جامعة نايف العربية للعلوم الأمنية
Naif Arab University for Security Sciences

Naif Arab University for Security Sciences
**Arab Journal of Forensic Sciences & Forensic Medicine**
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الجمعية العربية لعلوم الأدلة الجنائية والطب الشرعي
Arab Society for Forensic Sciences and Forensic Medicine

Review Article

# Forensic Characterization of Liquor Samples by Gas Chromatography-Mass Spectrometry (GC-MS): A Review

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*Received 10 Oct. 2016; Accepted 27 Dec. 2017; Available Online 31 Dec. 2017*

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## Abstract

Alcohol is a subject of forensic research across the world. The forensic characterization of alcoholic beverages is required in cases of death and crimes due to alcohol consumption. In many cases, determining the geographic origin becomes a very important part of the investigation. Therefore, it is important to develop more sensitive methods for the analysis of alcoholic beverages. In this review, an attempt has been made to summarize the work accomplished so far in the field of analysis and detection of alcoholic beverages.

In this review, various sample preparation techniques for GC-MS analysis of alcoholic beverages have been discussed along with its applications. GC-MS based analysis is less time consuming, more sensitive and more accurate.

**Keywords:** Forensic Sciences, Alcoholic beverages, Mortality, Analysis, GC-MS

## التوصيف الجنائي للمشروبات الكحولية باستخدام الكروماتوغرافيا الغازية المقترنة بمطياف الكتلة (GC-MS) : مراجعة علمية

## المستخلص

دائماً ما يكون الكحول موضوعاً للبحث العلمي الجنائي في جميع أنحاء العالم. ويكون التوصيف الجنائي للمشروبات الكحولية مطلوباً في حالات الوفاة والجرائم الناتجة عن تعاطي الكحول. وفي كثير من الحالات، يصبح تحديد المنشأ الجغرافي جزءً هاماً جداً من التحقيق. لذلك، من المهم تطوير طرق أكثر حساسية لتحليل المشروبات الكحولية.

في هذه المراجعة العلمية، تم مناقشة العديد من تقنيات طرق تحضير عينات المشروبات الكحولية من أجل التحليل بواسطة الكروماتوغرافيا الغازية المقترنة بمطياف الكتلة مع تطبيقاتها. وفي هذا المجال تبقى هذه التقنية هي واحدة من التقنيات الأكثر فعالية لتحليل المشروبات الكحولية وتوفر أفضل تحديد لنوعية المكونات المتطايرة المختلفة (من ماذا ؟ مما تم مقارنته به؟). كما تعد الأقل استهلاكاً للوقت والأكثر حساسيةً والأكثر دقةً.

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doi: 10.26735/16586794.2017.011

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**الكلمات المفتاحية:** علوم الأدلة الجنائية، المشروبات الكحولية، الوفيات، التحليل، GC-MS.

## 1. Introduction

Alcohol has been a part of human society and culture for millennia. It is believed that the first alcohol must have been produced when bacteria consumed plant material nearly 1.5 billion years ago. The first evidence of manufacturing of alcohol comes from Mesopotamia, modern day Iraq, around 3500 BCE. Alcohol serves different roles in the life of an individual as well as the society as whole [1]. Heath observed that alcohol can at the same time be a food, a drug and a highly elaborated cultural artifact with important symbolic meanings [2]. Alcohol is used as a beverage served with meals, a thirst quencher, a means of socialization and enjoyment and as a means of intoxication [3,4]. Despite the grand status of alcohol in history, it has grown into a big threat to the society. It is being abused widely, which has resulted in adverse social and health effects [5].

Based upon its use, ethanol can be differentiated into fuel, the one used for scientific (research laboratories), or technical purposes; and ethanol which is used in alcoholic beverages. Ethanol, which is the main psychoactive component in alcoholic beverages, has attracted a lot of attention in recent years for its utility as biofuel. Ethanol is a renewable resource which makes it a suitable substitute for petroleum products. Generally, absolute ethanol is mixed with gasoline for use as fuel [6,7]. Ethanol used for laboratory purposes is of a very high purity, 99% or above. Alcoholic beverages produced all over the world may be categorized into two categories: recorded and unrecorded alcohol [3]. Recorded alcohol is that part of alcohol which is consumed globally and is reflected in the official statistics on production, cross-border trade and sales figures of the country of production. However, a significant part of alcohol consumed in different parts of the world is not reflected or shown in such statistics and surveys. Such alcohols are known as "unrecorded alcohol". The unrecorded alcohol is further categorized into three types: a) (Licit) Informal alcoholic products (manufactured at small licensed factories using standard methods), b) Illicit alcoholic products (illegally produced in unlicensed small distilleries), c) Surrogate alcoholic products (preparations containing ethanol, which are not intended for human consumption).

According to WHO [8], about 25% of all alcohol consumed globally is unrecorded, but this figure is higher in some countries. Areas with the highest overall alcohol consumption are Europe, USA, and West Pacific Region, with a per capita alcohol consumption of 10.9, 8.4, and 6.8 liters per year, respectively. However, per capita consumption of unrecorded alcoholic beverage is highest in Europe, Africa and the Western Pacific Region (1.9, 1.8 and 1.7 liters pure alcohol, respectively). Unrecorded alcohol, as a proportion of total alcohol consumed, is highest in the Eastern Mediterranean (57%), South-East Asia (47%) and Africa (30%).

### 1.1. Forensic significance of liquors as evidence

Various economic, social, cultural and government policy factors are responsible for the increasing production and consumption of unrecorded liquors. Since the unrecorded alcohol is produced from readily available raw materials, they are cheap in comparison to licensed liquor. The production and consumption of unrecorded alcohol are major issues related to the beverage industry [4,9]. This problem is especially significant in developing countries. Another aspect of the liquor problem is the high mortalities related to disease caused by alcohol and due to consumption of hooch. Cases pertaining to drunken driving also add to the forensic cases. To make the situation worse, there is no internationally accepted standard method for analyzing liquor samples in forensic cases along with any type of database. In this review paper, an attempt has been made to summarize the current methods available for the analysis of various types of liquors [5].

