Methanol in Wine

1 Abstract

This paper examines the origins of methanol in grape wine and the quantities typically found in it, as well as in other foods such as unpasteurised fruit juices. The toxicology of methanol and the associated regulatory limits established by competent authorities in various parts of the world are also considered. It is concluded that such limits are not driven by public health considerations.

In conclusion, authorities are requested to consider the need for methanol analyses to be performed and reported on certificates of analysis as a condition of market entry for wine. Where methanol limits are still deemed to be necessary to achieve policy objectives, authorities are encouraged to establish them in the light of the levels of methanol typically found in grape wines produced by the full array of internationally permitted winemaking practices, and to consider harmonising their limits with those that have already been established by other governments or recommended by appropriate intergovernmental organisations.

2 Introduction

The origin and significance of methanol in wine, and the associated establishment of regulatory limits for its presence there, is a cause of much confusion and misunderstanding in international trade. This paper, produced by the FIVS[1] Scientific and Technical Committee, examines the topic in some detail, providing reference materials to assist with further study. It concludes that the levels of methanol commonly found in grape wines are broadly similar to those that may be found in many freshly squeezed and unpasteurised fruit juices if they are stored for a period of time after squeezing. It is further demonstrated, from a comparison of regulatory limits for methanol in wine with food safety risk assessments that have been conducted by reputable bodies, that the limits themselves do not serve any real food safety purpose. This is because many litres of wine per day or even per hour would need to be consumed (even if the product contained the highest content of methanol permissible in regulations) to even approach levels of any known toxicological concern. [2]

3 Chemical Properties and other information for Methanol

Methanol is chemically characterized as follows:[3]

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[1] FIVS (www.fivs.org) is an international federation serving trade associations and companies in the alcohol beverage industry from around the world. It provides a forum for its members to work collaboratively on legal and policy issues and communicates Federation views to national governments and international organisations.

[2] Andrew L. Waterhouse, Gavin L. Sachs and David W. Jeffery, *Understanding Wine Chemistry* (Chichester: John Wiley & Sons Ltd, 2016), 54.

[3] R. G. Todd eds., *Extra Pharmacopoeia (Martindale,) 25th Ed* (London: The Pharmaceutical Press, 1967), 85-86.

3.1 Chemical Formula, Synonyms, CAS Registry number

Chemical formula: CH_30H

Synonyms: Methyl alcohol, Carbinol, Wood alcohol

CAS Registry Number: 67-56-1

3.2 Physico-chemical properties

Physical appearance: methanol is a colourless liquid with characteristic odour

Melting Point: -98°C

Boiling Point: 65°C

Solubility in water: miscible

4 Origin of Methanol in wine

4.1 Action of Pectinase Enzymes

4.1.1 Action of natural pectinase enzymes on pectin in grapes

Methanol is produced before and during alcoholic fermentation from the hydrolysis of pectins by pectinase enzymes (such as methyl pectinesterase) which are naturally present in the fruit. More methanol is produced when must is fermented on grape skins; hence there is generally more in red wines than in rosé or white wines (See Section 5 below).

4.1.2 Use of exogenous pectinase enzymes in winemaking

Exogenous pectinase enzymes are permitted for use in winemaking (generally as clarifying agents) in at least the following countries: Australia, Canada, the 28 Member States of the European Union, Japan, the Republic of Georgia, New Zealand, South Africa, and the United States. Their use is also deemed to be an acceptable winemaking practice by the International Organisation for Vine and Wine (OIV). [4] As with the activity of pectinases naturally present in grapes, the use of exogenous pectinases as a winemaking practice will have the effect of increasing the levels of methanol in the resulting wine.

4.2 Treatment of wine with Dimethyldicarbonate

Dimethyldicarbonate (DMDC) is an effective pre-bottling sterilant, accepted for use in Argentina, Australia, Cambodia, Canada, Chile, the 28 Member States of the European Union, the Republic of Georgia, Hong Kong China, Myanmar, New Zealand, Russia, Singapore, South Africa, Thailand, Turkey and the United States, whose use is generally limited in international regulations and recommendations to a maximum treatment of 200 mg/L of wine.[5] For other alcoholic beverages and

[4] Data on wine production and pectinase usage. FIVS-Abridge, a database of national regulations and relevant international agreements for markets around the world, covering topics such as certification, composition, labeling, marketing, packaging, production, promotion, tariffs, taxation and transportation. http://www.fivs-abridge.org (accessed on August 5, 2016).

