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The Quantitative Analysis of Ethanol-based Hand Sanitizers and Prediction of Methanol Adulteration Using FTIR-ATR Technique

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Abstract **Background -** In this paper, a spectroscopic method is used to quantify the methanol and ethanol together present in the hand sanitizers with the help of the FTIR-ATR spectrometer using the Beers law quant method. **Objective**- The aim of this study is to determine the content of methanol as an adulterant in the ethanol-based hand sanitizers which are commercially available in the local market of Hapur with the help of FTIR –ATR technique. **Method**- In order to find out the methanol, seven synthetic hand sanitizers of ethanol contaminated with methanol were prepared and three for cross-validation as per the formulation of WHO for hand sanitizers. The calibration curves were constructed using Beers law by finding the peak area in the range 1020-1022 cm^{-1} & 1044-1046 cm^{-1} for methanol and ethanol respectively using Quant software. The linear curves so obtained have shown the correlation coefficient 0.997 and 0.996 for methanol and ethanol respectively. Five branded ethanol-based hand sanitizers were analyzed by FTIR-ATR. **Result**-The analysis of the locally purchased hand sanitizers shows less content of ethanol than claimed in most of them. However, none of the brands shows the presence of methanol as an adulterant. The validity of the method can be verified by the three synthetic sanitizers which were adulterated by methanol. **Conclusion**- With the widespread of Covid-19 the presence of methanol in hand sanitizers cannot be ruled out which can be harmful to health. In this paper, we have used a technique that is fast, cost-effective, and accurate to evaluate the adulteration of methanol in hand sanitizers.

Keywords: *ethanol-based hand sanitizers, COVID-19, FTIR-ATR, beers law, methanol adulteration*

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1. Introduction

In the midst of the coronavirus COVID-19 (SARS-CoV-2) outbreak [1] the demand for alcohol-based hand sanitizer has become high. Due to this reason, there is a critical shortfall of supply and the possibility of adulteration as well. To overcome this problem, the Food and Drug Administration (FDA) has produced a guidance document for the compounding of certain alcohol-based hand sanitizer products during this pandemic. There are two formulations recommended by the World Health Organization (WHO). They contain ethyl alcohol (80 % v/v) or Isopropyl alcohol (75 % v/v), Glycerol (1.45 % v/v), Hydrogen Peroxide (0.125 % v/v) with sterile or distilled water with remainder of volume. [2,3]. A hand sanitizer of less than 60% ethanol or IPA is not effective to kill all the microbes. Alcohol can attack and destroy the outer layer of the envelope protein of the virus including coronavirus. This protein is vital for a virus's survival and multiplication. Alcohol solutions containing 60% to 95% alcohol are the most effective. Notably, higher concentrations are less potent because proteins are not denatured easily in the absence of water. Alcohol-free hand sanitizers are also being reported to contain quaternary ammonium compounds (commonly benzalkonium chloride) instead of alcohol. However, these are less effective than alcohol-based hand sanitizers. Ethanol is a product of the distillation of grains or other carbohydrates. After the coronavirus crisis, a large number of distillers are involved in sanitizer production, by using "undenatured" alcohol, a food-grade ethanol that the industry has readily available.

Due to the involvement of a large number of companies in ethanol-based hand sanitizers, the issue of quality checks becomes important. The presence of methanol in hand sanitizer can be dangerous for human health. A large number of such hand sanitizers contaminated with methanol have been recently banned in the U.S. by FDA [4] (FDA updates the hand sanitizers consumers not to be used). Methanol exposure can result in nausea, vomiting, headache, blurred vision, permanent blindness, seizures, coma, and permanent damage to the nervous system or death. Hence it becomes essential to find methanol in ethanol-based sanitizers. In this context, the present method is a fast and accurate analysis for finding the

adulteration of methanol along with the quantity of ethanol in hand sanitizers.

The presence of methanol in ethanol can usually be quantified with GC-FID method [5] while the ethanol can be determined by capillary gas chromatography [6], sequential injection analysis with spectrophotometric [7], fluorescent chemical sensor [8] types techniques. All these methods mentioned are very expensive and time-consuming for finding the methanol and ethanol together. The use of FTIR with ATR is far better since the small volume of samples required, less time-consuming and user-friendly software.

