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Assessment of Adulterated Alcohols Chromatographic Analysis under Forensic Chemistry

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Abstract:

Alcoholic beverages are consumed heavily in almost all countries of the world and some common methods adopted to increase the profit margin by selling all such alcoholic products in particular countries like India include adulteration of wine to improve sweetness by adding cheaper sources of sugar than grapes. The main objective of this research work is to use alcohol chromatographic analysis which is a part of forensic chemistry and examine the health effects of such adulterated alcohol as well as strategies to determine the most touching, available and reasonable methods and techniques for determining such adulterated alcohol.

Introduction:

The alcohol is brewed legally under government supervisions and also illegally at unregistered breweries or homebrews, therefore not properly tested for safety and sold at low price to make money and its popular among low income communities, which can be proven as harmful sometimes. The chances of contamination are also there in illegal production due to errors in distillation or accidentally. Therefore, the addition of any foreign materials in alcohol like water, drugs, or sugars, Over the last few years the issues regarding the availability of alcohol and the prices it is being sold at to an everyday consumer has been a major concern for the Indian Government. A recent survey had been carried out and appeared to conclude that fatal levels of alcohol can be purchased. The strongest and cheapest products were found to be cider, with beer coming next and wine, vodka and gin following up next. According to the Health Service

Executive (HSE) the low-risk weekly guidelines for consuming alcohol for a healthy adult between the ages of 18 to 65 is seventeen standard drinks for men and eleven for women.

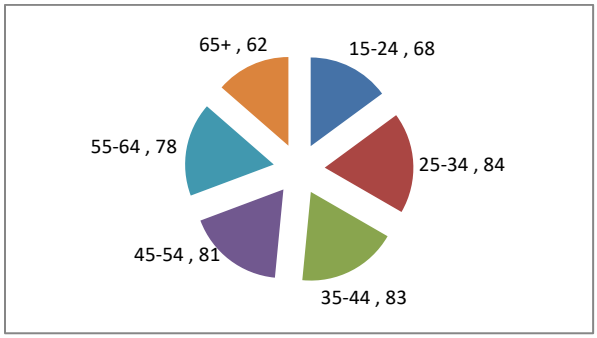

Fig 1 the percentage of alcohol consumed by adults aged 15 to over 65 over the twelve months of 2014-2015.

Consumers are purchasing more alcohol through Off-Licenses and other licensed supermarkets because it is a cheaper alternative to going out to a pub or nightclub where the case of adulterated alcohol is more common. Many methods of identifying the composition of alcohols have been adapted over the years, including site-specific natural isotope fractionation nuclear magnetic resonance (SNIF-NMR), Gas Chromatography-Mass Spectroscopy (GC-MS), Fourier-transform infrared spectroscopy (FTIR), High Performance Liquid Chromatography (HPLC), Ultra Violet-visible spectrophotometry (UV/VIS), different Gas Chromatography detectors such as Flame Ionization Detector, Electron Capture Detector and Thermal Conductivity Detector (GC-FID, ECD and TCD), and Ion Chromatography. **Wisniewska P et al [1]** used gas chromatography in studies of alcoholic beverages is presented. Due to numerous advantages such as good resolution and high sensitivity GC is becoming increasingly more popular in the analysis of samples with complex matrices. **De la Rosa Vazquez et al [2]** studied considering Tequila as sample and was found to be best analyzed using fluorescence spectroscopy. Although it is a suitable method for tequila, it may also be possible to detect other types of alcoholic beverages by fluorescence spectroscopy. **Lachenmeier et al [3,4] focused on** Vodka and rum suggested that these two alcohols can be easily detected using GC-FID or ion chromatography. Compounds such as ethanol, acetaldehyde, chloride, nitrate, n-propanol and iso-butanol were detected using gas chromatography. GC has developed over a period of time, to become more accurate and sensitive, and therefore more acceptable to use for determining alcohol purity.

Research Methodology

The present work is to find adulteration in various alcohols using different machines and techniques like SPME (**Solid - Phase Microextraction)**, LLE (**Liquid-Liquid Extraction)**, SPE (**Solid-Phase Extraction)** for various types of alcohol i.e. beers, wine and spirits. SPME is the technique in which the sorption of small amounts of samples onto a thin cylindrical layer of stationary phase coating a glass or quartz fiber. The fiber is placed inside a rust-free tube, which is located in the syringe needle. Such a setup enables mass exchange during the enrichment and release of the adsorbed compounds and pre-vents clogging. SPE is based on transferring the liquid sample into the solid phase using the water/solid sorbent partition coefficient for the analyzed organic compounds. The LLE technique is one of the most popular methods of sample preparation. The condition under which the extraction can be properly performed is the presence of two phases that are easily separated by mechanical means after the finished extraction. The extraction process is based on adding solvent to the mixture that contains the component to be extracted.

