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Review

Methanol in Grape Derived, Fruit and Honey Spirits: A Critical Review on Source, Quality Control, and Legal Limits

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Abstract: Spirits are alcoholic beverages commonly consumed in European countries. Their raw materials are diverse and include fruits, cereals, honey, sugar cane, or grape pomace. The main aim of this work is to present and discuss the source, quality control, and legal limits of methanol in spirits produced using fruit and honey spirits. The impact of the raw material, alcoholic fermentation, and the distillation process and aging process on the characteristics and quality of the final distilled beverage are discussed. In addition, a critical view of the legal aspects related to the volatile composition of these distillates, the origin and presence of methanol, and the techniques used for quantification are also described. The methanol levels found in the different types of spirits are those expected based on the specific raw materials of each and, almost in all studies, respect the legal limits.

Keywords: spirits; manufacturing processes; volatile composition; methanol; human health; legal limits; quality control

1. Introduction

Alcoholic beverages have been consumed since ancient times and possess a social, economic, and cultural role in modern societies. However, since they naturally contain some alcohols that can be harmful to human health, legal requirements establishing their maximum limits and good manufacturing practices have been developed. Therefore, distilled alcoholic drinks must comply with several national and international decrees and other standards. Methanol, an alcohol with an odor similar to that of ethanol, has been described to exist in low concentrations in the human organism and occurs naturally at a low level in most alcoholic beverages, without conferring health risk [1]. However, the contamination of alcoholic beverages with methanol claimed more than 750 lives in 2019, reassuring the importance of the strict regulation of its concentrations [2]. Methanol is toxic by two mechanisms: (i) direct depression of the central nervous system, similar to that of ethanol poisoning; (ii) the metabolization to formic acid, via formaldehyde, which inhibits mitochondrial cytochrome c oxidase, causing hypoxia at the cellular level, metabolic acidosis, and several other metabolic disturbances [3]. This review is mainly focused on the impact that the raw material, the alcoholic fermentation, the distillation processes, and the aging process have on the characteristics and quality of the final beverage, namely in the methanol content. Moreover, a critical view of the legal aspects related to the origin, presence, and quantification techniques of methanol and its effect on human health is also presented and discussed.

2. Spirits: Definition and Main Categories

Spirit drinks, included in the large group of alcoholic beverages [4], are strongly linked to the agricultural sector and represent a very important economic outlet. Therefore, the composition, quality, safety, and reputation of spirit drinks must be very well defined and regulated.

A spirit drink is produced by alcoholic fermentation followed by distillation of several raw materials, mainly different parts of plants.

The European Union Regulation No. 787 of 2019 [5] sets out definitions for 44 different categories of spirit drinks, among which are wine spirit, brandy or *weinbrand*, grape marc spirit or grape marc, fruit spirit, and honey spirit.

Bearing in mind that the different legal definitions [5,6] of the several categories of spirits are not totally coincident, it was decided, in the present work, to follow the definitions of the European Regulation [5]:

- Wine spirit—spirit drink "produced exclusively by the distillation at less than 86% vol. of wine, wine fortified for distillation or wine distillate distilled at less than 86% vol";
- Brandy—spirit drink "produced from wine spirit to which wine distillate may be added, provided that that wine distillate has been distilled at less than 94,8% vol. and does not exceed a maximum of 50% of the alcoholic content of the finished product";
- Grape marc spirit—spirit drink "produced exclusively from grape marc fermented and distilled either directly by water vapor or after the water has been added and both of the following conditions are fulfilled: (i) each and every distillation is carried out at less than 86% vol.; (ii) the first distillation is carried out in the presence of the marc itself; (iii) a quantity of lees may be added to the grape marc that does not exceed 25 kg of lees per 100 kg of grape marc used; (iv) the quantity of alcohol derived from the lees shall not exceed 35% of the total quantity of alcohol in the finished product";
- Fruit spirit—spirit drink "(i) produced exclusively by the alcoholic fermentation and distillation, with or without stones, of fresh and fleshy fruit, including bananas, or the must of such fruit, berries or vegetables (ii) each and every distillation shall be carried out at less than 86% vol.".
- Honey spirit—spirit drink "(i) produced exclusively by fermentation and distillation of honey mash; (ii) it is distilled at less than 86% vol".

In a simplified way, the three main steps for obtaining a spirit are the selection and harvest of the raw material, alcoholic fermentation, and the distillation processes.

Distillation can be carried out in batches or on a continuous basis [7]. Copper Charentais alembic (French style) and batch distillation columns (German-style) can be used [8–10]. Additionally, several previous studies showed the importance of some parts of the distillation apparatus being made with copper [7,8,11].

Despite a great European tradition in the production of wine spirits and brandies, its production is currently spread all over the world [12]. Regarding the grape marc spirit, its production has a strong tradition in many south European countries. There are several geographical indications registered for this spirit drink, namely *Orujo* in Spain, *Grappa* in Italy, *Tsipouro* and *Tsikoudia* in Greece, *Eaux de vie de marc* in France, *aguardente bagaceira* in Portugal, *Zivania* in Cyprus, and *Torkolypálinka* in Hungary [9].

In Europe, there is also an ancient tradition in fruit spirits production. For example, in Italy there are apple spirits [13]; in Greece mulberry spirits [14]; in Portugal *aguardente de medronho,* and in Spain *aguardiente de madroño*, a spirit made from *Arbutus unedo* L. fruits [11,15–17]. Additionally, in Greece, this spirit is produced with the traditional name of *koumaro* [18]. Other products like the plum *Prunus domestica* may be applied for the production of alcoholic beverages. This kind of distillates are traditional in different countries, having different designations depending on the country or geographic region, e.g., *pálinka* (Hungary), *rakia* (Balkan countries), *slivovica* or *slivovitz* in Eastern and Central European countries, being *sljivovica*, the most popular brandy in Bosnia and Herzegovina [19]. Nowadays, honey spirits are barely found on the market, but they have interesting characteristics and could be an alternative to outflow the honey production [15,20,21] given their higher content of sugars [22].

