installation. This compound, in small quantities, can be an indicator of the authenticity of traditional fruit distillates (Rodríguez, 2010).

By consuming small amounts of copper, it’s toxicity is rare. Intake of high levels of copper may cause gastrointestinal illness (Nieboer, 2004).

The analysis which aims the evaluation of quality parameters for fruit brandies are: alcohol concentration, relative density, total acidity, pH, total dry extract, as well some safety parameters like methanol content, superior alcohols, acetaldehyde, furfural, and also the quantitation of some toxic compounds like heavy metals and pesticides.

The aim of our study was to determine comparatively the quality and safety of some homemade fruit distillates (apple and plum brandies) originating from different counties of Transylvania area.

We have determined the alcohol concentration, relative density, total acidity, pH, total dry extract as quality markers and organo chlorinated pesticides and heavy metals (copper and lead) as safety markers.

MATERIALS AND METHODS

Nine samples of fruit distillates were collected between October 2008 and May 2010 from different regions of Transylvania such as: Maramureş, Cluj, Bistriţa Năsăud, Alba. All the samples were homemade fruit distillates and the type of fruit and the year of production were declared by the producers.

Tab. 1

The location, type and codification of the samples

Codification	Type	Location
1	Plum brandy (*ţuica)*	Tioltiur, Cluj
2	Plum brandy (*ţuica)*	Petreşti, Cluj
3	Plum brandy (*ţuica)*	Beclean, Bistriţa Năsăud
4	Plum brandy (*ţuica)*	Ciucea, Cluj
5	Plum brandy (*ţuica)*	Seini, Maramureş
6	Plum brandy (*ţuica)*	Morlaca, Cluj
12	Apple brandy	Coşbuc, Bistriţa Năsăud
13	Apple brandy	Ocoliş, Alba
14	Apple brandy	Câtcău, Cluj

1. Instrumentation and protocols for quality analysis

Determination of the alcoholic concentration and the relative density

The determination of the alcoholic concentration and the relative density (SR 184/2-2009) were made by the electronic densitometer type DDM2911, with digital display and measuring cell connected to an incorporated temperature regulator, made by Rudolf Research Analytical, series: 2045, measuring domain: 0-3 g/cm^3. The density is displayed with 5 decimals and alcoholic concentration with 2 decimals.

Determination of total dry extract and total acidity

The determination of the total dry extract was made according to the SR 184/3-2009.

The determination of the total acidity was made according to the SR 184/5-97 and SR 184/2-2009, through the potentiometrical method, by titration of the distillate sample with a solution of NaOH 0.1 n. Conventionally, acidity is expressed in g/l acetic acid, g/l sulphuric acid or in meq/l. For ethyl alcohol, the maximum value for total acidity is 1.5 g acetic acid/100 ml anhydrous alcohol.

2. Safety analysis

GC-FID determination of Organochlorine pesticides

The organochlorine pesticides were determined according to the specific gas-chromatopgraphic (GC-FID) procedure applied for water. A quantity of 250 ml of every sample (distillate) were twice extracted with 5 ml of n-hexane (every time). The extracts were unified and desiccated by passing through a column with anhydrous Na_2SO_4. The extract was dried using the rotary evaporator at 60^{o}C and re-solved in1 ml hexane for GC analysis.

The apparatus used was a Hewlett Packard GC 4890D equipped with electron capture detector (ECD), a separation column HP-608, of 30 m length and interior diameter of 0.53 mm. It was injected 1 µl from each sample.

Column temperature at 120^{o}C was maintained for 1 minute than raised with 10^{o}C/minute up to 250^{o}C; this final temperature it was maintained for 20 minutes. The injector temperature was 300^{o}C. The temperature of electron capture detector was 300^{o}C.

The components were identified, based on the retention time using a standard mixture of 20 pesticides or their derivatives.

The quantitative analysis was performed using an external standard method and standard quantitative mixtures. The concentration of the organochlorine pesticides, expressed in ppb (micrograms/kg) was calculated according to formula:

$$Cx = \frac{C_{ext} \times V_e}{V_s}$$

Where:

C_x –concentration of the organochlorinated pesticides, ppb
C_{ext} –concentration of the external standard, ppb
V_e – elution volume, ml
V_s – sample volume, ml

The detection limit was 0.005 µg/l.

The maximum allowed levels of organochlorine pesticides in drinkable water (according to STAS 12650-88 and STAS 12998/91) are 0.5 µg total organochlorine pesticides /l, and respectively, 0.03 µg aldrin or dieldrin, heptachlor and heptachlorepoxid /liter and 0,10 µg/l per each class of pesticide.

