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Analysis of Some Contaminants Commonly Found in Alcoholic Beverages

T. Osobamiro

Department of Chemical Sciences, Olabisi Onabanjo University,
P.M.B. 2002, Ago-Iwoye, Ogun-State, Nigeria

Abstract: Analysis of common contaminants in alcoholic beverages was carried out using the Gas-Chromatographic method. The purpose of this study was to determine the type and levels of contaminants present in alcoholic beverages commonly sold in major markets in Lagos, Nigeria. Five major contaminants; methanol, benzene, toluene, ethyl acetate and ethyl carbamate were analysed in ten different samples of local and imported alcoholic beverages. Six of the samples were spirit, two were wine and the remaining two were beer. None of the contaminants analysed were detected in beer and wine samples i.e. they were below the detection limit but, all of the contaminants analysed were found in spirit samples. Based on this findings, most of these spirit drinks might not be good for consumption especially samples A and E which contained toluene and benzene respectively that can lead to damage of nearly every organ and system in the body. Federal regulatory agencies such as NAFDAC should be encouraged to carry out routine analysis on commonly sold alcoholic beverages in markets in order to prevent sale of adulterated or contaminated drinks.

Key words: Alcoholic beverages · Gas chromatography · Contaminants · Benzene

INTRODUCTION

Any drinkable liquid that contains from5 to 95% ethanol is an alcoholic beverage. The major physiologically active component of most alcoholic beverages is ethyl alcohol (ethanol), the remaining fractions are often called congeners [1]. Congeners are biologically active chemicals (chemicals which exert an effect on the body or brain) and are often contained in alcoholic beverages. Congeners are produced in the process of fermentation or ageing, when organic chemicals in the beverage break down. They may also be added during the production process to improve the taste, smell and appearance of the beverage [2]. These include acetaldehydes, esters, ethyl esters and fusel oil. Fusel comes from the German language and literally means "bad spirits a by-product in the distillation of fermented alcohol [13]. They include carbonyl compounds, alcohols, esters, acids and acetals (An organic compound, $CH_3CH(OC_2H_5)_2$ formed by the condensation of two alcohol molecules with an aldehyde), all of them influence the quality of the finished product [3].

The presence of these congeners is undesirable as some of them are responsible for unpleasant organoleptic properties of alcoholic drinks. Acetaldehyde is the most toxic metabolite created by alcohol metabolism originating from fermented raw materials [4]. Acetaldehyde levels in distillates can increase during ageing due to the chemical oxidation of ethanol and further oxidation of acetaldehyde can result in the formation of small amounts of acetic acid. Methanol is formed by pectinolytic enzymes that split the methoxyl group from the pectin present in the crushed fruit. For this reason, the concentration of methanol in the final distillate spirit increases with the extraction time [5]. Ethyl acetate has a significant effect on the organoleptic characteristics of wines and distillates. At lower concentrations, ethyl acetate contributes to the fruity properties of the wine [6,7]. Storage under unfavourable conditions may expose alcohol to the risk of bacterial spoilage which can result in an increase in ethyl acetate. This also increases during ageing because of the continuous oxidation of ethanol to acetic acid and the esterification of this acid. The levels of these compounds are influenced by several processing factors, such as grape variety, fermentation conditions and

Corresponding Author: T. Osobamiro, Department of Chemical Sciences, Olabisi Onabanjo University, P.M.B. 2002, Ago-Iwoye, Ogun- State, Nigeria. Tel: +234-8056628102.

distillation techniques. Ethyl carbamate or urethane (CAS number 51-79-6) is the ethyl ester of carbamic acid. It can be found in fermented foods and beverages like spirits, wine, beer, bread, soy sauce and yoghurt. It can be formed from various substances such as hydrocyanic acid found in fruit stones or through reaction between urea and ethanol during yeast fermentation. Ethyl carbamate is genotoxic and a multisite carcinogen in animals and probably carcinogenic to humans (group 2A). Methanol is naturally found in some alcoholic beverages.