3. Methanol: Source and Impact on Human Health

Methanol is an alcohol, a small molecule with a boiling point of 64.7 °C, which is formed naturally from pectic substances, which exist in plants and fruits, particularly in the solid parts of the fruits [23,24]. Pectin is a branched heteropolysaccharide consisting of long-chain galacturonan segments and other neutral sugars such as arabinose, xylose, rhamnose, and galactose. It contributes to the cell structure and forms a matrix with cellulose and hemicellulose fibers [25,26]. In healthy individuals' methanol and formaldehyde, its short-lived oxidized products are naturally occurring compounds. The main sources of exogenous methanol in the healthy human organism are fruits, vegetables, and alcoholic beverages [27]. Indeed, methanol is usually present in alcoholic beverages (yet in much lower concentrations in the honey spirit) in a concentration that depends on the raw material used in their production [28].

When juices are extracted and during fermentation, the hydrolysis of chemical groups of pectic substances occurs naturally, through the action of pectin methylesterases (PME), enzymes that naturally exist in plants. Cleavage of methyl-ester bonds of the galacturonic acid units of the pectin backbone leads to the release of free methanol into the medium, which, being volatile, passes easily to the distillate during the distillation process [23,27].

In humans, methanol is metabolized by the alcohol dehydrogenase 1b (ADH1b) into toxic formaldehyde [29]. This metabolite is responsible for carcinogenesis and age-related damage to neurons in the brain [30].

Methanol and ethanol are very similar compounds from a biological point of view. Indeed, they have the same target structures, possessing a very similar organic effect [31]. However, while ethanol is oxidized to harmless acetate in the process including conversion to acetyl-coenzyme A and further oxidation via the Krebs cycle, formate is the last product of methanol oxidation. Formate is a chemical toxicant that can react with several target structures such as the mitochondrial cytochrome oxidase [32]. Besides that, formate is responsible for two typical manifestations of methanol poisoning: dysfunction of the retina followed by irreversible damage and metabolic acidosis [31,32]. Accumulation of methanol in the blood can cause hyperosmolality, and accumulation of its metabolites can cause an increase in the anion gap and a decrease in serum bicarbonate concentration and this abnormality is an important diagnostic clue in methanol intoxication. Furthermore, the accumulation of lactic and formic acids, formaldehyde, and ketones leads to metabolic acidosis and favors retinal damage [33].

Inhaled methanol is eliminated mainly by metabolism (70–97% of the absorbed dose); only a small fraction is eliminated unchanged in the urine and expired air (3–4%) [32,34]. The quantification of methanol and ethanol contents in the human breath after the consumption of different amounts of fruits and alcoholic beverages showed that methanol concentrations increased from a physiological level (0.4 to 2 ppm) a few hours after eating approximately 0.5 kg of fruits. Similar levels were found after drinking 100 mL brandy containing 24% ethanol and 0.19% volume of methanol [32].

As methanol is a neurotoxic substance, especially affecting the human retina, several situations of methanol poisoning have been detected, associated with the consumption of adulterated alcoholic beverages. For this reason, it is very important to know the factors that can influence the content of methanol in spirits, as well as to always determine its content before reaching the final consumer. Of paramount importance is also the establishment of legal limits for the concentration of methanol in alcoholic beverages (Table 1).

The maximum tolerable concentration (MTC) of methanol in an alcoholic beverage would be 2% (*v/v*) by volume in an adult who consumes 425 mL standard measures of an alcoholic beverage containing 40% alcohol by volume over a period of two hours. Nevertheless, this value only allows a safety factor of 4 to cover variation in the volume consumed and for the effects of folate deficiency, illness, and other personal factors such as ethnicity. For example, the EU general limit for naturally occurring methanol is 10 g methanol/L ethanol (corresponding to 0.4% (*v/v*) methanol at 40% alcohol volume) [1].

The ingestion of alcoholic beverages, even those of high analytical quality, always results in ethanol, methanol, and formaldehyde contents increasing in the human blood. Recently, a review paper [31] devoted particular attention to lifestyle diseases related to ethanol and methanol, toxicology, and metabolic disruptions of situations where ethanol is inadvertently or criminally replaced by methanol.

4. Methanol: Spirits Occurrence and Legal Limits

Upon leaving the alembic, the distillates obtained from different raw materials are mostly made up of alcohol (ethanol) and water.

In addition to these two ingredients, the distillates have in their composition large tens of volatile compounds. The most abundant volatile compounds in these distilled spirits are the fusel alcohols, the fatty acid esters, together with acetaldehyde and methanol, and sometimes these compounds are called major volatile compounds.

In the major volatile compounds, quantified in the spirits, the methanol is normally included, as can be observed in Table 1. This table shows the maximum and minimum levels of various major volatile compounds, quantified in different types of spirits, obtained in Portugal. The major volatile compounds usually include various alcohols that result from yeast metabolism during the fermentation process, namely 2-butanol, 1-propanol, 2-methyl-1-propanol, 2-propene-1-ol, 1-butanol, and the isoamyl alcohols. They also include an ester and an aldehyde, respectively ethyl acetate with a characteristic varnish aroma, and acetaldehyde with an oxidized or green apple aroma, which are also formed during fermentation [35]. In the case of acetaldehyde, its content may increase due to oxidation processes, which may occur when the fermented or distilled product is kept in contact with air [28]. On the contrary, the methanol appears in spirits in varying contents, but it originates from enzymatic reactions of the raw materials [23,27].

The volatile composition of the distillates will reflect the raw material used, the technological conditions verified during alcoholic fermentation, and the distillation technique, these being compounds that allow the differentiation of different products and the control of their quality [36].

Table 1 summarizes the maximum and minimum levels of various volatile compounds, quantified in different types of spirits produced in Portugal.

Taking into account the toxicity of methanol, several countries impose maximum limits on their levels in spirit drinks.