In the present review, various aspects of analysis of alcoholic beverages using gas chromatography – mass spectrometry (GC-MS) have been studied. Search engines like

**Table 1-** *Methods and parameters used in various studies for the analysis of various types of alcoholic beverages.*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Moutai Liquor | LLE using Diethyl ether and pentane (1:1) | Not reported (NR) | Set 1<br>Hp-Innowax<br>DB-Petro<br>Set 2<br>DB-Petro<br>DB-1701 | Helium | Set 1<br>50°C to 230°C (10min) at 2°C/min<br>Set 2<br>50°C to 260°C (30min) at 3°C/min | Inj - 250°C<br>Det - MSD<br>Ion Source: 220°C<br>Transfer line: 250°C | 1:30 | Hexanoic acid, butanoic acid, octanoic acid, pentanoic acid, ethyl ester of C1 - C10, 2- butanol, 2-nonanol, ethanol, 2-pentanone, 1,1-diethoxyethane, 1,1-diethoxy-2-methyl propane,2-octen-2-one, furfural, pyrazine and pyridine compounds | NR | [67] |
| 2. | Luzhou flavour raw liquor | LLE using Diethyl ether | Methyl octanoate and octanoic acid | HP-5ms cap column | Helium 1ml/min | 40°C (5min) to 200°C at 10°C/min to 220°C at 10°C/min | Inj - 250°C<br>Det - Quadrupole MS<br>Ion source - 230°C | 10:1 | 2-methylpropanoic acid, Butanoic acid, Pentanoic acid, Hexanoic acid, Nonanoic acid, 1-Propanol, 2-Pentanol, Isoamyl alcohol, 1-Pentanol, Phenylethyl alcohol, 1-Hexanol, Furfuryl alcohol, Ethyl acetate, n-Butyl formate, Ethyl lactate, p-Cresol, 2-pentanone, Heptadecane, Furfuryl Hexanoate | | [13] |
| 3. | Beer and Wine | Stir bar sorptive extraction using Ethylene glycol/ PDMS polymer | 3,4 - dimethylphenol in absolute alcohol | ZB-Wax column | Helium 2ml/min | 80°C (2min) to 230°C (5min) at 5°C/min | Inj - 230°C<br>Det - MSD<br>Ion source - 230°C<br>Transffer line - 280°C | 1:50 | Volatile phenols<br>4-ethyl phenol, 4-vinyl phenol, 4-ethyl guaiacol, 4-vinyl guaiacol | 95 - 104% in Beer<br>81% to 98% in wine | [54] |
| 4. | Five chinese premium liquors | HS-SPME using CAR/ PDMS fiber | 2-octanol | HP-Innowax | Helium 1ml/min | 50°C (2min) to 230°C (10min) at 6°C/min | Inj - 250°C | Splitless | Ethyl ester, furfuryl hexanoate, Ethyl hexanoate, Ethyl acetate, Ethyl propanoate, 1-Propanol, 2-Methyl-1-propanol, 1-Butanol, 3-Methyl-1-butanol, 1-Pentanol, 1-Heptanol, 1-Octanol, 2-Furanmethanol, Benzyl alcohol, Phenylethyl alcohol, Acetic acid, Butanoic acid, Pentanoic acid, Hexanoic acid, Octanoic acid, Benzoic acid, Pentanoic acid, Hexanoic acid, Octanoic acid, Benzoic acid, Acetaldehyde, 3-Methyl Butanol,Hexanal, Nonanal, Furfural, 2,4-Dimethyl phenol, Phenol, Pyrazines, Isoamyl alcohol | NR | [71] |

*Continued on the next page*

**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5. | Wines | SPME using DVB/CAR/ PDMS fiber | 3-octanol | DB-Wax capillary column + DB-17 ms column | Helium 1ml/min | 35°C (5min) to 250°C at 3°C/min | Inj - 250°C<br>Det - Time Of Flight MS<br>Ion source - 250°C<br>Transfer line - 250°C | Splitless | 2,3 - Butanediol, 4-Carene, 3-Penten-2-one, Diethyl succinate, β-Santalol, Diethyl malonate, Dihydro-2(3H)-thiophenone, Tetrahydro-2(H)-pyranone, Furfural, Nonanol, 3-Methyl-2(5H)-furanone, Ethyl-9-decanoate, Nerol.Octanol | 98% | [37] |
| 6. | Merlot Wines | SPME using DVB/CAR/ PDMS fiber | NR | Set 1<br>DB-Wax + DB-1ms Capillary column<br>Set 2<br>DB-5 + DB-Wax Capillary column<br>Set 3<br>DB-Wax + DB-17ms | Helium 1ml/min | 35°C (5min) to 120°C at 3°C/min to 200°C at 5°C/ min to 250°C/min | Inj - 250°C<br>Det - Time of flight MS<br>Ion Source - 250°C<br>Transfer line -250°C | Splitless | Propanol, Butanol, 2-methyl butanol, Pentanol, Heptanol, Hexanol, Butan-2,3-diol, Phenylethyl alcohol Acetic acid, Butanoic acid. Hexanoic acid. Octanoic acid, 2-Decanoic acid, Decanoic acid, Acetaldehyde, 2-Propenal, Butenal, Hexanal, Octanal, Decanal | Propanol, Butanol, 2-methyl butanol, Pentanol, Heptanol, Hexanol, Butan-2,3-diol, Phenylethyl alcohol Acetic acid, Butanoic acid. Hexanoic acid. Octanoic acid, 2-Decanoic acid, Decanoic acid, Acetaldehyde, 2-Propenal, Butenal, Hexanal, Octanal, Decanal | [37] |
| 7. | Mango Wines | LLE using n-Pentane | Methyl nonanoate in 11% Hydroalcoholic solution | HP-5ms capillary column | Helium 1ml/min | 50°C(4min) to 230°C at 4°C/min | Inj - 230°C<br>Det - FID<br>Det temperature - 230°C<br>Det - MS<br>Same parameters as FID | 1:10 | 102 compounds including 40 Esters, 15 alcohols, 12 terpenes, 8 acids, 6 aldehyde and ketones, 4 lactones, 2 phenols, 2 furans, and 13 miescellaneous compounds |  | [12] |

