Light-Assisted Detection of Methanol in Contaminated Spirits

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***Abstract*—The growing market of artisanal alcoholic beverages have faced challenges to assess the quality of the commercialized products. Contaminated beverages, resulting not only from an uncontrolled production process but also from deliberate adulteration, may contain nonsafe amounts of methanol leading to risks for consumers. Ethanol and methanol share similar physical-chemical properties. Both are colorless, soluble in water, and they have very close values of density. Although analytical laboratorial methods can precisely determine the alcoholic composition, rapid distinction between them is a conundrum. This paper proposes and compares two methods that can be used to fast detect the contamination of alcoholic beverages with methanol. Despite the proximity between densities of methanol and ethanol, as well as the close refractive indexes of methanol and water, it is shown that these macroscopic parameters can be used together to analyze the beverage composition. Additionally, using the fingerprinting molecular analysis provided by Raman spectroscopy and a statistical procedure based on principal component analysis, it is shown a rapid method for the detection of methanol presence in beverages above a pre-established level, without the need for addition of any standard to the sample. The performances of both methods were tested and validated with samples containing different amounts of water, ethanol, and methanol and beverages deliberately contaminated with methanol.**

***Index Terms*—Contaminated beverages, methanol contamination, Raman spectroscopy, refracto-densitometry.**

I. Introduction

ALONG the past years, not only the market for artisanal alcoholic beverages have experienced a worldwide expansion, but also the number of reported cases of intoxication by contaminated products. In the specific case of methanol, ingestion of contaminated beverages may cause health problems from simple nausea and vomit to serious blindness and even death. Consumption of methanol amounts ranging from 0.3 to 1 g per kilogram of body mass is considered lethal. However, there is a risk of intoxication even for the ingestion of methanol amounts far below this high level [1]. Considering the lethal amount and a person with a mass of 70 kg, this limit represents the ingestion of 200 ml of a contaminated beverage containing 70 g of methanol.

Owing to the serious risks to the citizens' heath, limits of methanol content in alcoholic drinks are established in different countries and must be followed by the industries.

In Brazil the maximum allowed concentration of methanol is 0.2 g/L of alcohol [2] while in the United States it would be 2.8 g/L [3]. Depending on local law, distilled beverages with alcoholic content in a predefined range can be considered a spirit. In Brazil, for example, this range lies between 38 °GL and 54 °GL – the percentage of alcohol per volume. All distributed products must be registered and have their processes controlled by the Ministry of Agriculture, Livestock and Supply [2]. Depending on the stage of the product lifecycle, from registration and classification to production control and inspection, standard tests are applied. Such set of rules are followed by the industries that produce drinks under rigid quality criteria. However, methanol concentration in illicit and even artisanal beverages may exceed the safe limit. In order to elevate the alcohol content, checked by densitometry, unscrupulous enterprises deliberately add methanol to alcoholic beverages. Methanol is used to tamper with the beverages, due to its similar density and lower price when compared to ethanol [4].

Besides, the manufacturing technologies employing traditional distillers in the production of home-distillated spirits may result in high levels of methanol content in the beverage [5]. Since methanol has a lower evaporation temperature (65 °C) than the ethanol (78 °C), depending on the fermentation that took place, the number of distillation cycles and the characteristics of the distiller apparatus and raw ingredients, as much as 10% of the yield (the first 10%) can be methanol. The heterogeneity in post separation batches could incur in concentrations higher than 10% in the final product. Low sampling rates for quality testing and the lack of appropriate laboratories and skilled personnel may introduce an additional setback for the adoption of corrective procedures. In such a scenario, many governments have warned their citizens, mainly the travelers, to the danger of drinking home-distilled spirits.

The required accuracy of the test used in the spirit analysis is highly dependent on its purpose. Several methods for alcohol analysis involving colorimetry with auxiliary chemicals, as well as demanding techniques employing cumbersome equipment for gas or liquid chromatography, rely on complex and/or time-consuming sample handling processes.

Considering that an unambiguous characterization often requires specialized laboratories and skilled manpower, not always readily available at the production or consume sites, a rapid method to assess the toxicity of beverages regarding the presence of methanol is of great concern for the sector.

Among the standardized methods used for a rapid assessment of conformity of alcohol-water based mixtures, are the densitometry and the refractometry. Densitometry is, for example, widespread used to determine the alcoholic content of ethanol fuel. Alcoholmeters give the total alcoholic content based on

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