The results of the determination of methanol, as well as other volatile compounds in spirits, are presented in relation to the ethanol content of the drink, expressed as compound weight per hL or L of 100% volume alcohol). Likewise, the legal limits established for methanol are expressed in g per hL of pure alcohol, with Table 2 showing the values for the different spirits.

Table 1. Major volatile compounds, quantified by GC-FID in different spirits analyzed in several research works.

Major Volatile Compounds (mg/L of 100% Volume Alcohol)	Wine Spirit [37]		Grape Marc Spirit [37]		Arbutus Spirit [16]		Honey Spirit [15]		Juniper Flavoured Spirit * [15,38]	
	Min.	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**	**Min.**	**Max.**
Ethanal	22.9	872.5	418.0	3549.2	180.0	580.0	31	33.6	0.0	1403.0
ethyl acetate	64.9	1976.7	619.1	5407.3	10,490.0	1170.0	291.1	303.7	0.0	3565.0
Methanol	**299.0**	**1239.1**	**3394.2**	**23,708.9**	**4870.0**	**8980.0**	**157.9**	**180.9**	**0.0**	**4550.0**
2–Butanol	0.0	266.7	0.0	233.9	0.0	0.0	0	0	0.0	0.0
1–Propanol	157.2	482.1	281.2	804.2	110.0	250.0	360.3	372.9	0.0	545.0
2-Methyl-1-propanol	340.9	956.3	395.2	1213.7	390.0	970.0	445.9	450.9	0.0	894.0
2-Propen-1-ol	0.0	47.7	0.0	26.1	0.0	0.0	0	0	0.0	0.0
1–Butanol	0.0	40.8	13.7	89.3	0.0	0.0	8.2	8.8	0.0	0.0
2 + 3-Methyl-1-butanol	1270.3	3138.7	514.2	4814.2	940.0	1650.0	3011.5	3118.7	55.0	5382.0

Min.—minimum; Max.—maximum; * a spirit made by macerating juniper berries in arbutus spirit, grape marc spirit, or wine spirit.

Table 2. Legal limits for methanol contents (in grams per liter of 100% vol. alcohol) in different spirits.

Country or Organization	Maximum Limit of Methanol (g/L of 100% Vol. Alcohol)	Spirit Beverage Applied
European Union [5]	2	Wine spirit and brandy
	10	Grape marc spirit
	10	Fruits spirits
	12	Fruits spirits produced from the following fruits: apricots (*Prunus armeniaca* L.), apple (*Malus domestica* Borkh.), plum (*Prunus domestica* L.), quetsch (*Prunus domestica* L.), peach (*Prunus persica* (L.) Batsch), mirabelle (*Prunus domestica* L. subsp. syriaca (Borkh.) Janch. ex Mansf.), pear (*Pyrus communis* L.), except for Williams pears (*Pyrus communis* L. cv 'Williams'), raspberry (*Rubus idaeus* L.), blackberry (*Rubus* sect. Rubus)
	13.5	Fruit spirits produced from the following fruits: quince (*Cydonia oblonga* Mill.), blackcurrant (*Ribes nigrum* L.), juniper berry (*Juniperus communis* L. or *Juniperus oxicedrus* L.), Williams pear (*Pyrus communis* L. cv 'Williams'), redcurrant (*Ribes rubrum* L.), elderberry (*Sambucus nigra* L.), rosehip (*Rosa canina* L.), sorb apple (*Sorbus domestica* L.), rowanberry (*Sorbus aucuparia* L.), wild service tree (*Sorbus torminalis* (L.) Crantz)
	-	Honey spirit
United States (Bindler et al., 1998) [39]	7	Grape white brandy
	7	Pear brandy
	7	Plum brandy
Australia and New Zealand (Pang et al., 2017) [40]	7	Other spirits, fruit wine, vegetable wine, and mead

In the United States, the allowed methanol concentration for distilled fruit spirits is 7 g/L of 100% volume [6,39]. In the same line, Australia and New Zealand proposed a limit of 7 g for the spirits [40]. Since 2008 [41], there have been EU limits on methanol (per liter of 100% vol ethanol) in different distilled spirits, which were recently updated [5] as follows: 13.5 g for some fruit spirits; 10 g for fruit marc spirits, and 2 g, the lowest allowed methanol content, for wine spirits and brandy. In the case of honey spirits, there is no limit for methanol content (Table 2).

Tables 3 and 4 present the methanol content found in wine spirits and brandies, grape marc spirits, fruit spirits, and honey spirits based on gathering data from several scientific publications.

Table 3. Methanol contents (in grams per liter of 100% vol. alcohol, % and g per liter) found in several fruit spirits (n-number of samples analyzed; min-minimum value; max-maximum value; avg—average result).

Fermented Product	g/L of 100 % vol. Alcohol				%		g/L			Reference
	n	min	max	avg	min	max	min	max	avg	
Plum	18	4.5	12.7							Coldea et al., 2011 [42]
	4				0.13	0.54				Tešević et al., 2005 [43]
	6	7.6	8.7							Satora et al., 2010 [44]
	29	2.9	11.4							Winterova et al., 2008 [45]
	5	1.0	5.5				0.55	4.17		Jung et al., 2010 [46]
	30	2.5	19.0							Kostik et al., 2013 [47]
	12	6.7	9.4							Popovic et al., 2019 [48]
	11	0.0	1.1							Balcerek et al., 2013 [49]
	24				0.19	2.39				Croitoru et al., 2013 [50]
Apple	4	6.0	11.9							Coldea et al., 2011 [42]
	13	6.8	10.1							Versini et al., 2009 [13]
	12	1.8	9.2							Winterova et al., 2008 [45]
	3				0.25	0.78				Croitoru et al., 2013 [50]
	10	4.6	9.9							Januszek et al., 2020 [51]
	12	4.3	11.5							Hang and Woodams, 2010 [52]
Pear	44	0.9	10.8							Winterova et al., 2008 [45]
	4	8.2	12.9							Coldea et al., 2011 [42]
	6	0.2	0.3							Garcia-Llobodanin et al., 2007 [53]
	9	4.3	10.4							Versini et al., 2012 [54]
	2				0.39	0.44				Croitoru et al., 2013 [50]
	10				0.61	0.96				Nikićević, 2005 [55]
Melon-juice	6	0.3	1.5							Hernandez et al., 2003, 2005, 2008 [56–58]
Melon-paste without skin	6	0.6	2.9							Hernandez et al., 2003, 2005, 2008 [56–58]
Melon-paste	6	1.0	4.7							Hernandez et al., 2003, 2005, 2008 [56–58]
Sweet cherry	31	4.5	10.7							Winterova et al., 2008 [45]
Sour cherry	21	4.4	8.8							Winterova et al., 2008 [45]
Apricot	16	6.7	12.1	0.00						Winterova et al., 2008 [45]
Jabuticaba	1	-		0.04						Asquieri et al., 2009 [59]
Red raspberry	1			1.14						Alonso et al., 2015 [60]
	1			1.14						Alonso et al., 2011 [61]
	1			3.50						Alonso et al., 2015 [60]
Blueberry (pulp)	1			2.61						Alonso et al., 2016 [62]
Black currant	1			1.67						Alonso et al., 2015 [60]
Black and red currant	5	2.7	6.0							Vulić et al., 2012 [63]
Orange	1									Croitoru et al., 2013 [50]
Cornelian cherry	5	2.4	7.7							Tešević et al., 2009 [64]
Passion fruit (pulp)	1			0.05						Viana et al., 2020 [65]