[5] Data on wine production and DMDC usage. FIVS-Abridge, a database of national regulations and relevant international agreements for markets around the world, covering topics such as certification, composition, labeling, marketing, packaging, production, promotion, tariffs, taxation and transportation. http://www.fivs-abridge.org (accessed on August 5, 2016).

mixtures of alcoholic and other beverages with an alcoholic strength by volume of less than 15%, the limit on usage is often set at 250 mg/L. The use of DMDC can be important in stabilizing lower alcohol products from additional fermentation in the bottle, and also allows a reduction in the quantity of sulphur dioxide that is used where the oxygen in wine is kept below 1 mg/L. DMDC breaks down rapidly in wine, producing carbon dioxide and leaving methanol at very low levels not harmful to health and other innocuous products in the wine. Methanol at a level of about 100 mg/L is created in wine from a DMDC treatment at the typical maximum treatment level of 200 mg/L.[6]

5 Typical levels of methanol in wine

It was noted above that the presence of low levels of methanol in wine is expected due to the action of pectinase enzymes that are naturally present in the grapes. A study of the literature indicates the following information concerning the typical levels of methanol that may be found in wine (these levels generally do not account for any additional amount that may result from a DMDC treatment):

- Red wines will tend to contain more methanol (between 120 and 250 mg/L of the total wine volume) than white wines (between 40 and 120 mg/L of the total wine volume), because of the longer exposure to grape skins during the fermentation.[7]
- Wines made from grapes that have been exposed to *botrytis cinerea* (e.g. late harvest wines, Sauternes) also have higher methanol levels than standard grape wines (as much as 364 mg/L of the total wine volume).[8]
- Wines made from non *vitis vinifera* grapes tend to contain more methanol than wine from pure *vitis vinifera* [9]

6 Typical levels of methanol in fruit juices

In comparison with the quantities found in wine, non-alcoholic fruit juices naturally contain an average of 140 mg/L of methanol, in a range from 12 mg/L to as much as 640 mg/L. This is quite similar to the average methanol level in white wine and within the range of values seen for red wines. [10,11,12]

7 Toxicology of methanol

Methanol is a toxic chemical. Acute methanol poisoning symptoms resemble those of ordinary alcoholic intoxication followed by the presence of severe upper abdominal pain, visual disturbance

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[6] EFSA Panel on Food additives and Nutrient Sources added to Food, "Scientific opinion on the re-evaluation of dimethyl dicarbonate (DMDC, E 242) as a food additive," *EFSA Journal 2015*, Volume 13, Issue 12, 11.

[7] W. R. Sponholz, "Der Wien 4.3. Fehlerhafte und unerwünschte Erscheinungen im Wein," *in Chemie des Weines*, eds. G. Würdig and R. Woller (Stuttgart: Ulmer, 1989), 385-411.

[8] B. Zoecklein et al, eds., *Wine Analysis and Production* (London: Chapman & Hall, 1995), 107.

[9] P. Ribereau-Gayon et al, eds., *Handbook of Enology Volume 2: The Chemistry of Wine Stabilization and Treatments 2nd Edition* (Chichester: John Wiley & Sons Ltd, 2006), 53.

[10] Chih-Yao Hou, Yeong-Shenn Lin, Yuh Tai Wang, Chii-Ming Jiang and Ming-Chang Wu, "Effect of storage conditions on methanol content of fruit and vegetable juices," *Journal of Food Composition and Analysis*, Volume 21, Issue 5, (August 2008), 410–415.

[11] NPCS Board of Consultants & Engineers*, The Complete Technology Book on Alcoholic and Non-alcoholic Beverages (Fruit Juices, Whisky, Beer, Rum and Wine,* (Delhi: Asia Pacific Business Press Inc., 2008), 712.

