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Forensic Examination of Methanol (Poisonous Alcohol) Detection in Local Beverages of Jharkhand State Using UV/Vis Spectroscopy and Different Chemical Detection Techniques: An Analytical Study for the Purpose of Police Investigation

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Abstract

The study of detection of alcohol in local beverage of Jharkhand state is very needful research for law enforcement agencies and state police authority, because Jharkhand state is very rich in culture and its maximum population in villages or in a small city the people use the local liquors for consumption and sometimes it seems that in certain cases in local beverage founding methanol concentration on it due to that the consumer suffers from it, that's this study is important for the purpose of helping in police investigation and detection of crime related to illegal liquors cases. In this research study we use both presumptive examination by performing color test and for confirmatory test we analyze by UV-vis spectroscopy.

Keywords: Population • Methanol concentration • Police investigation • UV-vis spectroscopy

Introduction

UV-Visible spectroscopy is a technique that measures the amount of light absorbed by a chemical substance. It is absorption spectroscopy or reflectance spectroscopy technique within the ultraviolet and visible regions of the electromagnetic spectrum. When continuous radiation is passed through a compound a portion of that compound is absorbed by the compound. The residual radiation after passing through the compound yields a spectrum with gaps in it due to absorption by the compound, this spectrum is called the absorption spectrum [1].

Absorption of UV-visible radiation results in the electronic transition of the compound, *i.e.,* an electron in the ground state (occupied orbital) is promoted to the excited state (unoccupied orbital) and the amount of radiation absorbed corresponds to the energy difference between the ground state and the excited state.

Principle of UV/Visible spectroscopy

UV-visible spectroscopy is a quantitative technique used in analytical chemistry to measure the amount of light absorbed by a substance. When light falls upon a substance it absorbs and reflects a certain amount of radiation. As the light passes through the sample, the amount of radiation absorbed by the substance is the difference between the incident radiation (I_0) and the transmitted radiation (I).

The amount of radiation absorbed is called absorbance (A) and transmittance (T), which is a fraction (I/I_0) indicating the amount of light that has passed through the sample.

Transmittance, $T=I/I_0$

Absorbance, $A=\log_{10}(I_0/I)=\log_{10}(1/T)=-\log_{10}(T)$

According to Beer-Lambert's law, the absorbance of a solution (containing the compound) is directly proportional to the concentration of the absorbing species (the compound) and the path length. This translates to, as the number of molecules (concentration) capable of absorbing the radiation at a given wavelength increases, the extent of absorption is increased. Also, the efficiency of the molecule (recorded by its molar absorptivity) in absorbing the radiation contributes to greater absorption [2].

The formulation for Beer-Lambert's law is given by,

$A=\varepsilon cl$ for a given wavelength

Where,

ε=molar absorptivity (also known as molar extinction

coefficient) c=molar concentration of the absorber (solute)

l=path length (length of the sample cell or cuvette in cm)

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The mathematical relation between absorbance and concentration established by the Beer-Lambert law allows direct measurement of the concentration of the absorber in a solution from absorbance for a fixed path length.

The instrumentation of UV-visible spectroscopy is called a UV-visible spectrophotometer. The spectrophotometer has a few key components namely:

- The light source emits broadband electromagnetic radiation across the UV-visible spectrum.
- The dispersion device or monochromator-it's a diffraction grating that separates the radiation into its component wavelength.
- A sample area-the radiation interacts with the sample as it passes through or reflects off.
- Detector-measures the reflected or transmitted radiation intensity.

Materials and Methods

Alcohol, sometimes referred to by the chemical name ethanol, is a psychoactive drug that is the active ingredient in drinks such as beer, wine and distilled spirits (hard liquor). It is one of the oldest and most common recreational substances, causing the characteristic effects of alcohol intoxication (drunkenness). Among other effects, alcohol produces happiness and euphoria, decreased anxiety, increased sociability, sedation, impairment of cognitive, memory, motor and sensory function and generalized depression of central nervous system function. Ethanol is only one of several types of alcohol, but it is the only type of alcohol that is found in alcoholic beverages or commonly used for recreational purposes; other alcohols such as methanol and isopropyl alcohol are significantly more toxic [3].

