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Actual applications of infrared spectrophotometry in determining the quality of daily products

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Abstract. Fourier transform infrared spectroscopy (FTIR) is a fast and non-destructive analytical method. Combined with chemometrics, it is a powerful tool for the pharmaceutical, cosmetics and food industries. This method can be used for qualitative and quantitative analysis of medicines, foods and other daily products. At the same time, IR spectroscopy is becoming a suitable technique in the processes of drug preparation and for monitoring the productive processes in quality control laboratories. In this paper, IR spectroscopy is used to determine the concentration of alcohol in hand sanitizers, which is essential for slowing the spread of viruses. The effectiveness of hand sanitizer is entirely determined by the volatile ingredient, alcohol, which must remain at a concentration greater than 60% (volume) to destroy bacterial and viral pathogens. The selected samples varied according to the initial concentration of ethyl alcohol, manufacturer, color, perfume and other ingredients, as well as the validity period.

Keywords: ethanol, hand sanitizer, infrared spectroscopy, standard addition, expiration date.

Aplicații actuale ale spectroscopiei în infraroșu în determinarea calității unor produse cotidiene

Rezumat. Spectroscopia în infraroșu cu transformată Fourier (FTIR) este o metodă analitică rapidă și nedistructivă. Asociată cu chimiometria, este un instrument puternic pentru industria farmaceutică, cosmetică și alimentară. Această metodă poate fi utilizată pentru analiza calitativă și cantitativă a medicamentelor, alimentelor și a altor produse utilizate în cotidian. Totodată, spectroscopia IR poate fi utilizată în timpul preparării medicamentelor și pentru monitorizarea procesului de producție în laboratoarele de control al calității. În lucrarea de față, spectroscopia IR este utilizată pentru determinarea concentrației de alcool în dezinfectantele pentru mâini, acesta fiind esențial pentru încetinirea răspândirii virusurilor. Eficacitatea dezinfectantului pentru mâini este în întregime determinată de ingredientul volatil, alcoolul, care trebuie să rămână la o concentrație mai mare de 60% (volum) pentru a ucide agenții patogeni bacterieni și virali. Probele de dezinfectant pentru mâini selectate, au variat după concentrația inițială de alcool etilic, producător, culoare, parfum și alte ingrediente, precum și termenul de valabilitate.

Cuvinte cheie: etanol, dezinfectant pentru mâini, spectroscopia în infraroșu, adăugare standard, date de expirare.

1. Introduction

Infrared spectroscopy (IR) is certainly one of the most important analytical techniques available to scientists [1]. Being an improved method over time, at present, it allows the practical study of different types of samples [2]. The major advantage of IR spectroscopy over other spectroscopic techniques is that all the compounds virtually have absorption (emission) and thus can be analyzed both qualitatively and quantitatively [3].

Fourier-transform infrared spectroscopy (FTIR) was originally a spectroscopic technique used to identify the functional groups of chemical substances, but in recent years it has been widely used to identify, control quality and monitor the manufacturing process of drugs [3], assess the quality of agricultural products, in particular foodstuffs [4], as well as in the field of forensics for the identification of traces and fingerprints [5].

The principle of IR spectroscopy is to measure the amount of IR radiation that is absorbed (or emitted) by a sample as a function of wavelength [3]. IR spectrum measurement can be performed in transmission or reflectance mode, the former being the most popular. This method is easy to use in the analysis of pharmaceutical, food, and cosmetic components because it often requires minimal preparation or even testing of the unprepared sample. This paper represents one of the areas of the use of IR spectroscopy, namely how to use IR spectroscopy to determine the concentration of alcohol in hand sanitizers.

Ethanol or isopropyl alcohol with the concentration of 60-95% (volume) is an active ingredient in all alcohol-based hand sanitizers. The given ethanol concentration has been tested and shown to be effective against common bacteria, including Serratia marcescens, Pseudomonas aeruginosa, Escherichia coli, Salmonella typhosa, Staphylococcus aureus, and Streptococcus pyogenes [6, 7]. In the presence of ethanol, the hydrophobic forces that keep the cell membrane intact are weakened because ethanol is less polar than water, causing an increase in membrane permeability and leakage of life-sustaining intracellular components [8]. It is important to note that 60% alcohol is the lowest concentration that remains effective against these common bacteria, however, 100% alcohol is ineffective against Staphylococcus aureus and Streptococcus pyogenes, as high alcohol concentration will cause clotting of the peptidoglycan layer, which protects bacteria from further damage [9].

In terms of viral pathogens, the usual hand sanitizer with 60-80% ethanol is effective against protein capsid viruses, such as coronavirus. Concentrations greater than 60-95% are required for efficacy against non-encapsulated viruses, such as poliovirus and adenovirus [10].