*Continued on the next page*

**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8. | Pinotage wines | HS-SPME using CAR/ PDMS fiber | NR | VF-1 Capillary column+ Sol gel- Wax capillary column | Hydrogen 0.8ml/min | 40°C (0.2min) to 225°C (10min) at 3°C/min | Inj - 275°C<br>Det - Time of Flight MS<br>Ion Source - 225°C<br>Transfer line - 250°C | Splitless | 206 compounds including 67 esters, 40 alcohols, 22 aldehyde, 16 ketones, 8acida, 6 acetals, 8 furans and lactones, 5 sulphur containing compounds, 6 nitrogr=en containing compounds, 24 terpenes, 2 phenols, and 2 pyrans | | [26] |
| 9. | Grappa beverage | SPME using following fibers<br>1) DVB/CAR/ PSDMS<br>2) DVB/ PDMS<br>3) Polyacrylate fiber | NR | DB-5ms capillary column | Helium 1ml/min | 45°C(3min) to 150°C at 12°C/min to 230°C at 18°C to 250°C (4min) at 19°C | Inj - 230°C<br>Det - MSD MS<br>Ion source - 290°C<br>Transfer line - 250°C | Splitless | Ethanol, 2-Butnaol, Diethyl ether, 3-Methyl butanol, 2-Methyl butanol, Hexanal. Furfural. 1-Pentanol, 2-Propyl-1-pentene, 1-Hexanol, 1-Pentanol, Styrene, 1,1-Dietoxy-ethane, Benzaldehyde, 2-Pentyl furan, Hexanoic acid, Ethyl esters, D-Limonene, β-Linalool, Diethyl succinate, Ethyl decanoate, Octanoic acid ethyl ester, Octanoic acid methy ester, α-terpineol, Nonanoic acid, α-Bisabolo oxide, Dodenoic ethyl ester, α - Cubebene, Decanoic acid methyl ester, Tetradecanoic acid ethyl esters, Linoleic acid ethyl ester, Hexadecanoic acid ethylNo extraction ester | | [36] |
| 10. | Khadi (Unrecorded beverages) | Direct injection | 2-pentanol | ZB-FFA Capillary column | Nitrogen 2ml/min | 35°C(3min) to 40°C (2min) at 2.5°C/min to 80°C(4min) at 20°C/min to 140°C (5min) at 20°C/min to 220°C (1min) at 20°C/min | Inj - 300°C<br>Det -FID<br>Detector temperature - 300°C | Splitless | Ethyl acetate, Ethanol, 2-Methyl-1-Propanol, 3-Methyl-1-butaol, Ethyl lactate | | [66] |
| 11. | Raki, an illegally produced liquor | Direct injection | NR | HP-FFAP capillary column | Helium | 60°C (4min) to 160°C (4min) at 6°C/min | Inj - 250°C<br>Det - Quadrupole MS<br>Ion Source - 280°C | 1:100 | Methyl alcohol, Ethanol, Isoamyl alcohol, t-Anethole, Propionic acid, 1-Butanol, 1-Propanol, Ethyl acetate, Formic Acid, Formamide, Acetaldehyde, Methyl amine, 2-Propanol, Methyl formate, Trioxan | | [68] |

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**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12. | Homemade commercial samogon, tequilla, whiskey, cognacs | Direct injection | Cyclohexane | HP-FFAP capillary column | Helium 1ml/min | 70°C (5min) to 190°C (20min) at 10°C/min | Inj - 240°C<br>Det.- FID<br>Det. temp. - 220°C<br>Det. - MS<br>Ion source - 240°C<br>Transfer line - 180°C | 1:15 | Diethyl ether, Acetaldehyde, Acetone, Ethyl acetate, Methanol, Isopropanol, Methyl Ethyl Ketone, t-Butanol, 1-Propanol, Crotonaldehyde, Methyl butyl ketone, Isobutanol, Ethanol | | [52] |
| 13. | Alcoholic beverae produced by Whey fermentation | LLE using Dichloromethane | 4-nonanol | CP-Wax capillary column | Helium | 60°C (5min) to 250°C (20min) at 3°C/min to 255°C at 1°C/min | Inj - 20°C to 250°C at 180°C/min<br>Det – Ion trap MS | Splitless | Acetaldehyde, Ethyl acetate, Ethanol. 2-Butanol, 1-Propanol. 2-Methyl-1-propanol, 2-Methyl-1-butanol, Acetic acid, 3-Methyl-1-butanol, 4-Nonanol | | [53] |
| 14. | Mezcal | Direct injection for major components and SPME using Car/ DVB fiber for minor components | 2-Pentanol | HP-Innowax capillary column for major components<br>HP-FFAP capillary column for minor components | Helium 1.5ml/min | 40°C (3min) to 120°C at 3°C/min to 200°C at 6°C/ min | Inj - 220°C<br>Det. – FID<br>Det. Temp. - 250°C<br>Det. – Mass selective detector<br>Ion Source - 230°C<br>Trnsfer line - 230°C | Splitless | Ethanol, Methanol, n-Propanol, 2-Butanol, 2-Methyl-propanol, 2-Methyl-1-butanol, 3-Methyl-1-butanol ethyl ester, Acetic acid | | [56] |
| 15. | Chinese rice wines | HS-SPME using following fibers<br>1) DVB/CAR/ PDMS<br>2) DVB/ PDMS<br>3) PDMS | 2-Octanol | DB Wax capillary column | Helium 2ml/min | 50°C to 80°C at 20°C/min to 230°C at 3°C/min | Inj - 250°C<br>Det. – Mass selective detector<br>Ion source - 250°C<br>Transfer line - 230°C | Splitless | 97 Compounds including 28 ester, 1 acid, 3 ketones, 13 alcohol, 8 acid, 17 aromatic compound, 3 lactones, 6 phenols, 3 sulphides, 9 furans, 6 nitrogen containing compounds | | [24] |
| 16. | Spirit germam fruit spirit and Mexican fruit | Static headspace with trap enrichment | t-Butanol | Rtx-1701 capillary column | Nitrogen | 37°C (6min) to 100°C at 10°C/min to 200°C at 20°C/ min | Inj. - 220°C | Splitless | Methanol, 1-Propanol, 1-Butanol, 2-Butanol. Isobutanol, 2/3-Methyl-1-butanol, Ethyl acetate, Ethyl lactate, Benzaldehyde, 1-Hexanol, Ethyl octanoate | | [28] |
| 17. | Surrogate Alcohol of Russia | Direct injection | Acetone-D6 | HP-FFAP capillary column | Helium | 60°C (4min) to 110°C at 5°C/min | Inj. - 200°C<br>Det – Mass selective Detector<br>Ion source - 230°C<br>Transfer line - 280°C | Splitless | Ethanol, 1-Propanol, Isobutanol, Isoamyl alcohol | | [55] |