Table 3. *Cont.*

Fermented Product	g/L of 100 % vol. Alcohol				%		g/L			Reference
	n	min	max	avg	min	max	min	max	avg	
Arbutus unedo fruits	1			3.21						Alonso et al., 2011 [61]
	1			3.21						Alonso et al., 2015 [60]
	15	4.9	9.0							Caldeira et al., 2019 [16]
	2	8.1	10.2							Versini et al., 2011 [66]
		2.7	11.5							Soufleros et al., 2005 [18]
	4	8.3	10.2							Botelho et al., 2015 [67]
	6	7.6	8.6							Santo, 2010 [68]

Table 4. Methanol content (in grams per liter of 100% vol. alcohol, % and g per liter) found in wine spirits, brandy, grape marc spirit or grape marc and honey spirit (n-number of samples analyzed; min-minimum value; max-maximum value; avg—average result).

Spirit Type	Fermented Product	g/L of 100% vol. Alcohol				%		g/L			Reference
		N	Min	Max	Avg	Min	Max	Min	Max	Avg	
Wine spirits	Grape juice	38	0.3	1.2							Luis et al., 2011 [37]
		15	0.2	1.8							Belchior et al., 2015 [36]
		50								0.2	Garreau, 2008 [69]
Brandy	Grape juice	45	0.0	12.1							Kostik et al., 2013 [47]
		35	0.4	12.8							Kostik et al., 2013 [47]
		20	0.4	2.2							Kostik et al., 2013 [47]
Grape marc spirit or grape marc	Red grape marc	14						5.6	9.6		Geroyiannaki et al., 2007 [70]
		28								4.54	Cortés and Fernández, 2011 [71]
	Grape marc	15	0.4	7.2							Hang et al., 2008 [72]
		4	25.3	39.4							Da Porto et al., 2003 [73]
		8						2.2	6.3		Gerogiannaki-Chrisopoulou et al., 2004 [74]
		19	4.3	7.5				1.9	3.2		Diéguez et al., 2005 [75]
		11			7.5					3.4	Silva et al., 2000 [76]
		25	4	6.4							López-Vázquez et al., 2010 [77]
		4	5.8	7.9							López-Vázquez et al., 2010 [78]
		5	4.3	7.5				1.9	3.2		Diéguez et al., 2005 [75]
		6	1.7	14.9							Diéguez et al., 2001 [79]
		6	5.9	9.2				3.1	5.2		Orriols et al., 1991 [80]
		10	0.6	1.4							Apostolopoulou et al., 2005 [81]
					12.2					8.9	Silva et al., 2000 [76]
		48	3.4	23.7							Luis et al., 2011 [37]
		7	2.0	8.8							Rodríguez-Solana et al., 2012 [82]
		51				0.12	0.92				Da Porto, 2012 [9]
		6						0.9	4.5		Lukić et al., 2011 [83]
		38	7.4	7.9							Orriols et al., 2008 [84]
		13	0.7	2.4							Borsa et al., 2008 [85]
		24	4.3	6.2							Arrieta-Garay et al., 2014 [86]
		4						3.3	6.9		Cortés et al., 2010 [87]
		3	2.9	3.4							Lukić et al., 2011 [88]
	White grape marc	14						1.7	4.5		Geroyiannaki et al., 2007 [70]
		33								6.39	Cortés and Fernández, 2011 [71]
Honey spirit	Mead	2	0.16	0.18	0.17						Anjos et al., 2020 [15]
	Mead	6	0.0	0.14				0.0	0.06		Anjos et al., 2020 [21]

Taking into account that the methanol results from enzymatic reactions and the enzymes are present in the raw materials [89], the majority of the spirits present methanol, as displayed in Table 1, Table 3, and Table 4. An interesting exception is the honey spirits, which possess null or very low amounts of methanol. In fact, it has been reported that mead contains very low amounts of methanol (maximum of 136.87 g/L of 100% vol. alcohol, Table 1), which is expected to increase little when the fermentation is performed in the presence of pollen [90]. Bee pollen naturally occurs in honey and may also be added throughout the fermentation process to promote yeasts' growth. The presence of pollen, which contains low amounts of organic matter may explain the very low amounts of methanol that is detected in the honey spirits. Several factors have been reported to influence the amount of methanol of the fermented beverages among which: the temperature, the size of the raw material, the content of pectin, and the activity of pectin methylesterase, and the yeast strain involved in the fermentation process [91]. The content of pectin in bee pollen is residual, which may justify the lower methanol content of honey-based fermented products, in comparison to those developed using fruits.

The amount of methanol in these beverages could be also a good fingerprint to detect adulterations.