Result and Discussion

Table 1 - Gas chromatography results of suspicious vodka sample sold as Smirnoff and reference Smirnoff and German vodka samples. ND = Not Detected

Suspicious Vodka Sample			**Reference Vodka Sample**		
	Smirnoff 1	**Smirnoff 2**	**Smirnoff 3**	**Authentic Smirnoff**	**Authentic German Vodka**
Relative Density	0.9537	0.9538	0.9538	0.9538	0.9536
Ethanol	37.4	37.3	37.3	37.3	37.5
Chloride	8.0	8.7	9.3	ND	9.3
Nitrate	14.5	14.4	12.8	ND	15.5
Isoamyl Alcohol	1.6	1.9	1.6	1.5	1.4
Acetaldehyde	2.1	2.2	2.2	2.6	2.2

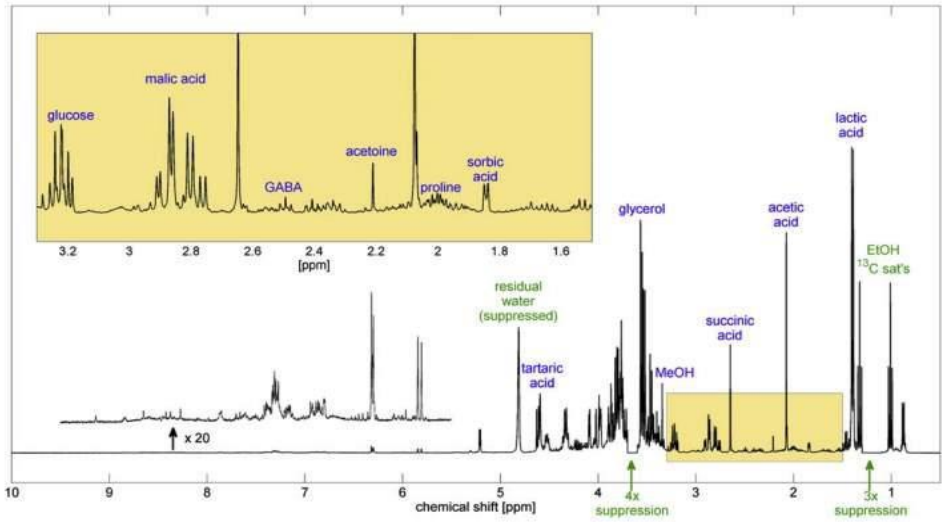

Fig. 1 -A proton NMR spectrum showing the separation of peaks depending on the type of acid present. There is a presence of tartaric acid, glycerol, MeOH, succinic acid, acetic acid, lactic acid, malic acid, glucose, GABA, proline and sorbic acid.

The method of SNIF-NMR is also useful for analysing beer samples for the distribution of deuterium in ethanol. Although there is a lack of literature for analysing and authenticating beer in comparison to wine, it can be of interest to test it to differentiate certain types of beer or to determine different malt types used in the beer. Other methods apart from SNIF-NMR can be used such as FTIR and Proton NMR. Since beer adulteration is not harmful to a consumer, the development of analysing it has not taken place in recent years and it may remain that way due to the lesser importance of it compared to the authenticity of wines and spirits.