*Continued on the next page*

Table 1- *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18. | Surrogate alcohol from South-Eastern Nigeria | LLE with Dichloromethane | NR | CB-Wax capillary column | Helium 1ml/min | 50°C (1min) to 160°C at 5°C/min to 220°C(10min) at 25°C/min | Inj. - 220°C<br>Det – MS/ MS triple quadrupole MS<br>Ion Source – 200°C<br>Transfer line - 280°C | Splitless | Ethanol, Methanol, Acetaldehyde, 1-Propanol, 2-Butanol, Isobutanol, Amyl alcohol, 2-Phenlethanol, Ethyl acetate, Ethyl lactate | | [64] |
| 19. | Whiskey and Gao-Liang | Direct injection | 2-Pentanol and Acetonitrile | CP-Wax 58 CP Megapore capillary column | Nitrogen 3ml/min | 30°C (2min) to 65°C at 5°C/min to 250°C (1min) | Inj - 210°C<br>Det – FID<br>Det. Temp. - 280°C | Spitless | Methanol and Ethanol | 94 – 103% for Methanol<br>95 – 97% for Ethanol | [88] |
| 20. | Greek distilled alcoholic beverages | Direct injection | Pentanol in absolute ethanol | CB Wax 57 capillary column | Helium 2ml/min | 40°C (5min) to 200°C (20min) at 30°C/min | Inj. - 200°C<br>Det. – FID<br>Det. Temp. - 200°C | 1:60 | Acetaldehyde and Methanol | | [60] |
| 21. | Wine and Whiskey | Direct injection | Acetonitrile | CP-Wax 58CB capillary column | Nitrogen 3ml/min | 38°C (3min) to 250°C (1min) at 50°C/min | Inj. – 210°C<br>Det. – FID<br>Det. Temp. - 280°C | Splitless | Methanol and ethanol | 101-107% for Wine<br>94-103% for Whiskey | [85] |
| 22. | Chinese Dahuaxiang liquors | 1) LLE using Dichloromethane<br>2) SPME sol gel fiber of γ-methylryloxypropyl | n-Butyl acetate and 2-Octanol | HP-5 capillary column | Helium 1.2ml/min | 37°C (8min) to 50°C at 3°C/min to 100°C at 4°C/min to 210°C (10min) at 5°C/min | Inj. - 250°C<br>Det. – Mass selective detector<br>Ion source – 230°C | Splitless | 57 compounds including 5 alcohols, 30 esters, 6 acids, 3 aldehydes, 4 acetals, 5 aromatic compounds, 2 ketones, 2 miscellaneous compounds | | [50] |
| 23. | Turkish Raki | SPME | 2-Octanol | GL Science High Resolution TC-Wax capillary column | NR | 35°C to 80°C (2min) at 2°C/min to 150°C (2min) at 2°c/min to 195°C at 2°C/min to 250°C at 4°C/min | Inj. - 150°C<br>Det. – FID<br>Det. Temp. - 250°C | Splitless | Acetaldehyde, Ethyl acetate, Methanol, 2-Propanol, 1-Propanol, Butyl acetate, Amyl acetate, 3-Pentanol, n-Butanol, 2-Butanol, 3-Methyl-1-penatnol, 1-Pentanol, Ethyl lactate, 1-Hexanol, p-Allylanisole, t-Anethole, p-Anisaldehyde, p-Anisyl alcohol | | [59] |
| 24. | Lemon liquor (Limoncello) | SPME using PDMS fiber | NR | SLB – 5ms capillary column | Helium | 40°C to 250°C (2min) at 3°C/min | Inj. - 250°C<br>Det. – MS<br>Ion source - 200°C<br>Transfer line - 250°C | 1:10 | Terpenes | | [35] |