[12] J. J. Clary, *The Toxicology of Methanol* (Chichester: John Wiley & Sons Ltd, 2016), 48.

sometimes proceeding to incurable blindness and prolonged coma, which may terminate in death from respiratory failure. The fatal dose varies but is usually from 100 mL to 200 mL. Permanent blindness has been claimed to have been caused by as little as 10 mL. The toxicological properties of methanol are mediated by those of ethanol, and patients suffering from methanol poisoning may sometimes be treated by administration of ethanol. [13,14]

According to a paper produced by the United Nations World Health Organization International Programme on Chemical Safety[15], it is difficult to do a risk assessment on methanol because the chemical itself and its primary metabolites of concern are naturally present in humans – a fact that pre-supposes a certain level of these substances poses no toxic risk. In this paper, the authors propose a level of methanol intake that is of insignificant risk to humans, in that it causes no increase in the most toxic metabolite (formic acid) above the normal background levels found in humans. That intake level is a single oral exposure of 20mg/kg body weight. This represents 1400mg for an individual weighing 70kg. To receive this amount of methanol from a wine containing 400 mg/L methanol (the methanol limit for red wines recommended by OIV – see Section 8), that individual would need to consume 3.5 litres of wine in a single oral exposure.

According to the European Union Scientific Committee on Food,[16] a healthy individual can metabolize 1500 mg per hour of methanol without showing any ill effects. Note that 1500mg of methanol is approximately the amount of methanol contained in 3.75 litres of a wine with a methanol content of 400mg/L (the methanol limit for red wines recommended by OIV – see Section 8). This volume of wine would have to be consumed in one hour to ingest more methanol than a healthy individual could metabolise with no ill effects.

The Food and Drug Administration of the United States of America (FDA) reported that the No Observed Adverse Effect Level (NOAEL) in humans for methanol is 71 to 84 mg/kg body weight (bw)/day. Because this NOAEL was derived from studies in humans, the FDA developed an Acceptable Daily Intake (ADI) of 7.1 to 8.4 mg/kg bw/day by using a safety factor of 10.[17] Note that an individual weighing 70kg would have to consume about 1.25 litres of wine (almost 2 bottles) a day with a methanol content of 400 mg/L (the methanol limit for red wines recommended by OIV – see Section 8) to reach the low end of this ADI range.

8 Regulatory limits established for methanol levels in wine

The table below summarizes the limits set for methanol in wine in different global markets. It is clear that most economies and regions have established limits that take account of the levels of methanol

[13] Public Health England. *Methanol: Toxicological Overview*, (August 2015), 3.
[14] Public Health England. *Methanol: Incident Management*, (May 2016), 8.
[15] United Nations Environment Programme, International Labour Organisation, World Health Organization. International Programme on Chemical Safety, *Environmental Health Criteria 196: Methanol*, (1997). http://www.inchem.org/documents/ehc/ehc/ehc196.htm (accessed August 5, 2016).
[16] European Commission Scientific Committee on Food. *Opinion of the Scientific Committee on Food on the use of dimethyl dicarbonate (DMDC) in wines*, (2001). http://ec.europa.eu/food/fs/sc/scf/out96_en.pdf (accessed August 5, 2016).
[17] Federal Register 58, No. 204, (January 26 1993), 6088–6091.

typically found in wine, and make additional allowances for the possible use in production of exogenous pectinase enzymes and of DMDC, as mentioned earlier in this paper.[18]

Methanol limits based on volume of wine	
Argentina, Chile, China, India, Vietnam, OIV	400 mg/L of wine (Red) 250 mg/L of wine (White and Rosé)
Canadian Provinces (Ontario, Quebec)	400mg/L of wine
Japan, Korea, USA	0.1% (or about 1000mg/L) of wine
Republic of Georgia	0.05 mg/kg
South Africa	300 mg/L of wine
Switzerland	300mg/L of wine (Red) 150 mg/L of wine (White and Rosé)
Thailand	420 mg/dm^3
Turkey	10 mg/kg (about 10mg/L) of wine
Limits based on alcohol content of wine	
Australia, Mexico, New Zealand, Singapore,	3 g/L of ethanol
Chinese Taipei	2 g/L of ethanol
Indonesia	0.1% based on ethanol

9 Purpose of Methanol Limits for Wine

Comparing the toxicological information in Section 7 with the limits that have been established for methanol in wine (Section 8), it seems clear that the purpose of these limits is not to protect public health. This is because an individual weighing 70 kg would have to drink 1.25 litres of red wine a day containing the OIV recommended limit amount of methanol (400mg/L) in order to reach the lowest ADI value derived by the FDA. According to the paper produced by the World Health Organization International Programme on Chemical Safety, a single oral exposure to 3.5 litres of this wine would not cause an increase in background levels of formic acid (the most toxic metabolite of methanol) in that consumer. Finally, the European Commission Scientific Committee on Food data suggests that the individual would have to consume 3.75 litres of the same wine in an hour to ingest more methanol than the 1500 mg that individuals can metabolize without ill effects.