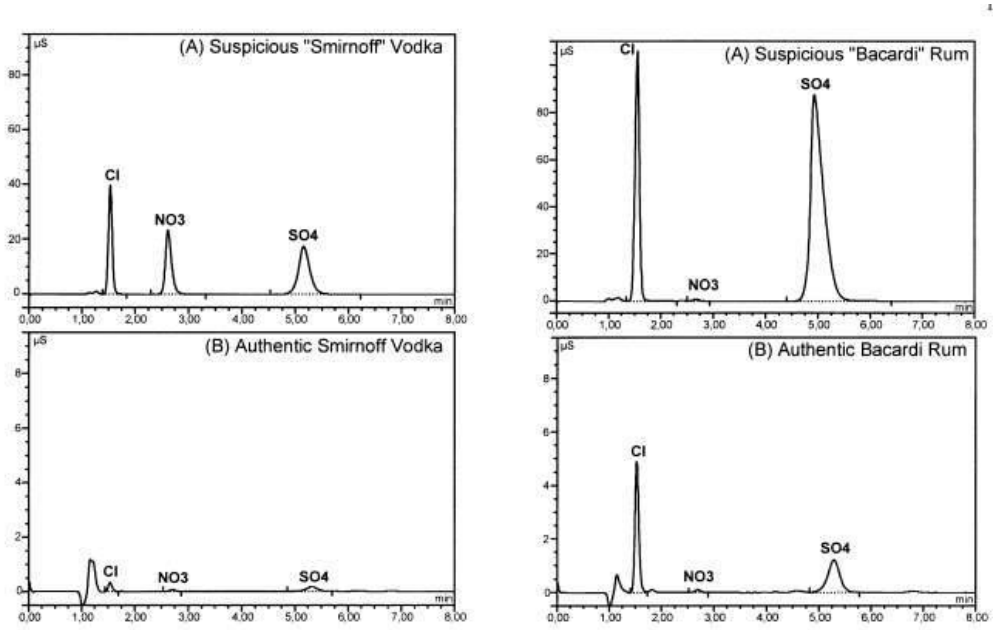

Fig. 2- Ion chromatogram of vodka samples with (A) Suspicious vodka sold as Smirnoff and (B) Authentic Smirnoff

One method used for the authentication of vodka, rum and brandy is ion chromatography. In this study it was stated that gas chromatography is normally used to identify substances that are volatile. However, a new and improved method of using ion chromatography can determine the ionic content of domestic water and brand-specific spirit water used for distillation which show different compositions. It was concluded that ion chromatography is an easy way to determine the ionic composition as it requires very little sample and very little sample preparation. High sensitivity, reproducibility and selectivity are shown during the analysis which is a must have to produce accurate results. The study also concluded that a GC analysis was carried out for the vodka and run samples which only showed acetaldehyde and isoamyl alcohol present in the vodka samples.

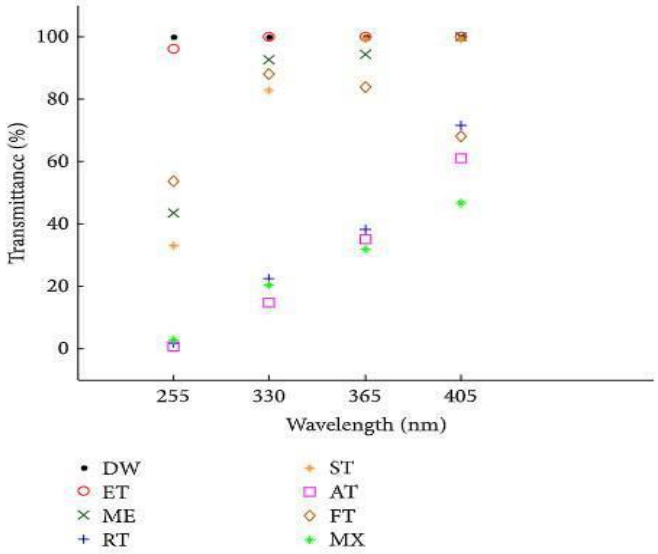

Fig. 3- A Fluorescence spectroscopy spectrum of distilled water (DW), ethanol (ET), methanol (ME), aged tequila (AT), rested tequila (RT), mixed tequila (MT), silver tequila (ST), and fake tequila (FT), at 255nm, 330 nm, 365 nm and 405 nm

It had been concluded from the results that the fluorescence excited at 255nm could be used to show the adulterated tequila from the original tequila. The method could be improved by the measurement of spectral transmittance in the 255 to 405nm wavelength interval. Over all the use of fluorescence spectroscopy is a very practical method in determining the adulteration of alcoholic beverages, specifically tequila.

Conclusion

1. For analyzing alcohols for adulterants it can be said that different types of alcohol i.e. beers, wines and spirits (such as vodka, rum, tequila, brandy and whiskey), can be analyzed using different machines and techniques.
2. The technique that both wine and beer have in common is the SNIF-NMR. It can detect geographical origins and varieties of grapes. Beer can be tested using other methods such as FTIR and Proton NMR to distinguish its type and if there may have been brand fraud.
3. Vodka and rum can be easily detected using GC-FID or ion chromatography. Compounds such as ethanol, acetaldehyde, chloride, nitrate, n-propanol and iso-butanol were detected using gas chromatography. GC has developed over a period of time, to become more accurate and sensitive, and therefore more acceptable to use for determining alcohol purity.

4. Tequila was found to be best analysed using fluorescence spectroscopy. Adulterated tequila could be distinguished from genuine tequila by comparing the wavelengths.
5. Sample preparation through SPME, LLE and SPE gave many similar advantages and disadvantages. The advantages included the low cost of the equipment required and the simplicity of the preparation. The major disadvantage concluded was the loss of material.

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