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**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25. | Lemon flavour liquor | LLE using hexane | NR | SE 52 capillary column | Helium | 50°C to 70°C (8min) at 4°C/min to 200°C (6min) at 5°C/min to 300°C at 5°C/min | Inj. – 250°C<br>Det – FID<br>Det. Temp. - 300°C | 1:45 | Lactic acid, Oxalic acid, Malonic acid, Phosphoric acid, Succinic acid, Malic acid, Citric acid, Ascorbic acid, Glycerols, meso-erithryol, mio-inositol, L-arabinose, rhamnose, fructose, glucose, saccharose, ethanol, acetaldehyde, ethyl acetate, methanol, propanol, i-butanol. | | [86] |
| 26. | Apple fermented beverages | Direct injection | Heptanoic acid | ZB-Wax capillary column | Nitrogen 2.5ml/min | 40°C (5min) to 150°C (10min) at 10°C/min to 200°C (5min) at 10°C/min to 220°C at 10°C/min | Inj. - 220°C<br>Det. – FID<br>Det. Temp. - 230°C | 1:12 | Ethyl ethanoate, Ethyl butanoate, 3-Methylpropyl ethanoate, Ethyl hexanoate, Butyl ethanoate, 3-Methylbutyl ethanoate, Hexyl ethanoate, 2-Hydroxy ethyl propanoate, Ethyl octanoate, Ethyl decanoate, Diethyl butanedioate, Ethyl dodecanoate, Ethanal, Butanoic acid, Octanoic acid, 3-Methyl-1-butanol, 1-Hexanol, 2-Hexanol, 2-Phenulethyl alcohol, 2-Hexanone, 2-Octanone | | [57] |
| 27. | Sparkling wines | 1) HS-SPME using DVB/CAR/PDMS fiber<br>2) Simultaneous distillation extraction using Pentane and Dichloromethane (3:1)<br>3) Closed loop stripping analysis using activated charcoal | 2-Octanol | Supelco wax 10 capillary column | Helium 1ml/min | 40°C (10min) to 200°C (1min) at 2°C/min to 250°C (10min) at 2°C/min | Quadrupole Trace MS | NR | Lilial octanal, 2-Octanone, Isopropyl disulfide, Methylthiophen-3-one, α-Amyl-cinnanaldehyde, Ethyl-2-furancarboxylate, 2-Acetyl-furan, 5-Methylfurfural | | [17] |
| 28. | Wines | HS-SPME using PDMS/DVB fiber | NR | GL-Science TC-Wax capillary column | Nitrogen 1ml/min | 40°C (2min) to 150°C (1min) at 4°C/min to 200°C (1min) at 4°C/min to 220°C (5min) at 15°C/min | Inj. - 250°C<br>Det. – ECD<br>Det. Temp. - 300°C | Splitless | 2,4-Dichloroanisole, 2,4,6-Trichloroanisole, 2,3,4,6 – Tetrachloroanisole, Pentacloroanisole, 2,4,6 – Trichlorophenol, 2,3,4,6 – Tetrachlorophenol, Pentachlorophenol | 92 – 102% | [34] |

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**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 29. | Whiskey | 1) LLE using Dichloromethane<br>2) SPME using CAR/PDMS | Octan-3-ol + Methylpentan-2-ol in hydroalcoholic solution (1:1 v/v) | DB-Waxetr capillary column | Helium 1ml/min | 40°C (1min) to 120°C (2min) at 1°C/min to 180°C (1min) at 1.7°C/min to 220°C (10min) at 25°C/min | Inj. – 260°C<br>Det. – FID<br>Det. Temp. - 300°C | Splitless | Propen-1-ol, 2-methyl propan-1-ol, Butan-1-ol, 2-Methyl butan-1-ol, Hexan-1-ol, Methanol, 2-Phenylethanol, Benzyl alcohol, Isoamyl acetate, Ethyl butanoate, Ethyl hexanoate, Ethyl lactate, Ethyl octanoate, Ethyl decanoate, Diethyl succinate, Ethyl dodecanoate, Hexanoic acid, Octanoic acid, Decanoic acid, Acetaldehyde, Syringaldehyde, Furfural, 5-Methyl-2-furfual, Guaiacol | >80% | [18] |
| 30. | Maldova Sun and Muscat wines | 1) SPME using following fibers<br>a) CAR/DVB/PDMS<br>b) PDMS<br>c) CAR/PDMS<br>d) DVB/PDMS<br>e) Polyacrylate<br>2) Solid phase extraction using C-18 isolute cartridge | 2[H]7 – Geraniol in ethanol | Supelcowax – 10 capillary column | Helium 0.8ml/min | 40°C (1min) to 200°C at 5°C/min to 230°C (9.5min) at 20°C/min | Inj. - 220°C<br>Det. – Quadrupole MS with triple axis detector<br>Ion source - 220°C<br>Transfer line - 240°C | Splitless | Geranic oxide 1, Geranic oxide 2, 1,3,5,5 – Tetramethyl-1,3-cyclohexadiene, Isoterpinolene, β-Myrcene, α-Terpinene, Limonene, β-cis-ocimene, m-Cymene, Terpinolene, Cis Rose oxide, Cis-lineleol oxide, Linalool, Hotrienol, Ocinenol-1, Ocimenol-2, α-Terpineol, β-Citronellol, 4,5,9,10 – Dihydroisolongfolene |  | [77] |