Swiss tolerable values in various brandies are set, depending on the beverage, at 2-15 g/L of pure alcohol and 0.15-0.3 g/kg for wines[8]. Much higher levels had been obtained in cases of adulterated wines in Italy in 1985, following deliberate addition of methanol. Consumption of such beverages provoked several deaths or permanent blindness[8]. Acute methanol toxicity is well known, the toxic mechanism relates to the formation of formaldehyde and formic acid. The minimal human lethal dose has been estimated within a range of 0.3-1.0 g/kg BW. Chronic toxicity is not well characterized. Methanol has been described to be the most common cause for surrogate toxicity [8,9], while acetaldehyde may contribute to the carcinogenicity of alcoholic beverage [10]. Benzene is a known human carcinogen. Benzene is one of the food contaminants with the highest level of evidence for carcinogenicity [11]. Benzene can form in beverages when ascorbic acid combines with either sodium or potassium benzoate, with certain additional conditions present, such as heat, ultraviolet light and metallic ions in the mixture. The longer a product is in the market (shelf-life), the greater the potential for benzene formation if its precursors are present. Trace levels of metal ions, such as copper and iron, may act as catalysts in benzene formation in beverages in the presence of benzoic acid sources and ascorbic acid. Quality drinking water should have less than 10 parts of benzene per billion parts of water (ppb), or 10 micrograms per litre. There is no specific legal limit for benzene in food and drink. The World Health Organization (WHO) guideline value of 10 µg/L in drinking water has been taken as a pragmatic limit [12]. Gas chromatography is a simple, sensitive way to characterize the volatile compounds in alcoholic beverage products.

The purpose of this study was to determine the type and levels of contaminants present in some common alcoholic beverages sold in major markets in Lagos, Nigeria and determine whether these levels were within the maximum permissible levels of each contaminant in alcoholic beverages.

MATERIALS AND METHODS

Ten different samples of alcoholic beverages (both local and imported) were purchased from an open market in Oshodi, Lagos State. Six samples were spirit, two were wine and the remaining two were beer. The samples (with ethanol %) include; A(30), B(43), C(11.5), D (5.2), E(40), F(40), G(45), H(12.5), I(7.5) and J (40). They were refrigerated until analysis. Reagents used for this analysis include; Ethanol, methanol, benzene, toluene, ethyl acetate and cyclohexane with purity of 99 % GC grade and were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Gas Chromatographic Conditions: Analyses were carried out on the gas chromatograph Crystal5000 (JSC SDB Chromatec, Yoshkar-Ola, Russia) equipped with FID, a split/splitless injector, liquid autosampler, Unichrom software (New Analytical Systems Ltd., Minsk, Belarus), capillary column Rt-Wax, 60 m x 0.53 mm, phase thickness 1µm (Restek, Bellefonte, PA, USA). The oven temperature was: initial isotherm at 75 °C (9 min) and raised to 240 °C at rate 7 °C/min with final isotherm. Carrier gas was nitrogen. Gas flow was 4.5 mL/min; injector temperature 240 °C; detector temperature 240 °C; injector volume 1.0µL and split ratio 1:20. This high split ratio was chosen to achieve good separation between peaks of cyclohexane and ethanol. The recovery of all the contaminants analysed fell within this range 100.4±9.4%.

RESULTS AND DISCUSSION

The composition and concentration of by-products found in alcoholic beverages can vary widely. Some compounds appear in high concentrations (hundreds of mg/l), while a large part appear at significantly lower levels [3].

The results in table (1) show that some of the alcoholic beverages analysed contained some levels of contaminants. None of the contaminants analysed were detected in beer (D and I) and wine(C and H) i.e. they were below the detection limit but, all of the contaminants analysed were found in spirit samples.