The FTIR is increasingly used for the determination of sugars in aqueous mixtures, adulteration of honey [9,10] fruit juice and various ethanolic beverages [11,12], spirit drink, and beer [13]. These methods are based upon calculations like PLS-1 (Partial Least Square Algorithm –1); PLS-2 (Partial Least Square Algorithm –2); PCR (Principal Component Regression) and are quite complicated. But in the present method, we have used the simple Beers law quant method. In this method, we have selected the peak area as the basis of our calibration curve for both the ethanol and methanol present in the synthetic mixture of hand sanitizers. During the literature survey, we found that none of the methods is reported so far to find methanol adulteration in ethanol-based hand sanitizers using the FTIR-ATR technique based on the Beers law quant method.

2. Materials and Methods

Ethanol (99.9%, Omnis, SD fine) Methanol (HLPC grade, Merck) and Water HPLC grade (Merck) were used to prepare the synthetic standard mixtures for calibration and validation sets. The synthetic mixture of Ethanol based hand sanitizers adulterated with different percentages of methanol was prepared. The maximum ethanol % is varied from 40% to 77.5% while that of methanol is varied from 40% to 2.5% keeping the percentage of overall alcohol not more than 80%. Each standard was made up such that all contained the same quantity of glycerol and hydrogen peroxide (1.45 and 0.125 % v/v respectively). Solutions were made up to 100 mL using HPLC grade water as per WHO formulation.

Fourier transform infrared spectra were recorded using an ATR module on the model Spectrum two of Perkin Elmer, UK equipped with DTGS detector. ATR is composed of diamond crystal. The spectrometer is completely software controlled with the facility of Beer law quant software. The calculations of peak area were performed using the algorithm Beers law quant software. The spectrum of each sample has been obtained by taking the average of 4 scans at a resolution of 4 cm^{-1} for each sample. Each sample was scanned from the range of 4000 cm^{-1} to 400 cm^{-1}. One drop of the sample was placed using a Pasteur pipette in direct contact with the crystal. ATR crystal was carefully cleaned with n-hexane twice followed by drying with an appropriate tissue paper before measurement of the next sample.

Five ethanol-based hand sanitizers were also purchased from the local market of Hapur for analysis. Three more synthetic samples for cross-validation adulterated with methanol were also evaluated by FTIR-ATR. The FTIR absorption spectra of seven synthetic samples of ethanol-based hand sanitizers adulterated with methanol were recorded. FTIR –ATR absorption curve for seven synthetic samples is given in Figure 1 only from the range 1200-800 cm^{-1}. In order to test the performance of Beer law, specified and calculated values were checked and compared as given in Table 1.