Alcohol has a variety of short-term and long-term adverse effects. Short-term adverse effects include generalized impairment of neurocognitive function, dizziness, nausea, vomiting and hangover-like symptoms. Alcohol is addictive to humans and can result in alcohol use disorder, dependence and withdrawal. It can have a variety of long-term adverse effects on health, such as liver damage and brain damage and its consumption is the fifth leading cause of cancer. The adverse effects of alcohol on health are most important when it is used in excessive quantities or with heavy frequency. However, some of them, such as increased risk of certain cancers, may occur even with light or moderate alcohol consumption. In high amounts, alcohol may cause loss of consciousness or in severe cases, death.

Alcohol and brain (reactions)

Alcohol works in the brain primarily by increasing the effects of a neurotransmitter called γ-aminobutyric acid or GABA. This is the major inhibitory neurotransmitter in the brain and by facilitating its actions, alcohol suppresses the activity of the central nervous system. The substance also directly affects a number of other neurotransmitter systems including those of glutamate, glycine, acetylcholine and serotonin. The pleasurable effects of alcohol ingestion are the result of increased levels of dopamine and endogenous opioids in the reward pathways of the brain. Alcohol also has toxic and unpleasant actions in the body, many of which are mediated by its byproduct acetaldehyde.

Methanol

Methanol (methyl alcohol) was originally produced by heating wood chips in the absence of air. Some of the carbohydrates in the wood are broken down to form methanol and the methanol vapor is then condensed. This process led to the name wood alcohol as another common name for methanol. Methanol is synthesized commercially by a catalytic reaction of Carbon Monoxide (CO) with Hydrogen gas (H_2) under high temperature and pressure. Methanol has a high-octane rating and a low emission of pollutants characteristics that make it a valuable fuel for automobile engines. From the late 1960s until 2006, the cars at the Indianapolis 500, the automobile race held annually at the Indianapolis Motor Speedway, were powered by methanol-burning engines. Methanol was once under consideration as a commercial motor fuel because it is cheaper than ethanol and can be made from natural gas and coal resources. However, increasing interest in ethanol-based fuels and difficulties involving the solvent properties of methanol, which cause problems with fuel systems especially in fuel-injected cars have resulted in diminished commercial interest in methanol fuels. Methanol tends to dissolve the plastic and rubber components employed in modern fuel systems and different materials must be used that can survive exposure to methanol over long periods of time without dissolving or cracking.

Pure methanol is an important material in chemical synthesis. Its derivatives are used in great quantities for building up a vast number of compounds, among them many important synthetic dyestuffs, resins, pharmaceuticals and perfumes. Large quantities are converted to dimethylaniline for dyestuffs and to formaldehyde for synthetic resins. It is also used in automotive antifreezes, in rocket fuels and as a general solvent. Methanol is also a high-octane, clean-burning fuel that is a potentially important substitute for gasoline in automotive vehicles. The methanol derived from wood is used chiefly for rendering industrial ethyl alcohol unfit to drink [4].

Characteristics of methanol or methyl alcohol

- It is a colorless liquid that boils at 64.96° celsius and solidifies at 93.9° celsius. When mixed with air or comes in contact with air it forms explosive mixtures and burns with a non-luminous flame. Methanol is completely miscible in water its order is similar to that of ethyl alcohol.
- Methanol's odor resembles that of ethyl alcohol, an intoxicant of alcoholic beverages but along with this, it is also a very dangerous poison. It was also said to cause death if consumed.
- It appears as a colorless, fairly volatile liquid. The vapors of methyl alcohol or slightly heavier than air and I travel to some distance to a source of ignition and flashback. With this characteristic, if there is an accumulation of zippers in confined spaces in the buildings or any other confined places such as sewers, it may explode if ignited.
- Methanol works as an amphiprotic solvent (define). It is majorly known as alkyl alcohol, which is the one-carbon compound and also a girl child organic compound which categorizes as primary alcohol as well. It is the conjugate acid of methoxide.