There are some fruits in which only the pulp is used for alcoholic fermentation and distillation, among these is passion fruit [92]. A similar procedure was used to produce wine spirit and brandies, which can explain their low amounts of methanol (Table 4). On the other hand, some spirits are produced after a fermentation process in the presence of peel and other solid parts of the raw material. This is the case of grape mark spirit and some fruit spirits such as arbutus spirit and that can explain the high values shown in Tables 3 and 4. In the development of melon spirits [56–58], it is also verified that the use of melon paste as a raw material originated in a spirit with high amounts of methanol (Table 3). However, most of the samples complied with the legal limits of Table 2.

5. Factors that Influence the Methanol Content in Spirits

The overall quality of the spirit, and, in this specific case, its methanol content, is influenced by several factors, namely the quality of the raw material, the conditions of the fermentation process, the time and the conditions between fermentation and distillation and, finally, the technological conditions during the distillation process.

5.1. Raw Material

Several fruits have been used to produce high-quality spirits such as banana, orange, guava, melon, and kiwi [7]. It is not possible to produce quality spirits without high-quality raw material, meaning that the plants, fruits, or honey used in the fermentation process must always be spoilage free (without deterioration). In addition, the state of ripeness of the fruit influences the quality of the spirits and the fermentation process. In the case of wine spirits, the grapes must be harvested with high acidity to allow good control of the fermentation process [36].

The use of pectinases in raw materials has been focused on by several authors. Usually, the application of enzymes intends a suitable fruit disintegration and an easy juice extraction. The influence of pectinase treatment on fruit spirits from apple mash, juice, and pomace was studied. Significantly higher methanol concentrations were obtained when the apple pomace is used. Moreover, higher methanol concentrations were found in spirits obtained from the pectinase treated mash, juice, and pomace of Crispin apples [93]. In another study, apple pomace spirits were made from dry pomace and selected yeast strains. According to the results of this study, treatment with enzymes with pectin methylesterase activity led to excessive levels of distilled methanol. Contrarily, lower concentrations of methanol were produced by the indigenous yeasts. Furthermore, apple pomace drying contributes to its preservation, allowing it to take advantage of the great quantity of raw material during a short season time [94].

Nikićević [55] and Andraous et al. [95] also verified that pectolytic enzyme addition to crushed Bartlett pear fruit resulted in an increase in methanol content of the pear spirits. Similar results were reached in works with apple spirits [95] and grape spirits [96].

The inhibition of enzymatic activity was also tested in order to reduce the methanol content in the spirits. Kana et al. [97] studied the heat treatment of must and verified a decrease of methanol when heat was applied to must in the absence of grape skins. The pasteurization of apple juice prior to alcoholic fermentation could significantly reduce the methanol content of the obtained spirit [52].

In pears spirits, it was verified that the methanol concentration is much higher in the distillations of fermented juices compared to the ones from concentrate juice. This may be related to the degradation of pectins which are removed from the concentrated pear juice during the production process [98].

In studies carried out with arbutus fruits, it was found that the use of very ripe fruits produced spirits with a higher methanol content [33], and in fact, several studies have shown that the enzymatic activity causes methanol increases during fruit ripening. Pectin methylesterases interact with PMEIs (pectin methylesterase inhibitors) to influence fruit development and ripening [99]. Moreover, fifteen distinct distillates were obtained from ten clones and five seedlings of *Arbutus unedo* L. and distillate composition variability seemed to be associated with the plant's variability [16].

Several works detected a significant effect of the fruit cultivar used in the methanol contents of the corresponding spirits. Janusek et al. [51], Hang et al. [52], and Versini et al. [13] detected a significant effect of apple cultivar in the methanol contents of the corresponding apple spirits. Additionally, differences in methanol amounts were assigned in grape marc spirits when using different marcs proceeding from different grape varieties [75,77,78,83] and in plum spirits from different plum varieties [48]. The fruit spirits produced from three black currant cultivars also presented differences in the methanol amounts [63], as well as in pear spirits produced from diverse pear varieties [54].

5.2. Alcoholic Fermentation

The technology and fermentation conditions will largely determine the quality of the spirit, namely its composition in methanol. Thus, for spirits that are originated from fermented products in which contact with the solid parts of the fruits or plants occur, and where there are naturally more pectic substances, the natural existence of a higher methanol content is expected. This group includes grape marc spirits and arbutus spirits, so their levels are usually higher (Tables 3 and 4), as well as the legal limits. In the case of wine spirits, in which the fermentation of white or red grapes always occurs with an open spout [36], that is, without contact with the solid parts, the levels of methanol are usually lower (Table 4), and the legal limit as well (Table 2). In the case of honey spirits, we start from a mead that usually does not contain methanol and, therefore, the corresponding distillate has zero or very low levels (Table 4), so there is no need to establish a legal limit (Table 2).

As mentioned for wine spirits, fermentation must take place without the use of sulfur dioxide in grapes or must, since its use would cause mercaptans to appear during distillation, with the development of unpleasant aromas. Microbial protection by fixing the acidity to high levels must be ensured up to the moment of distillation [36].

The influence of different yeasts isolated from fresh blue plum fruits (*Aureobasidium* sp.) and spontaneously fermenting plum musts (*Kloeckera apiculata* and *Saccharomyces cerevisiae*), as well as commercial wine and distillery strains, on the fermentation and volatile profile of plum brandies was also studied [44]. The most rapid fermentation occurred in musts inoculated with *S. cerevisiae*. Nevertheless, the highest concentration of ethanol was detected in samples after spontaneous fermentation (8.40% *v/v*). In fact, plum brandies obtained after spontaneous fermentation (carried out by *Kloeckera apiculata*) followed by distillation contained from 66.3 up to 74.3% *v/v* ethanol. After spontaneous fermentation, samples presented high levels of acetoin, ethyl acetate, and total esters, as well as low levels of methanol and fusel alcohols. *S. cerevisiae* strains resulted in increased levels of alcohols while non-Saccharomyces yeasts produced higher concentrations of esters and methanol. The final products obtained with distillery strain of *S. cerevisiae* were characterized by a well-harmonized taste and aroma and reached the highest scores on sensory analysis.