Atomic absorption analysis of heavy metals (copper and lead)

It was used an atomic absorption spectrometer AVANTA ∑, A5018 series with auto sampler PAL 3000, graphite furnace. For copper determination it was used a lamp flux 3 mA, wavelength 324.8 nm, and based on peak height, the calibration was quadratic. For lead determination it was used a lamp flux 5 mA, wavelength 283.3 nm, slot 0.5 mm, method of measuring: peak area, method of calibration:. The injected sample volume was 20 µl in both cases, all samples were diluted 1:100 before analysis. The calibration curves were registered between 10-50 µg/l for lead and copper, separately. The maximum limit for lead was 300 µg/l and for copper 5 mg/l. The standardized method used was SR EN 14082:2003.

RESULTS AND DISCUSSION

Alcohol concentration and relative density

Tab. 2 shows the values registered for Relative density, g/ml and Alcohol concentration, % vol. All the samples had values, which were included in the normal standard limits for fruit brandies.

Tab.2

Alcoholic concentration and relative density of brandy samples

Sample code	Relative density, g/ml	Alcohol concentration, % vol
1	0,93330	48,37
2	0,92916	50,5
3	0,93342	48,31
4	0,93395	48,03
5	0,92551	52,32
6	0,93061	49,76
12	0,92976	50,19
13	0,92461	52,76
14	0,93411	47,94

The highest value was noticed for apple brandy nr.13, from Ocoliş, Alba county, while the lowest value was found at another apple brandy, nr. 14, from Câţcău, Cluj county.

Total dry extract

Tab. 3 represent the total dry extract values, which were very different, ranging from 0.002 to 0.014%. Generally, the values were very low, but were similar to other publications (Beceanu, 2009).

Tab. 3

Total dry extract for brandy samples

Sample code	Total dry extract
	%
1	0.002
2	0.015
3	0.008
4	0.011
5	0.014
6	0.002
12	0.013
13	0.004
14	0.002

Total acidity and pH

Tab. 4 represents the values registered total acidity and pH values.

Tab. 4

Total acidity and pH

Sample code	Total acidity, g acetic acid/100 ml anhydrous alcohol	pH
1	0.20	4.04
2	0.21	4.06
3	0.10	4.74
4	0.04	5.16
5	0.25	4.12
6	0.13	4.63
12	0.09	4.94
13	0.28	4.00
14	0.17	4.09

According to the Romanian legislation, the results for total acidity are included in the maximum admissible range of values.

GC-FID determination of organochlorine pesticides

We found that three samples contained residues of organochlorine pesticides and these were plum brandies no. 2, 3 and 5, from Petreşti (Cluj), Beclean (Bistriţa-Năsăud) and Seini (Maramureş), as it is shown in the chromatograms below (Fig. 2, Fig. 3, Fig. 4).

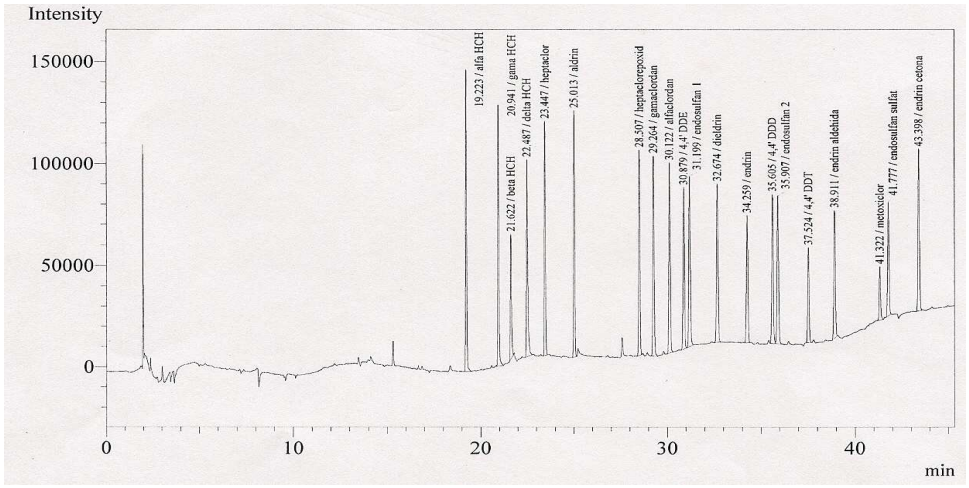

Fig. 1.The GC-FID chromatogram recorded for the standard mixture of pure organochlorine pesticides.