*Continued on the next page*

**Table 1-** *(continued)*

| No | Type of Beverage | Extraction method used | Internal standard used | Column used | Carrier gas and flow rate | Ramp Cycle | Injector and detector temperature | Split ratio | Major compounds reported | Recovery | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 31. | Chinese Moutai and Gujingyong liquor | 1) LLE using Diethyl ether<br>2) HS-SPME using CAR/ PDMS | 4-Methyl-2-pentanol | 1) DB-Wax capillary column<br>2) HP-5 capillary column | Helium 2ml/min | 50°C (2min) to 230°C (15min) at 4°C/min | Inj. - 250°C<br>Det. – Mass selective detector<br>Ion source - 230°C | Splitless | 2,5-Dimethyl purazine, 2,6-Dimethyl pyrazine, 2-Ethyl pyrazine, 2,3 – Dimethyl pyrazine, 2-Ethyl-6-methyl pyrazine, 2-Ethyl-5-methyl pyrazine, 2-Ethyl-3-methyl pyrazine, 2,3,5-Trimethyl pyrazine, 2,6-Dimethyl pyrazine, 2,5-Dimethyl-3-ethyl pyrazine, 2,3-Dimethyl-5-ethyl pyrazine, 3,5-Dimethyl-2-ethyl pyrazine, 2,3,5,6-Tetramethyl pyrazine, 3,5-Dimethyl-2-methyl pyrazine, 2,3,55-Trimethyl-3-isobutyl pyrazine, 2-Methyl-6-vinyl pyrazine, 2-Acetyl-3-methyl pyrazine, 2-Butyl-3,5-dimethyl pyrazine, 2-Methyl-6-cz-1-propyl pyrazine, 2-Acetyl-3,5-dimethyl pyrazine, 2,5-Dimethyl-3-pentyl pyrazine, 2,3-Dimethyl-5-(Z-1-propenyl) pyrazine | 83 – 119% for synthetic liquor<br>85 – 100% for Moutai liquor<br>92 – 117% for Guijingyong liquir | [63] |
| 32. | Gerenache Red wine | LLE using Freon 113 | 4-Methyl-2-Pentanol and 2-Octanol | DB-Wax capillary column | Helium 1ml/min | 40°C (5min) to 200°C (100min) at 2°C/min | Inj. - 30°C to 200°C at 150°C/min<br>Det. – Ion trap MS | Spitless | 45 compounds including 8 acids, 7 alcohols, 5 aldehydes and ketones, 15 esters, 5 lactones, 5 phenols, 2 thiols | | [76] |
| 33. | Ciders | Microextraction using C 18 sorbent | 4-Methyl pentan-2-ol | BP-20 capillary column | Helium 1ml/min | 35°C to 240°C at 5°C/min | Inj. - 240°C<br>Det. – Ion trap MS<br>Ion source - 150°C<br>Transfer line - 270°C | 1:5 | 2-Methyl propano-1-ol, Butan-1-ol, 3-Methylbutyl acetate, 4-Methyl pentan-2-ol, Heptan-2-one, Isopentan-1-ol, Ethyl hexanoate, 1,2,4-Trimethyl benzene, Propan-1-ol, Hexyl acetate, Acetoin, Ethyl lactate, Hexan-1-ol, Nonan-2-one, Ethyl octanoate, Acetic acid, 2-Methyl propanoic acid, Ethyl decanoate, Butanoic acid, Diethyl succinate. Methional. 2-Methyl butanoic acid. 2-Phenyl ethyl acetate, Hexanoic acid, Benzyl alcohol. 2-Phenylethyl alcohol, 4-Ethyl guaiacol, Octanoic acid, 4-Ethyl phenol, Decanoic acid | | [62] |

Google Scholar, ScienceDirect and PubMed were searched using combinations of keywords such as gas chromatography-mass spectrometry (GC-MS), alcoholic beverages, wine, whiskey, illicit liquor, geographic origin, characterization, etc. for literature published after 2000.

## 2. Qualitative analysis

Qualitative analysis or identification of components of different alcoholic beverages can be done using comparison of analytical parameters such as MS spectra with standards stored in the form of databases. Most common MS databases are provided by the National Institute of Standards and Technology (NIST) and Wiley. Although these databases provide a definite identification, it is advisable to run standard compounds to compare the retention times with that of an analyte in the samples. Running standards and comparing their retention time also helps in differentiating isomeric compounds such as 1-butanol and 2-butanol, 1-pentanol, 2-pentanol and 3-pentanol, etc.

## 3. Quantitative analysis

Apart from qualitative analysis, the determination of the concentration of the components is also important for identifying an alcoholic beverage. This process includes addition of internal standards to calculate the recovery percentage. Standards are also used to prepare the calibration curves which again help in quantifying the components. These parameters are discussed below.

## 4. Internal Standard

To compensate for variations in the analytical method, a known concentration of an internal standard is added to the sample during calibration and validation of the method as well as in practical application. The response coefficient of the internal standard is known or arbitrarily fixed [10]. Its concentration is in about the same range as that of the analyte(s) of interest. It is added prior to any chemical derivatization or any other treatment of the sample [11,12,13]. The internal standard must not be present in the sample and there must be no compound present that has the same retention time in the chromatogram. It should elute near the peak of interest. It must be chemically similar to the analytes of interest and must not react with any sample components. In Table-1, the internal standards used in the analysis of alcoholic beverages have been summarized. 2-octanol and 2-propanol are the most commonly used internal standards.

## 5. Sample Preparation

### 5.1. Solvent Extraction

Extraction methods employing solvents such as liquid - liquid extraction, etc. are time consuming and involve many steps. Such methods have the need to rinse the organic extract with an aqueous solution of different pH to remove acids and non-volatile compounds from the sample, which might result in downsizing of the extraction procedure. The removal of non-volatile substances from the samples is necessary because of the risk of chromatographic column contamination, and possible artifact formation in the hot injector [14]. Liquid-liquid extraction using ammonium sulphate and dichloromethane [15], 4-ethylphenol and 4-ethylguaiacol [16], pentane and dichloromethane (3:1) and carbon disulphide [17], sodium sulphate and dichloromethane [18], pentane, pentane-diethyl ether (2:1 v/v) and have been reported. Castro et al. used rotatory and continuous liquid-liquid extraction for the extraction of volatile compounds of ‘fino’ sherry wines [19].

### 5.2. Headspace Extraction

Headspace sampling is essentially a separation technique in which volatile components of the gas phase above a liquid or solid sample matrix are analyzed. Headspace can be either static or dynamic. Both static [20] and dynamic [21] have been successfully used for the analysis of alcoholic beverages. Static headspace has shown great advantage in which intermediate trap phases were involved [22,23]. Headspace can be combined efficiently with SPME to produce better results [24-26].

Some variants of the headspace technique are the purge and trap methods. In purge and trap analysis, a sample is continuously purged with an inert gas, and volatiles are transported from the sample to a trap with sufficiently high retention power. After purging, the trap is heated and the trapped volatiles are released onto a GC column [27,28]. Using purge and trap extraction, Mamede and Pastore extracted 25 volatile components in the aroma of the Chardonnay and Pinot Noir fermented grape musts [29]. Static headspace and Purge and trap extraction was used by Kleinova and Klejdus for extraction of volatiles in beer [30]. Trap materials used include Carbotrap and Carbosieve sandwich trap. By this process, the volatile analytes are pre-concentrated prior to GC separation, so that a splitless transfer is possible. The process of loading absorbent as well the sample is simple and easy to operate. This trap enrichment results in significant high peak areas. It has been observed that single trap extraction cycle results in an increase of almost 33–35 times in peak areas compared to static headspace [28].