The pH level during the fermentation also has a significant influence on the methanol content of the obtained spirits [57]. Gerogiannaki-Chrisopoulou et al. [74] verified that the addition of citric acid before alcoholic fermentation diminished the methanol amount in the distillates of the fermented pomace of Moschato of Limnos, Moschato of Patras, Savatiano, and Asyrtiko.

Since the arbutus spirit making technology has been scarcely studied, a 2-year study in order to study the influence of water addition to fruits before its alcoholic fermentation was conducted [100]. The statistical analysis displays a significant effect of the water addition on the composition of the distillates. The distillates resulting from the fermentation of fruits with a water mixture presented higher pH, lower acidity, lower acetaldehyde quantities, and higher amounts in some fusel alcohols than those resulting from fruits fermented without added water.

5.3. From Fermentation to Distillation

During the period between fermentation and distillation, various chemical and enzymatic reactions may occur. Consequently, the composition of the fermented product may change, usually with negative consequences for the quality of the distillate. Therefore, it would be preferable that the distillation took place immediately after the end of fermentation.

In particular, and in the case of grape marc spirits, previous studies showed that the silage ensilage conditions greatly influence the quality of the spirits, with the reduction of the ensilage time being the most effective way to reduce the methanol content of the final beverage [36,76,79,87,101,102]. Equally, for the arbutus spirit, the recommendation is to reduce the time between fermentation and distillation as a good manufacturing practice [11]. Moreover, another study showed that increasing the storage time of fermented must before distillation enhanced the methanol content in plum spirits [103].

5.4. Distillation Process

Distillation technology is another factor that determines the quality of the distillate. In the fruit spirits production, the initial material for distillation is a fermented mash (or juice or must) that contains ethanol and water as its main compounds and a large number of other volatile compounds with different boiling points (e.g., acetaldehyde 20.8 °C and benzaldehyde 179 °C). These compounds, globally, are often referred to as congeners, and they confer authenticity and flavor. Some congeners are desirable in small quantities while others should be removed as much as possible during the distillation process, in head and tail fractions. It is difficult to measure the relative volatility for each individual component in a multicomponent mixture. According to Spaho (2017) [8], some reasons for that are the following: i) the aroma compounds are highly dependent on ethanol content in the liquid phase from which they vaporize; ii) the composition and concentration of compounds varies continuously with time, and; ii) compounds interact with themselves and between each other.

Several studies have shown that the composition of spirits is influenced by distillation conditions. At the beginning of the distillation process, the high volume of ethanol comes out of the still together with high volatile compounds. Though the time volume of alcohol is decreased followed by water, and low volatile compounds increase. During the whole process, the distillate is cut to three cuts or fractions: the head, the heart, and the tail [8,11,16,104]. The head contains a higher concentration of low boiling point components, mainly undesirable compounds that could provide distillates with an unpleasant, strong, and sharp flavor. In the first cut, there is a higher concentration of some toxic compounds, such as methanol, and consequently, such fraction must be rejected. The most valuable part of the run is the middle part of the distillation, the final spirit, known as the heart fraction. This possesses high ethanol content, with a pleasant scent and fruity aroma compounds. The last cut is the tail fraction, rich in unpleasant fatty and oil compounds, that must be eliminated. Water is the carrier of the longer molecules, which are frequently unpleasant [8]. Commonly, tail fractions (with or without head adding) are collected and redistilled, because they present a reasonably high concentration of alcohol and congeners which can be recovered.

In addition, the correct separation of the various distillation fractions (heads, hearts, and tails), as well as the correct maintenance of the distillation equipment are other important points [11,36]. The distillation fractions have a very different composition [16,21,33,105] knowing that unpleasant aromas are associated with the tails (final part of distillation), which detract from the quality of the spirit [105].

A similar methanol pattern of variation during the distillation was assigned for different spirits [16,36,40,70,80,81,88,105,106]. The methanol content varies throughout the distillation (Figure 1), with a tendency for a slight decrease, but remaining present throughout the distillation. Since the decrease in ethanol over distillation is more pronounced (Figure 1A1) than that of methanol when it is expressed in relation to pure alcohol, we can say that the methanol content increases during distillation. The distillation system used seems to have no effect on the methanol contents [86].