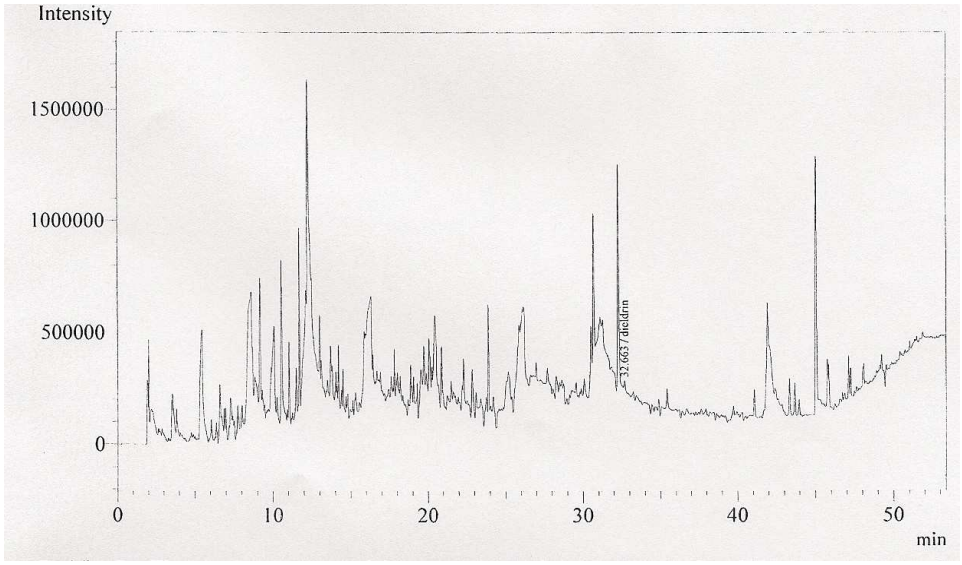

Fig. 2.The GC-FID chromatogram of sample 2 – plum brandy – Petreşti, Cluj

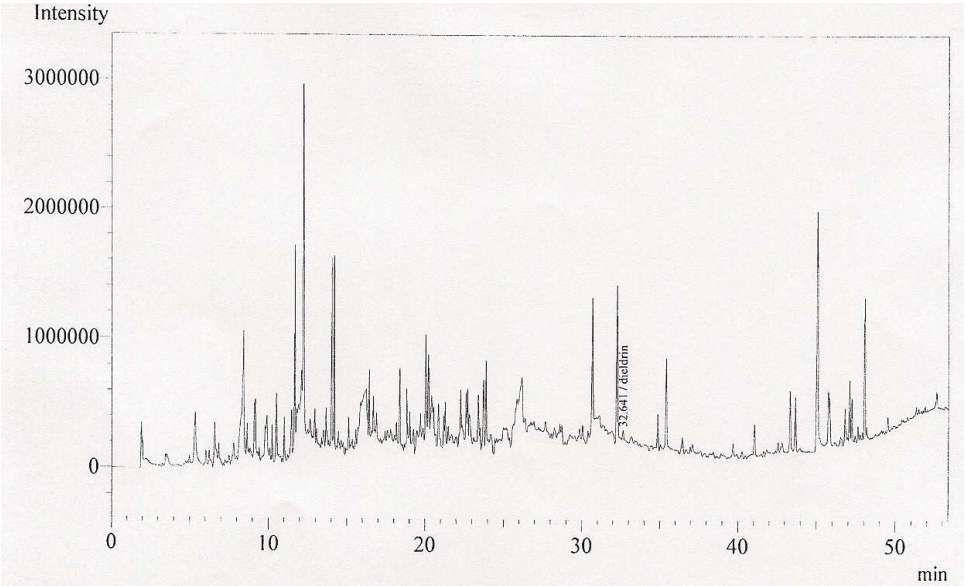

Fig. 3. The GC-FID chromatogram of sample 3 –plum brandy– Beclean, Bistriţa-Năsăud