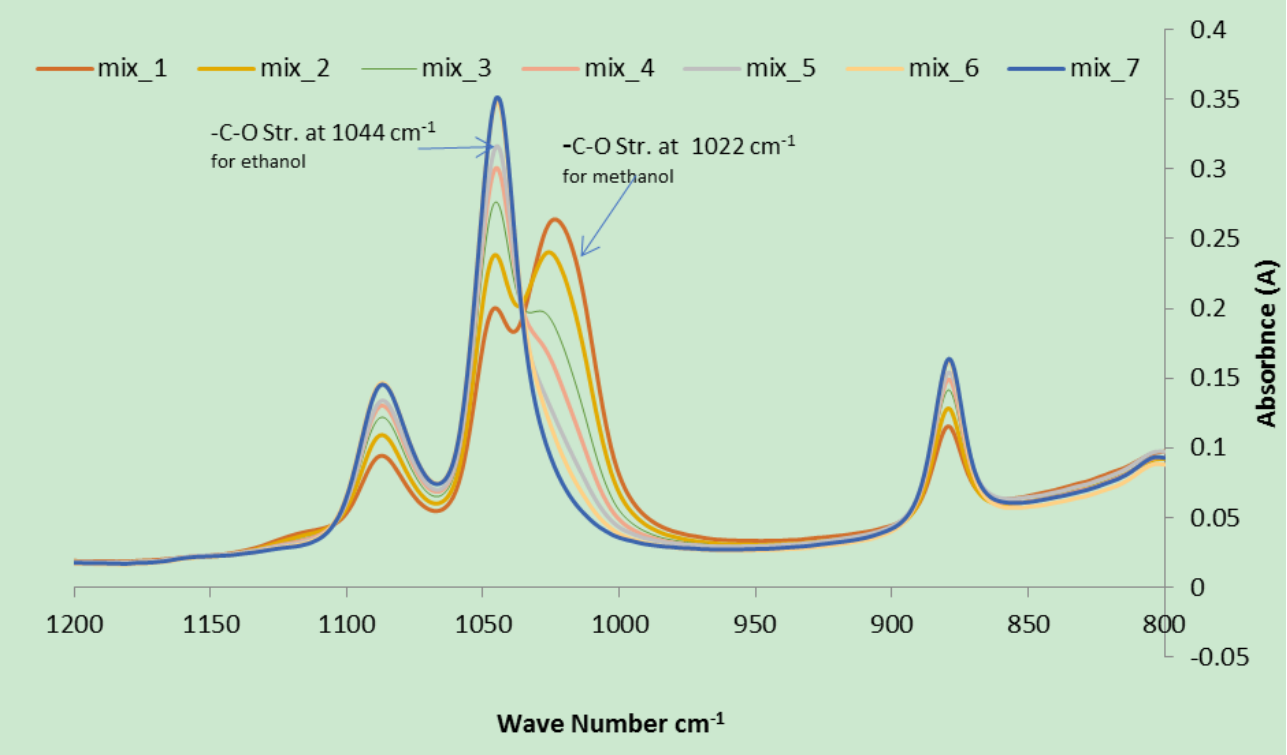

Figure 1. FTIR- ATR Absorption spectra of the seven synthetic ethanol-based hand sanitizers adulterated with methanol

Table 1. Percentage of ethanol and methanol specified and calculated with residual amount using the quant software

Ethanol Specified %	Ethanol Calculated %	Residual	Methanol Specified %	Methanol Calculated %	Residual
40.0	40.955	-0.954989	40.0	38.3978	1.60225
50.0	49.70	0.299988	30.0	31.5621	-1.56207
60.0	58.8159	1.18412	20.0	21.2899	-1.28995
65.0	64.7596	0.240352	15.0	15.1454	-0.145388
70.0	69.0357	0.96431	10.0	8.92051	1.07949
75.0	76.3586	-1.35856	5.0	5.3328	-0.332795
77.5	77.8752	-0.375221	2.5	1.85154	0.648464