### 5.3. Solid Phase Microextraction (SPME)

SPME has three modes of operation: the direct-immersion extraction (DI-SPME), headspace extraction (HS-SPME), and membrane protected SPME [31]. While selecting fibers, parameters such as sensitivity, lack of affinity for interfering compounds, fast desorption, and low sample carry over must be taken into consideration [32,33]. Stashenko et al. [32] reported seven types of SPME fibers available commercially, which include 1) Non-polar polydimethylsiloxane (PDMS), 2) Polar Polyacrylate (PA), 3) Polar Carbowax/Divinyl benzene (CAR/DVB), 4) Carbowax/Templated resin 5) Mixed polarity polydimethylsiloxane/divinyl benzene (PDMS/DVB), 6) Mixed polarity Carbowax/Polydimethylsiloxane (CAR/PDMS), and 7) Mixed polarity Divinyl benzene/Carbowax/Polydimethylsiloxane (DVB/CAR/PDMS).

In alcoholic beverages, a major portion is constituted by volatile components. Therefore, the SPME is often used in combination with headspace [26,27, 34-39]. The most common fiber used is Polydimethylsiloxane (PDMS) [19,24,30,36,40-45]. Polydimethylsiloxane (PDMS) fibers often provide the highest efficiency along with extracting the maximum number of compounds for volatile polar compounds [31]. Carboxene/polydimethylsiloxane (CAR/PDMS) fiber can also be used for the extraction of trans-level volatile components from alcoholic beverages [18,19,39,42,43]. The Polyacrylate fiber [19,42] is another type of fiber commercially available for extraction of volatile compounds. However, polyacrylate as well as divinylbenzene fibers show a considerable affinity to ethanol and are therefore less suited for the extraction of other volatile components from alcoholic beverages [65].

From a theoretical point of view, the amount of analyte extracted into the fiber coating is the same at equilibrium for direct immersion and headspace sampling provided that the sample vial and the volume of the liquid sample and the gaseous headspace are the same. However, headspace has the large advantages of excluding non-volatile substances and of avoiding fiber corrosion by the liquid phase. Due to the accumulation of the analyte on the fiber, much more analyte can be injected into the GC-MS than by static headspace injection, which leads to strongly increased sensitivity. However, SPME suffers from a lack of precision and high fiber to fiber variations. Highest reproducibility is attained only when all calibration and measurements are performed continuously with the same fiber and by use of deuterated internal standards. Moreover, the high price of fibers along with their fragile nature makes them less preferable. Furthermore, the variety of coatings currently available commercially for extraction procedures is limited. Due to this, the number of components which can be extracted using this method is severely limited.

### 5.4. Stir-Bar Sorptive Extraction (SBSE)

To overcome the limitations of SPME, SBSE was developed in which a magnetic stir bar, coated with polydimethylsiloxane (PDMS), is rotated in an aqueous sample. Once the equilibrium is reached, the magnetic stir bar is first rinsed with distilled water to remove the excess of the sample adhering to the outer surface of the magnetic bar. Then, the magnetic bar is placed on the liner of thermal or liquid desorption system to enable GC analysis [27,46]. This extraction technique is new, and its application in the field of beverage analysis is yet to be explored. At present, the only polymer commercially available as stir-bar coating is that of polydimethylsiloxane (PDMS)[47]. Coelho et al. [46] used SBSE with liquid desorption (SBSE-LD) followed by large volume injection and subsequent qualitative and quantitative analysis with GC-MS of varietal and fermentative volatiles in sparkling wines. SBSE extraction greatly influenced the quantitation of major as well as minor components. A stir bar recovery of polar analytes is low. Therefore, a stir bar coated with materials that shows higher affinity for polar compounds would improve SBSE flexibility and selectivity while maintaining its concentration capacity [47,48].

### 5.5. Selecting an appropriate extraction method

The analytical performance of an extraction method may greatly affect the results of (GC-MS) analysis. A good extraction technique must have good linearity, a wide range of extracted components, low detection limits, high recovery for more components and high sensitivity [49]. As discussed above, several isolation and concentration methods developed for isolation and concentration of analytes include solvent extraction, headspace extraction, SPME and SBSE. With solvent extraction, all volatile compounds require solvent evaporation, which might result in loss or degradation of some of the components and formation of adducts originally absent in the sample [29]. Headspace techniques are fast and no sample preparation is required, but they suffer from a disadvantage of low sensitivity. SPME and SBSE are effective extraction techniques and can be used for both direct extraction and extraction through headspace. Contrary to SPME, where numerous fiber coating materials are available commercially, only one type of stir bar coating is available for SBSE i.e. of non-polar medium polydimethylsiloxane (PDMS). This limits the sensitivity and number of compounds extracted using SBSE [31].

Caldeira et al. [18] observed that out of LLE and HS-SPME, HS-SPME produces better results in terms of number of components extracted as well the quantity extracted. Wang et al. [50] compared the analytical efficiency of SPME using sol-gel and LLE method in identifying the components of alcoholic beverages. SPME appeared to be a better technique for extraction of volatile components from alcoholic beverages.

Demyttenaere et al. [51] compared SPME using three fibers with newly developed SBSE. Qualitatively, both SPME and SBSE performed equally; however, SBSE showed better enrichment of identified components, even when higher split ratios were used. This was the result of a higher amount of polymer that covers the bar, proving higher sensitivity of SBSE. However, SBSE suffers from the limitation of ineffective desorption. When used with split desorption-split injection mode, because of lacking desorption device, it does not improve significantly the results obtained by SPME.