Sample collection

Collection of samples is one of the major steps in the research work or even in the lab works. Without doing the proper collection process of any sample whether it was for study purpose or for the case the finding could not be done accurately. When we follow the proper step the result or the finding is accurate. Each sample should be collected in a different way so different process are applied for different sample. The sampling method used in this study was stratified random sampling method. The collection of samples was done simultaneously from the different shops in the district of Jharkhand. Collection method of sample was done as per the description in the literature. The alcohol sample has to be collected in a bottle or in a container. For the purpose of collection of samples, we need the following materials:

- Plastic container
- Gloves
- Labels

Steps involved:

- The gloves were worn.
- The alcohol sample was taken in a plastic container.
- The plastic container has to be labeled containing certain details (place, date, type of alcohol should be written on it).

Labels are put on the container so that during the time of analysis we may not get confused but n number of sample.

Results and Discussion

Procedures

For that particular research we performed some chemical tests for detection of methanol and instrumentation analysis also that is UV-Vis spectroscopy [5].

Chemical test

There are different types of chemical test are performed for the detection of methanol in the sample. The chemical test which are performed only give positive result when the sample contain methanol in it. 10 samples were taken and were analysed on the basis of this chemical test. The chemical test which are performed are:

- Chromotropic acid test
- Schiff's test
- Sulphomolybdic acid test

Chromotropic acid test

Chromotropic acid test is specific test for the detection of methanol from the sample. If the result of this test is positive then the given sample contain methanol in it.

Procedure for hadiya (rice beer) (sample1, S1):

- Firstly, take the 2 ml of hadiya sample in the test tube.
- Then, add 2 ml of potassium permanganate solution to the test tube containing the sample. The purple colour appears in the test tube.
- Add freshly prepared 5 ml chromotropic acid into the test tube.
- After that add drop wise conc. H_2SO_4 in the side wall of the test tube.
- The appearance of violet colour in the test tube.

Result: The appearance of violet colour indicates the presence of methanol in the hadiya.

Sample (Hadiya)+2 ml potassium permanganate=Purple colour+5 ml chromotropic acid+2-3 drop conc. H_2SO_4=Violet colour

Note: Same procedure is repeat for the other sample of S4, S5 and S10 which has been collected from the other places of Jharkhand.

Procedure for mahua (S2):

- Firstly, take the 2 ml of Mahua sample in the test tube.
- Then, add 2 ml of potassium permanganate solution to the test tube containing the sample. The purple colour appears in the test tube.
- Add freshly prepared 5 ml chromotropic acid into the test tube.
- After that add drop wise conc. H_2SO_4 in the side wall of the test tube.
- The appearance of violet colour in the test tube.

Sample (Mahua)+2 ml potassium permanganate=Purple colour+5 ml chromotropic acid+2-3 drop conc. H_2SO_4=Violet colour

Same procedure is repeat for the other sample of S6 and S7 which has been collected from other places of Jharkhand.

Procedure for toddy (S3):

- Firstly, take the 2 ml of toddy sample in the test tube.
- Then, add 2 ml of potassium permanganate solution to the test tube containing the sample. The purple colour appears in the test tube.
- Add freshly prepared 5 ml chromotropic acid into the test tube.
- After that add drop wise conc. H_2SO_4 in the side wall of the test tube.
- The appearance of violet colour in the test tube.

Sample (Toddy)+2 ml potassium permanganate=Purple colour+5 ml chromotropic acid+2-3 drop conc. H_2SO_4=Violet colour

Same procedure is repeat for the other sample of S8 and S9 which has been collected from other places of Jharkhand (Figure 1) [6].