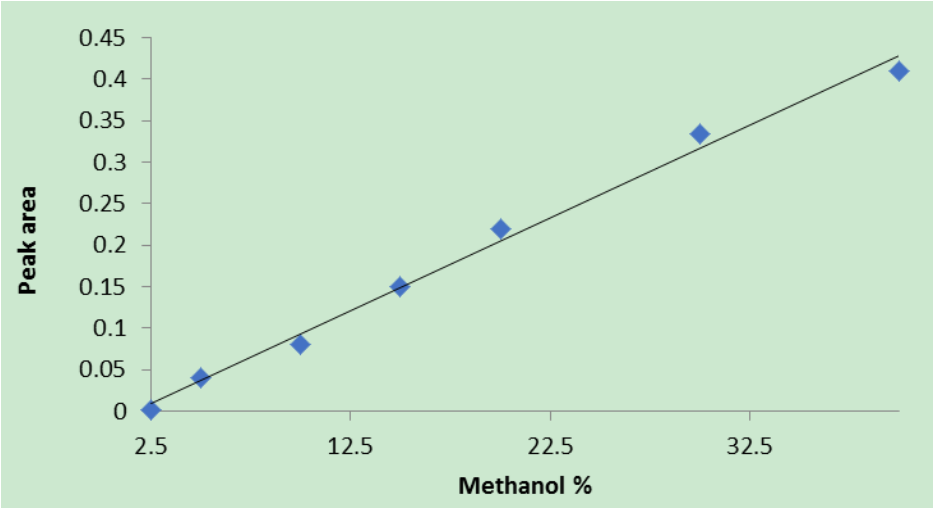

Figure 2. Methanol calibration curve in the mixture

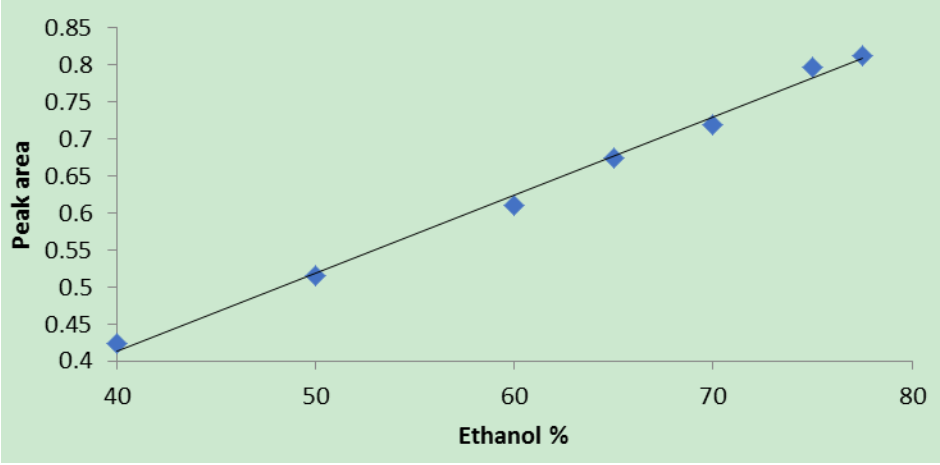

Figure 3. Ethanol calibration curve in the mixture

The calibration curve for both methanol and ethanol between the peak area versus percentage are plotted in Figure 2 and Figure 3 respectively. The peak area from 1042-1044 cm^{-1} (C-O str.) is selected for ethanol and 1020 -1022 cm^{-1} (C-O str.) for the methanol. Both the peaks don't overlap and can be easily distinguished and can be used for quantitative purposes.

3. Result and Discussion

The Beer law was used to generate the calibration curve for the synthetic ethanol-based sanitizer contaminated with methanol. From the regression analysis, the correlation coefficient and SEP for methanol 0.9962, 1.9431 and that for ethanol 0.9975, 1.4491 were found as given in Table 2. The ethanol and methanol both fit linearly with a good correlation coefficient in their mixture. The method is also cross-validated with the three different synthetic mixtures of ethanol-based hand sanitizers adulterated with methanol. The amount of added methanol is confirmed by FTIR –ATR technique in the synthetic hand sanitizers as given in Table 3. Thus, the result of cross-validation is also good. Five different brands of sanitizer were purchased from the local market of Hapur. These were brought to the laboratory for the analysis of the methanol adulteration but none of them reported the significant presence of the methanol. However, they have less content of ethanol than claimed as given in Table 3. Thus, the current method can be highly beneficiary, non-expensive, fast technique for the identification of methanol in hand sanitizer and the quantitation of ethanol.

Table 2. Calibration Results from the plot between Peak areas vs. % conc

S. No.	Parameters	Ethanol	Methanol
1	Correlation coefficient	0.99752	0.996251
2	Standard Error	1.03714	1.29529
3	Standard Error of Prediction (SEP)	1.44915	1.9431

Table 3. Predictions of % ethanol and methanol in five brands and three synthetic mixtures For Validation

Brands and synthetic mix. for validation	Ethanol Specified %	Ethanol Calculated %	Methanol Specified %	Methanol calculated %
Brand-1	80	76.96	Nil	ND*
Brand-2	80	72.23	Nil	ND*
Brand-3	80	81.97	Nil	ND*
Brand-4	80	79.22	Nil	ND*
Brand-5	80	76.12	Nil	ND*
Mix15:1	75	76.35	05	5.3328
Mix14:5	70	69.035	10	8.9205
Mix 11:5	65	66.48	15	13.52

ND*- Not Detected.

4. Conclusion

From the above discussion, it is clear that the adulteration of hand sanitizers with methanol can be confirmed with the help of FTIR-ATR techniques in just a few seconds without any use of expensive chemicals. Thus, the current method is fast, cost-effective, and accurate to determine the adulteration of methanol and the quantitation of ethanol in hand sanitizers.

Conflicts of Interest

There is no conflicts of interest.

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