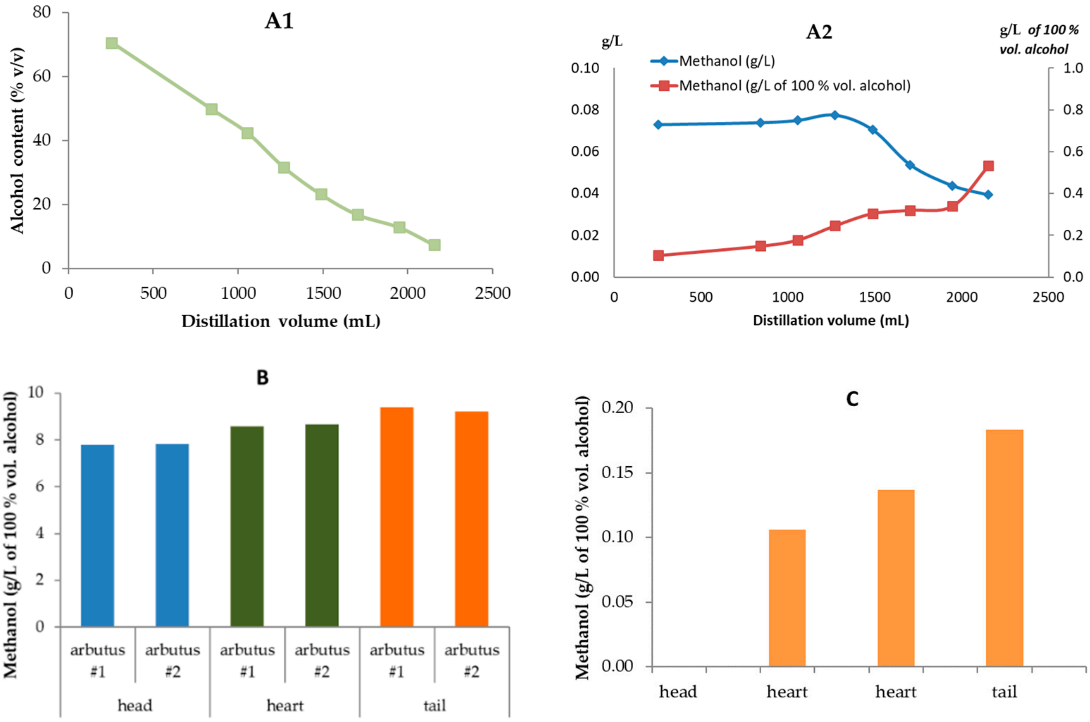

Figure 1. Variation of ethanol (**A1**) and methanol (**A2**,**B**,**C**) contents over distillation to obtain different spirits (**A**-wine spirit; **B**-arbutus spirit and **C**-honey spirit).

The distillation of some spirits could be done in the presence or absence of the lees and that could also influence the composition of the obtained spirit. In pear distillates, it was verified that methanol diminishes or does not change its concentration when the distillation was in the presence of lees, for all of the distillation equipment tested [53].

Since the methanol is present during all the distillation, some researchers applied re-distillation processes in order to reduce the methanol content of the obtained spirits [107].

5.5. Wood Aging Process

Some types of spirits are generally placed in appropriate wooden casks, where the spirit is kept for a certain period aiming to refine its sensory profile and to improve its chemical quality. This process is called aging or maturation.

The maturation of distilled beverages in wooden casks is an important step of the production process. Indeed, the sensory profile of fresh spirit is quite different from those obtained after the aging time. Several physicochemical interactions between the wood and the spirit during aging, including migration of volatile and non-volatile compounds of wood to spirit. During maturation, the evolution of phenolic compounds, beverage oxidation, color and flavor modifications, and the development of new sensory notes, such as woody, vanilla, and others contribute to the richness and complexity of the distilled beverage's aroma [108–110].

The quality of fresh spirit is very controlled before aging and consequently, the methanol content must respect all the limits mentioned in Table 2. Accordingly, most aging studies are more focused on volatile compounds that come from the wood and only a few works evaluated the methanol evolution during the aging process. Some studies reported a tendency for low amounts of methanol in more aged spirits [111,112]. The authors attributed this decrease to the methanol oxidation and subsequent acetalization reaction with the formation of diethoxymethane. In fact, Puech et al. [112] found high amounts of 1,1- diethoxymethane in spirits with many years of aging. This is corroborated by the null changes in methanol content of cider spirits throughout the entire maturation period when inert containers are used without the presence of oxygen [113]. Additionally, Balcerek et al. [114] verified a decrease in the concentration of methanol in the majority of samples during the aging time with alternative aging processes applied to plum spirits.

6. Methanol Quantification in Spirits

6.1. Current Methods

Methanol is a volatile compound that should be well monitored in spirit drinks according to the aforementioned standards and regulations. The determination of methanol is usually carried out using high-performance gas-liquid chromatography [115]. Methanol concentrations expressed in grams or milligrams per liter (mg/L) or mg/L of 100% vol. alcohol is usually evaluated using the Internal Standard (IS) method [116,117]. The IS more frequently used are the 4-methyl-2-pentanol or 2-octanol as IS [37,78,109,118]. However, 1-octanol [119], 2-pentanol [120], or 4-nonanol [121] could also be used as the IS.

Because the introduction of the IS compound in low dose is not easy given its volatility, the method of External Standard (ES) is also used [122]. Nevertheless, in both methods, it is mandatory to determine alcohol strength by volume (% *v/v*) of the analyzed sample [116,117].

In summary, the fulfillment of good manufacturing practices in the production of spirits, whatever its origin, has two advantages that should be highlighted: the reduction of the content of methanol and other constituents harmful to its quality (analytical and sensory) and to increase the guarantee of a final product complying with the legal limits.

6.2. Methanol Quantification by Vibrational Spectroscopy

Methanol content could also be detected by vibrational spectroscopy. Vibrational spectroscopy (namely NIR, FTIR ad RAMAN) has been used in numerous studies to forecast the chemical composition of different beverages due to the accessibility of quick results, the minimum sample preparation, and the consequent low associated costs [123,124]. Besides, the use of vibrational spectroscopy leading to a specific and characteristic spectrum for each sample or matrix to be connected to the molecular bonds of its chemical constituents [124] and different methodologies give additional information. As an example, in Figure 2, there is spectra of wine spirit aging in oak for six months, acquired with Fourier transform infrared (FTIR) spectroscopic method with attenuated total reflectance (ATR), near-infrared spectroscopy (NIR), and FT-RAMAN. These techniques have been used to assess spirits' features and some studies are focused in the methanol determination given their importance and legal limits.