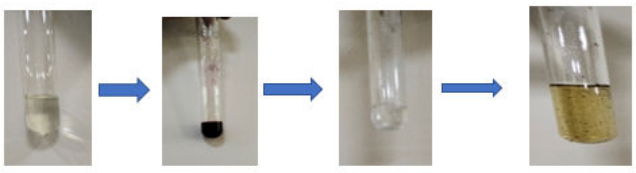

Figure 1. The result of the test perform on laboratory.

Schiff's test

Schiff's test is used for the detection of methanol in the sample. This method takes long time for showing the result.

Procedure for s1 sample:

- Firstly, the sample is taken in a test tube.
- Add 0.5% of ethanol to the sample.
- Then, add 3 ml potassium permanganate to the test tube.
- Add 2 ml of ortho phosphoric acid to the test tube and left the sample for 10 min.
- After that add 1 ml of 10% phosphoric acid to the test tube and left it for 10 min.
- Add 1 ml conc. H_2SO_4 and left the sample for 10 min. The solution colour disappears.
- Then, finally add Schiff's reagent to the test tube.
- Appearance of purple colour.

Result: The appearance of purple colour indicates the presence of methanol.

Same procedure is repeat for the other sample of S4, S5 and S10 which has been collected from other places of Jharkhand.

Procedure for s2 sample:

- Firstly, the sample is taken in a test tube.
- Add 0.5% of ethanol to the sample.
- Then, add 3 ml potassium permanganate to the test tube.
- Add 2 ml of ortho phosphoric acid to the test tube and left the sample for 10 min.
- After that add 1 ml of 10% phosphoric acid to the test tube and left it for 10 min.
- Add 1 ml conc. H_2SO_4 and left the sample for 10 min. The solution colour disappears.
- Then, finally add Schiff's reagent to the test tube.
- Appearance of purple colour.

Result: The appearance of purple colour indicates the presence of methanol.

Same procedure is repeat for the other sample of S6 and S7 which has been collected from other places of Jharkhand.

Procedure for s3 sample:

- Firstly, the sample is taken in a test tube.
- Add 0.5% of ethanol to the sample.
- Then, add 3 ml potassium permanganate to the test tube.
- Add 2 ml of ortho phosphoric acid to the test tube and left the sample for 10 min.
- After that add 1 ml of 10% phosphoric acid to the test tube and left it for 10 min.
- Add 1 ml conc. H_2SO_4 and left the sample for 10 min. The solution colour disappears.
- Then, finally add Schiff's reagent to the test tube.
- Appearance of purple colour.

Result: The appearance of purple colour indicates the presence of methanol.

Same procedure is repeat for the other sample of S8 and S9 which has been collected from other places of Jharkhand (Figure 2) [7].

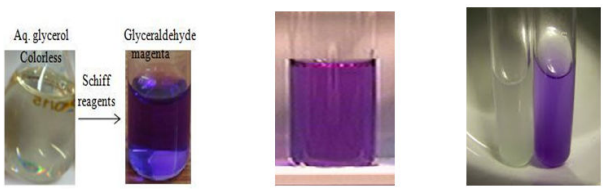

Figure 2. The result of the test perform on laboratory.

Instrumental method (UV-Vis spectrophotometer)