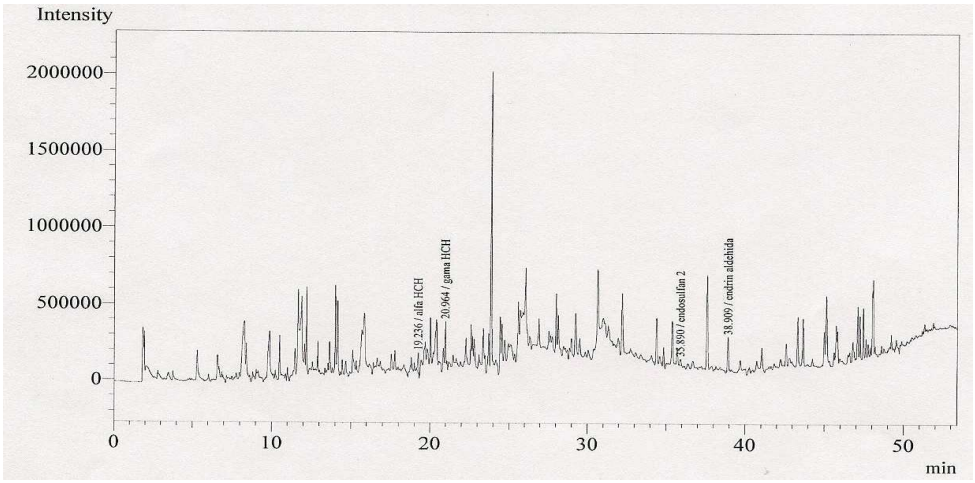

Fig. 4. The GC-FID chromatogram of sample 5 – Plum brandy – Seini, Maramureş

Tab. 5 shows the amounts of pesticides found in the samples 2, 3 and 5.

Tab. 5

The quantity of total organochlorine pesticides found in the samples 2, 3 and 5 (ppb)

Organochlorine pesticides, unit mark (ppb)	2	3	5
Alfa HCH	-	-	20.467
Gama HCH	-	-	42.283
Beta HCH	-	-	-
Delta HCH	-	-	-
Heptaclor	-	-	-
Aldrin	-	-	-
Heptaclorperoxid	-	-	-
Gamaclordan	-	-	-
Alfaclordan	-	-	-
4,4'DDE	-	-	-
Endosulfan 1	-	-	-
Dieldrin	6.337	14.402	-
Endrin	-	-	-
4,4'DDD	-	-	-
Endosulfan 2	-	-	9.908
4,4'DDT	-	-	
Endrin aldehyde	-	-	53.515
Metoxiclor	-	-	-
Endosulfan sulfat	-	-	-
Endrin ketone	-	-	-

Tab. 6 includes the values of individual organochlorine pesticides found in samples 2, 3 and 5, expressed in µg/l.

Tab. 6

Quantity of individual organochlorine pesticides found in samples 2, 3 and 5, expressed in µg/l

Sample	Organochlorine pesticides, µg/l				
	Dieldrin	α-HCH	γ-HCH	Endosulfan 2	Endrin aldehyde
2	0.025	-	-	-	-
3	0.057	-	-	-	-
5	-	0.082	0.169	0.039	0.214

The values registered for samples 3 and 5, were higher than the maximum permitted limits.

Heavy metals determination

Tab. 7 includes the values of lead and copper concentrations found in the analyzed samples.

Tab. 7

The values of lead and copper found in the analyzed samples

Sample code	Metals	
	Pb, µg/l	Cu, mg/l
1	29	6.16
2	800	2.57
3	99	4.53
4	147	2.18
5	148	4.62
6	77	6.25
12	246	1.54
13	177	2.33
14	151	6.13

The highest level of lead was found at sample 2, significantly over the critical limit. The copper highest concentration was recorded at sample 6 from Morlaca (Cluj). Other two samples (1 and 14 from Tioltiur-Cluj and Câţcău –Cluj, respectively) had copper concentration values over the critical limit.

CONCLUSION

There were investigated some quality parameters (alcohol concentration, relative density, total dry extract, pH and total acidity) as well two safety markers (organo chlorinated pesticides and heavy metals - lead and copper) from nine different homemade brandies. The methods used were routine determinations for quality analysis while, gas-chromatographic (GC-FID) quantitative evaluation of organochlorinated pesticides and atomic absorption analysis for heavy metals. We found generally acceptable quality parameters, included in the standardized limits, while for safety, three samples contained residues of organochlorine pesticides and all were plum brandies: Petreşti (Cluj), Beclean (Bistriţa-Năsăud) and Seini (Maramureş). We noticed that Ocoliş *pălinca* it has the highest alcoholic concentration, with no organochlorine pesticides detected and with the levels of Pb and Cu in the acceptable limits. Câţcău *pălinca* had the lowest alcohol concentration but with no organochlorine pesticides detected and with the levels of Pb and Cu in acceptable limits. Further investigations will be focused more on safety parameters of a larger number of samples from Transylvania.

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