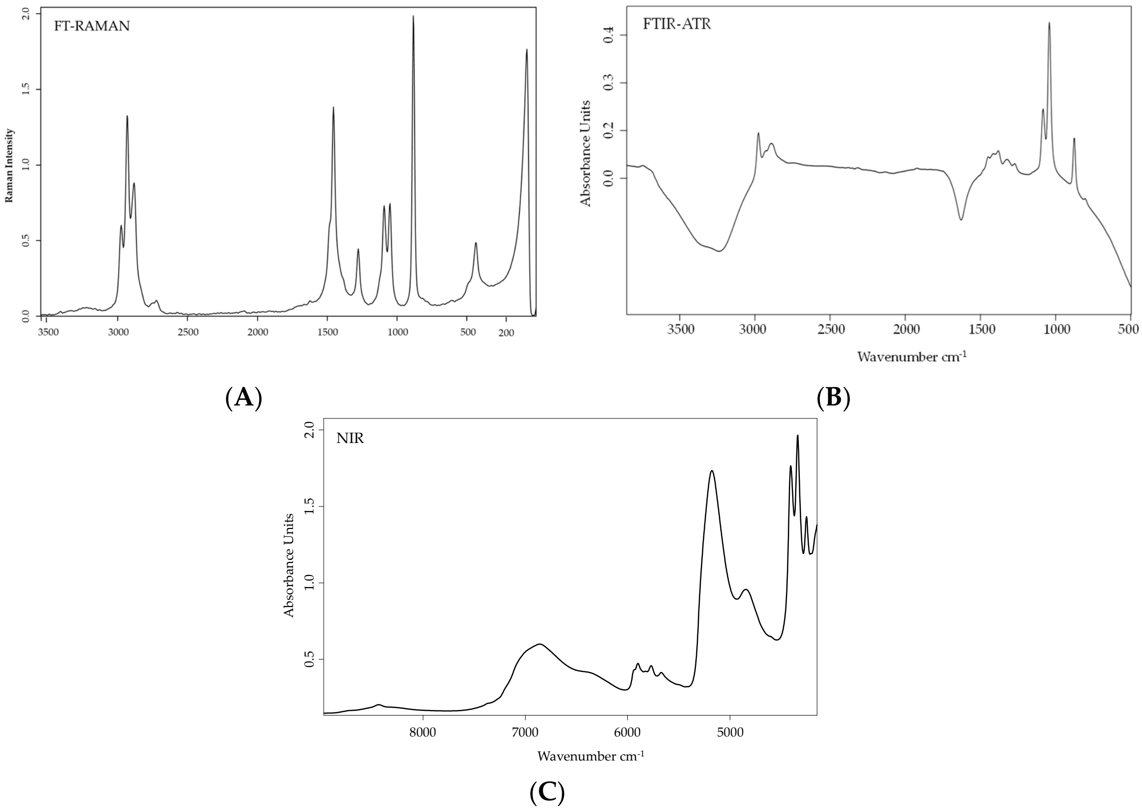

Figure 2. Spectra of wine spirit with 3 months of aging in wood collected in (**A**) FTIR-ATR [125]; (**B**) FT-RAMAN [21] and (**C**) NIR [126].

The NIR technique has been used to estimate the alcohol and methanol contents in brandies and other distilled beverages [127,128]. Nordon et al. [129] in their work made the comparison between Raman spectrometry and NIR to assess the alcohol strength of whiskies, vodkas, and other alcoholic drinks. Only a small number researchers used vibrational techniques to quantify or identify methanol content in spirits and are listed below separated by technique.

(a) Using FTIR-ATR:

- Lachenmeier [130] applied the FTIR spectroscopy in combination with multivariate data analysis to assess the quantification of parameters density, ethanol, methanol, ethyl acetate, propanol-1, isobutanol, and 2-/3-methyl-1-butanol of spirit drinks. The calibration model obtained presented an r^2 of 0.997 for cross-validation and 0.981 test-set validation;
- Coldea et al. [131] applied FTIR spectroscopy and chemometrics techniques to evaluate the quality of fruit spirits traditionally produced in Romania. In this study, the methanol fingerprint was identified in the 1020 and 1112 cm^{-1}. Using PLS regression, these authors found that the FTIR spectra could be useful for authenticity control of the provenience region and the type of the fruit spirit;
- Anjos et al. [132] used FTIR-ATR in the spectral region of 4000 to 400 cm^{-1} to forecast the alcoholic strength, methanol content, acetaldehyde, and fusel alcohol content of grape mark and wine spirits, applying partial least square (PLS). For methanol content, a very good model was obtained using the peaks at 1085 and 1043 cm^{-1} corresponding to the C–O stretch absorption bands, with r^2 of 99.2 and ratios of performance to deviation (RPD) of 11.1.

(b) Using RAMAN:

- Boyaci et al. [133] proposed a method for direct quantification of ethanol and methanol in distilled alcoholic beverages. In this research, calibration models for ethanol and methanol concentrations in the ranges of 0–7 M and 0–10 M, respectively, were performed. An r^2 value of 0.998 for ethanol and 0.998 for methanol for linear correlations were plotted. The aforementioned authors used the important bands of methanol at 1019 cm^{-1} that corresponded to C–O stretching;
- Goes et al. [134] used Raman spectroscopy and a statistical procedure based on principal component analysis to determine the presence of methanol content in beverages;
- Song et al. [135] used handheld Raman spectroscopy, with an excitation laser emitting at 1064 nm to online detect methanol content in a spirit. For their analysis, they used the spectral information located at 1074.6 cm^{-1} (bending vibration of C-O-H). The prediction of methanol concentration was made with an r^2 of 0.999. More recently, Ellis et al. [136] proposed a methodology for through-container detection of fake spirits and methanol quantification with handheld Raman spectroscopy. These authors used the peak at 1030 cm^{-1} assigned to the methanol C–O stretching vibration, to make their validation. In this study, the PLS model developed had an r^2 between 0.9518 and 0.9734.

(c) Using NIR:

- Yang et al. [128], applied multivariate calibration in data collected with two-dimensional NIR, to make the determination of methanol in white spirit. In this study, the N-way partial least squares technique was applied to the impure methanol solution; the obtained average relative error and root mean square error was 2.97 and 0.064%, respectively. They concluded that the adulteration level by methanol was taken in the region of 4300– 4450 cm^{-1}.

7. Conclusions

Methanol is a naturally occurring substance in all fruit spirits and honey spirits, although in honey spirits, the average quantity is much lower. From the point of view on human health, it can be concluded that according to practically all the bibliography referred across this paper, the spirits produced are safe for the consumer, respecting the legal limits imposed for methanol. The good manufacturing practices followed during the production chain of spirits have assumed a fundamental role to achieve products of suitable quality. With this revision, it was intended to contribute to the global vision on the importance of continuing to carry out rigorous work with high analytical control, based on classical (gas chromatography) or new approaches, such as vibrational spectroscopy (e.g., NIR, FTIR, RAMAN), to guarantee the quality of the spirits produced worldwide.

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