Table 1: contaminants present in the analysed samples

Sample	Methanol (mg/L) X± S	Ethyl Acetate (mg/L) X± S	Benzene (mg/L) X± S	Toluene (mg/L) X± S	Ethyl Carbamate (mg/L) X± S
A (spirit)	21.62 ±0.03	N.D	9.63 ±0.02	N.D	N.D
B (spirit)	18.25 ±0.09	10.54±0.07	N.D	N.D	N.D
C (wine)	N.D	N.D	N.D	N.D	N.D
D(beer)	N.D	N.D	N.D	N.D	N.D
E (spirit)	N.D	N.D	N.D	156.01±3.48	N.D
F (spirit)	N.D	N.D	N.D	N.D	40.65 ±0.13
G (spirit)	N.D	30.19 ±0.008	N.D	N.D	40.28 ±0.21
H (wine)	N.D	N.D	N.D	N.D	N.D
I (beer)	N.D	N.D	N.D	N.D	N.D
J (spirit)	176.17 ± 5.17	N.D	N.D	N.D	38.73 ±2.16

ND is value below the limit of detection, X =Mean and S= Standard deviation.

Methyl alcohol (also known as: methanol) is the simplest, lowest molecular weight alcohol, yet it is the most toxic of all, due to its metabolic products-formaldehyde and formic acid [7]. It's concentration was found to be highest in sample J (176.17mg/L) followed by sample A(21.62mg/L) and sample B contained the lowest level (18.25mg/L). The concentration of methanol in sample B is about ten times the amount found in sample J. All these levels were found to be higher than the permissible standard set by National Agency for Food and Drug Administration and Control, NAFDAC (0.05mg/L) [14]. According to several authors [6,13,14], ethyl esters (mainly ethyl acetate), alcohols with three or more carbon units and acetaldehyde, are the major agents responsible for the flavor of alcoholic beverages and their amounts determine the quality of the distillate. Ethyl acetate, for example, has a significant effect on the organoleptic characteristics of distillates. The presence of this ester results in a pleasant aroma with fruity properties, which turns vinegary at levels above 150 mg/l, adding spoilage notes to the beverage [6,15]. The concentration of ethyl acetate found in sample G was (30.19mg/L) and sample B was (10.54mg/L). The levels detected in the two samples (i.e. G and B) were below 150 mg/l which also corresponds with the permissible level set by NAFDAC [14].

Benzene was only found in sample A (9.63mg/L) and this level is about 10 times the WHO (0.01mg/L in drinking water) about ten times higher than the WHO recommended permissible level (0.01mg/L) in drinking water. Acceptable level while, sample E was the only sample found to contain toluene (156.01mg/L) and this is far higher than the permissible level of toluene even in drinking water (1.0mg/L) [16]. The amount of toluene detected in sample E was sixteen times the concentration of benzene found in sample A. Based on NAFDAC recommendation, toluene and benzene must not be found even in traces in any alcoholic beverage [14]). Levels of ethyl carbamate were found to follow this order F (40.65mg/L)> G (40.28mg/L)> J (38.73mg/L). These levels were higher than the maximum permissible level of NAFDAC (1.50mg/L) [14] and the Canadian limit of 0.15 mg/L for distilled spirits [12]. Ethyl carbamate was detected in only 7.3% of beer samples analysed by FAO/WHO [16], while in wine it was 51.6% and spirit 69.4%.

This work is of significance to the producers, the consumers, the law enforcement agencies and researchers as well as general public. It will help to monitor the amount of contaminants present in alcoholic beverages and improve the quality of the production of alcoholic beverages. It will also help to reduce the effect and risk of those contaminants by enlightening the consumers of the effect to human health AS Long-term use of alcohol in excessive quantities is capable of damaging nearly every organ and system in the body [17].

This study has shown that most alcoholic beverages (spirit) contain contaminants either below or above the permissible level that has been set by regulatory bodies. The adverse of drinking alcoholic beverages may not show forth presently but rather in the future because these contaminants have tendency to bio-accumulate in the body.

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