## 6. Detector conditions

Detectors are an integral part of any chromatographic technique. Different detectors provide differing sensitivities and have been successfully used to identify the separated components. Detectors used include FID [57-61], ECD [34], and MS [62-64]. Mass spectrometric detectors provide high sensitivity, low detection limits and high qualitative capabilities. Mass spectrometers use the differences in mass-charge ratio i.e. m/z ratio of ionized atoms or molecules or fragments for separation. The fragmentation pattern of a compound is very specific and can be used for qualitative and quantitative identification. There are various types of analyzers available, for e.g. quadruples, time of flight analyzers, magnetic sectors, fourier transform, and quadruple ion traps. However, quadruple and time of flight mass analyzers are most common. Various detectors used for the analysis of alcoholic beverages include Flame ionization detector [12,52,66,67], time of flight mass detector [25,36,37,67], and quadruple mass detector [13,68]. Quadruple mass analyzers produce classic mass spectra with good reproducibility. These are relatively low cost systems. However, quadruples produce low resolution mass spectra and their peak height vs. mass response must be tuned.

Time of flight (TOF) MS are the fastest mass analyzers, significantly reducing the analysis time and highest practical range of all other mass analyzers. Ion trap mass analyzers have the best resolution of all mass analyzers. Ion trap mass analyzers help in non-destructive ion detection and produce a stable mass calibration. However, ion trap mass analyzer suffers from the limitation of narrow dynamic range, and the results are comparatively less reproducible [69].

## 7. Applications of GC-MS

### 7.1. Identification and characterization of aroma components of alcoholic beverages

The volatile fraction of liquors is responsible for the organoleptic properties of the liquors and their quality. Therefore, the characterization of the volatile fraction becomes an important part in maintaining the quality of liquors [70,71]. Some volatile components are universally found in all liquors and some volatile components are specific to a certain type of alcoholic beverage. Such volatile components can be used in differentiating the different liquors [13]. A gas chromatography with mass spectrometric detector is used to create component profiles of various alcoholic beverages traditionally manufactured in different countries. Volatile components of beer [72,73], wine [24,74-77] whiskey [78], rum [79], tequila [80] and other traditional alcoholic beverages [56,71,83] and other alcoholic beverages [88,50,53,56,71,72] have been reported. Table 1 illustrates the different types of components reported in different studies.

### 7.2. Congener analysis

Congeners are all compounds in an alcoholic beverage other than water and ethanol that assist in the distinctive aroma, flavor and appearance of the beverage [81]. These congeneric products which distil along with the ethanol after fermentation provide a “fingerprint” that can assist in identifying the type of spirit. The final concentration of congeners in the alcoholic beverage broadly depends on the raw materials used for fermentation, various parameters of fermentation used, and the distillation process. Around 600-800 congeners have been reported in beer, spirits and wines. The concentration of different congeners and their relative concentration must be taken into consideration while interpreting the results of congener analysis [82]. Congeners can be produced either by the cross-reaction of different fermentation products [25, 83] or by degradation of amino acids [81]. The production of congeners is also affected by availability of amino acids, presence of other carbon sources such as carbohydrates, and different strains of yeast fermenting at variable rates consequently producing different congener profiles. Another factor affecting congener profiles is the distillation. Although distillation results in decrease of total congener volume in an alcoholic beverage, the relative congener concentration produced during the fermentation is increased. Most of the congeners having boiling points similar to ethanol are retained [81]. Maturation and secondary fermentation can also result in a change in the concentration of congeners in alcoholic beverages.

### 7.3. Geographic origin of alcoholic beverages

Determination of geographic origin of different alcoholic liquors is an important aspect of forensic investigation. Determination of geographic origin is a method of authenticating the liquor samples. By application of chemometric tools such as principal component analysis (PCA), linear discriminant analysis (LDA), cluster analysis (CA), partial least square discriminant analysis (PLS-DA), stepwise linear discriminant analysis (SLDA), etc., the alcoholic beverages from different geographical origins can be differentiated. These chemometric tools process the data obtained from GC-MS and overcome the resource limitations of detecting equipment to provide statistical separation of different categories [45]. High accuracy rates of classification (above 80% in every case) have been reported by Cheng et al. [45], Counet et al.[84], Cynkar et al. [85], and Berna et al. [86]. More research must be done in this field to validate the available results.

### 7.4. Adulteration of alcoholic beverages

Methanol is cheap and readily accessible; therefore, it is one of the most common adulterants used in alcoholic beverages, especially in developing countries. These have been used in the production of imitated spirits and wine [87]. Its accidental intake results in severe intoxication due to formation of formic acid, which has a long half-life and results in severe acidosis. There have been several methods reported for qualitative and quantitative analysis of methanol in alcoholic beverages. Wang et al. used direct injection capillary gas chromatography for rapid determination of methanol [87]. Simultaneous determination of ethanol and methanol in alcoholic beverages have been reported by Zhang et al. [61] and Wang et al. [88]. The determination of methanol and its derivatives in illegally produced unrecorded alcoholic beverages have been studied using GC-MS [60,68].

### 7.5. Analysis of unrecorded and surrogate alcohols

Unrecorded alcohols consist of illicit liquors and traditional alcoholic beverages. The main purpose of manufacturing such alcoholic beverages is tax evasion, profit, and to impede law enforcement agencies. The alcohol content varies significantly, and their quality is suspicious. Traditional alcoholic drinks are location specific and are manufactured using raw materials found in that area. Unrecorded alcoholic beverages have been analyzed using gas chromatography–flame ionization detection by Mapitse et al. [66]. Surrogate alcohols include alcohol containing medicines and other spirits such as fluids for lighting fires and aftershaves [55,64].

## 8. Conclusion

The forensic analysis of alcoholic beverages constitutes a very important position in many toxicological cases. In this review, various methods for extraction of various volatile components were discussed along with their advantages and limitations. Furthermore, the application of GC-MS in qualitative and quantitative determination of volatile components of alcoholic beverages was discussed. From the literature review, SPME is the best extraction method available. It is evident that far too little analytical work has been done in the field of determining geographic origin using aroma components of liquors. More work is being done in this field and, therefore, the present review is an important addition to knowledge in this area.

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