If the methanol limits that have been established for wine do not represent a public health protection measure, it may be asked what purpose they actually serve. In practice, it seems possible that at one time they were intended to serve as an index of appropriate fruit handling in harvest and subsequent processing. In Section 4.1.1., the action of endogenous pectinases in forming methanol in wine was reviewed. Such enzymes will be liberated, and methanol generated, whenever fruit is damaged during its growth, its journey from the vineyard to the winery and in subsequent processing. It is recorded that fungal diseases that attack grapes in the vineyard most likely result in higher levels of methanol in the resulting juice and wine[19], and in Section 5 it was noted that late harvest wines (where fungal

[18] Data mostly taken from wine composition tables in FIVS-Abridge, a database of national regulations and relevant international agreements for markets around the world, covering topics such as certification, composition, labeling, marketing, packaging, production, promotion, tariffs, taxation and transportation. http://www.fivs-abridge.org (accessed on August 5, 2016).

[19] Maynard Andrew Amerine and Maynard Alexander Joslyn, *Table Wines: The Technology of Their Production*. (California: University of California Press, 1970), 435.

pressures will be more pronounced as the grapes remain longer in the vineyard) tend to have higher methanol contents. Therefore, methanol content in wine may be expected to be higher where the fruit has been damaged either by moulds in the vineyard or by rough handling at harvest and during transportation to the winery.

The possibility of methanol limits historically serving as indices of appropriate fruit handling in wine production seems to be supported by the fact that many authorities differentiate between red wines on the one hand, and white wines and rosés on the other, establishing different methanol limits in each case. If the limits were purely set for toxicological reasons, there would be no need to do this; a single limit for methanol in wine would be appropriate regardless of whether it was white, rosé or red.

In Section 4 it was mentioned that it is widely permitted to add exogenous pectinase enzymes in wine production and also to use DMDC as a pre-bottling sterilant, and that both of these processes, if used, will contribute somewhat to the total methanol content of wine (in recognition of which, governments and other appropriate intergovernmental bodies have increased their limits for methanol in wine). It is clear, therefore, that there will no longer necessarily be such a clear relationship between a wine's content of methanol and the appropriateness of fruit handling in the harvest and production of that wine.

As we have seen, even wine containing the maximum allowable methanol content by regulation never has a high enough concentration to give rise to public health concerns.

10 Conclusions

Methanol is produced quite naturally in wine by the action of endogenous pectinase enzymes on the grape pectins. The possible use of exogenous pectinase enzymes in the winery, as well as possible treatment of the wine with dimethyldicarbonate just prior to bottling, will have the effect of increasing the methanol content of the wine to varying degrees. Many competent authorities around the world have chosen to establish limits for the methanol content of wine, and many have chosen to establish different limits for red wines compared with white and rosé. Yet in each case, when compared with toxicological data, it is clear that the limits do not really serve to protect public health, because the methanol content in wine does not become sufficiently high to even approach a safety concern.

At least two possible future directions are suggested by the observations in this paper:

First, there is no public health necessity for competent authorities to require methanol analysis of wine as a condition of market entry, since no additional consumer safety will be obtained by such measures. It is true that there have been rare wine adulteration incidents involving wine historically but a wholesale requirement for methanol analysis at the border seems an excessive and costly approach to mitigate the possibility of such an event, which in any case may remain localized and not cross national boundaries.

Second, if authorities determine that it is necessary to retain these limits, international trade could be greatly facilitated by pursuing the following steps:

- Establishing limits that take account of the levels of methanol typically present in grape wines, and taking account of the full range of permitted winemaking practices that may be applied in their production.
- Given the wide variety of numerical values for existing methanol limits in wine, and of methods chosen for the expression of those limits (as revealed in the table in section 8), consider harmonising limits with those established by other competent authorities or appropriate intergovernmental bodies.

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