Ultraviolet-Visible (UV-Vis) spectrophotometry is a technique used to measure light absorbance across the ultraviolet and visible ranges of the electromagnetic spectrum. When incident light strikes matter it can either be absorbed, reflected or transmitted. The absorbance of radiation in the UV-Vis range causes atomic excitation, which refers to the transition of molecules from a low-energy ground state to an excited state. Before an atom can change excitation states, it must absorb sufficient levels of radiation for electrons to move into higher molecular orbits. Shorter bandgaps typically correlate to absorption of shorter wavelengths of light. The energy required for molecules to undergo these transitions, therefore, are electrochemically-specific. A UV-Vis spectrophotometer can use this principle to quantify the analytes in a sample based on their absorption characteristics. Ultraviolet/Visible area (UV-Vis) measurements span wavelengths from around 200 nm to 800 nm. The absorption by a molecule of ultraviolet or visible radiation results in transitions between the molecule's electrical energy levels. The optical and electronic properties of different materials, such as films, powders, monolithic solids and liquids are suitable for characterization. UV-Vis spectroscopy is a cost-effective, simple, versatile, non-destructive, analytical technique suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV-Vis spectrophotometers measure the absorption or transmission of light that passes through a medium [8].

Principle of UV-Vis spectroscopy

The Beer-Lambert law: This law states that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is actually proportional to the concentration of the solution and the incident radiation [9].

This law is expressed through this equation:

$A=\log (I_0/I)=ECl$

where, A stands for the absorbance, I_0 refers to the intensity of light upon a sample cell, I refers to the intensity of light departing the sample cell, C stands for the concentration of the solute, L stands for the length of the sample cell and E refers to the molar absorptivity.

Procedure

- Firstly, we should start the UV-Vis spectrophotometer apparatus so that the calibration process starts.
- Then, put the sample in the cuvette and take another cuvette in which we will put the standard sample.
- Then, put the cuvette in the machine.
- If the machine is calibrated then we will click on start button.

- We can also set all the parameter of the measurement.

Result: Graph has been obtained which help in determining the range of methanol present in it (Figure 3) [10].

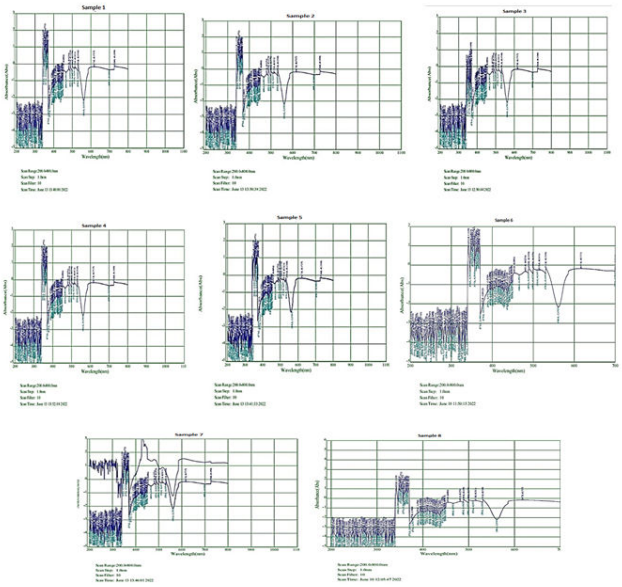

Figure 3. UV-VIS spectroscopy outputs of samples 1 to 8.

The graph, represent the different samples which has been collected from the different places of Jharkhand state. All sample absorbance come under 340 nm-360 nm which means that the sample contain methanol.

In the graph, sample 7 represent the two-samples run at a time in which one is the standard sample and the other one is the suspected sample but the peak of both samples came at a fixed point. In this graph, sample 8 represent the standard sample of methanol to check the range in the UV-Vis spectrophotometer. The standard sample absorbance is 340 nm [11].

Conclusion

The chemical test which are performed are chromotropic acid test in this all the sample give positive result of the detection of methanol the appearance of violet colour indicate that methanol is present. The colour is dark that means the concentration is high. Each and all steps are performed in an appropriate manner and the appearance of violet colour in the sample indicate the presence of methanol in the sample and the intensity of colour indicate that the concentration of methanol is also quite high in comparison to the branded one.

In the instrumental method we perform UV-Vis spectrophotometer. In this the graph of the sample is analysed with the standard sample and it was found that the sample contains methanol in it and its concentration is also determined.

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