Law enforcement agencies, which are responsible for detaining inefficient products, need a reliable and practical method of determining the ethanol content in hand sanitizer to assess whether the amount of ethanol matches the value indicated on the „product label".

Several techniques are known to measure the ethanol concentration, including redox titrations [11], flow injection electroanalytical analysis [12], amperometric biosensors [13], and gas chromatography coupled mass spectrometry [14]. Although effective, these techniques take a long time, extensive preparation, and are destructive to the sample. That is why Fourier transform (FTIR) infrared spectroscopy (FTIR) was chosen for this study, being accessible, easy to use, and with high accuracy.

Sample A	Sample B	Sample C	Sample D
70%	73%	75%	70%
02.2021	10.2022	04.2025	09.2023

Figure 1. Hand sanitizer samples examined and 20 ml ampoules with diluted hand sanitizer solution.

When determining the concentration of ethanol in water, it is important to consider the similarities between the two molecules. Both can form hydrogen bonds due to the presence of hydroxyl groups, however, ethanol has a carbon-oxygen bond that can be identified using FTIR and is displayed at 1044-1045 cm^{-1} in the transmission spectrum [15]. This methodology of using the C-O bond was used by „FTIR manufacturers Perkin Elmer and Shimadzu to determine the efficiency of estimating the percentage of ethanol in hand sanitizer solutions" [16, 17]. Both studies are based on the calibration curve technique, preparing samples with high ethanol concentration based on WHO (World Health Organization) guidelines for hand sanitizer, using water as a control sample [18, 19]. This approach can produce a matrix effect in which the analytical signal is altered due to a non-analyte component of the hand sanitizer.

The study aims to determine the concentration of alcohol in a series of hand sanitizers (Figure 1). The concentration of alcohol in the nominated hand sanitizers was determined by the method of standard additions of known concentration of ethyl alcohol, to the diluted sample of hand sanitizer and monitoring the change in the intensity of the C-O band in the alcohol.

2. Materials and methods

Materials: 70% ethyl alcohol was purchased from LUXFARMOL SRL (product code 220890910). Four samples of hand sanitizers with different expiration dates, were purchased (Figure 1): (A) Septophan, 65-75% (02.2021) - blue liquid; (B) Compact, 73% (10.2022) - transparent gelled solution; (C) Ecco, 75% (04.2025) - blue liquid; (D) Vitanic, 70% (09.2023) - colorless liquid. To prevent evaporation of the alcohol, the sample vials were covered throughout the experiment.

Table 1. Addition of standard to A-D hand sanitizer samples

Sample	Hand sanitizers information	Dilute Samples	V_o (ml)	V_t of ethanol in V_o , ml	V_s, ethanol, ml	V (ml)	$I_{(s+x)}$	$C_i \cdot V_s / V_0 \cdot 100$	$I_{(s+x)} \cdot V/V_0$
A	70%, 02.2021	A1	13.0	3.5	0	13	1057.72	0.000	1057.72
		A2	13.0		1	14	1138.50	0.054	1226.08
		A3	13.0		2	15	1179.76	0.107	1361.27
		A4	13.0		3	16	1246.44	0.161	1534.09
		A5	13.0		4	17	1285.89	0.215	1681.56
B	75%, 10.2022	B1	13.0	3.75	0	13	1179.27	0.000	1179.27
		B2	13.0		1	14	1305.88	0.054	1406.33
		B3	13.0		2	15	1378.32	0.107	1590.38
		B4	13.0		3	16	1442.45	0.161	1775.32
		B5	13.0		4	17	1462.44	0.215	1912.42
C	73%, 04.2025	C1	13.0	3.65	0	13	1163.44	0.000	1163.44
		C2	13.0		1	14	1216.62	0.054	1310.21
		C3	13.0		2	15	1279.96	0.107	1476.88
		C4	13.0		3	16	1322.71	0.161	1627.95
		C5	13.0		4	17	1369.88	0.215	1791.39
D	70%, 09.2023	D1	13.0	3.5	0	13	1061.68	0.000	1061.68
		D2	13.0		1	14	1174.50	0.054	1264.85
		D3	13.0		2	15	1262.48	0.107	1456.71
		D4	13.0		3	16	1344.50	0.161	1654.78
		D5	13.0		4	17	1400.44	0.215	1831.35

Preparation of A-D samples and addition of standard: 5 mL of sample (hand sanitizer) were pipetted to a 20 mL vial with a stopper. To the given sample 8 mL of distilled water was added, and the closed vial with a sieve was stirred gently (sample A). We note the initial sample of diluted hand sanitizer as ”A1.....”, A - the letter corresponding to the sample. The background spectrum of the diluted sample A1 (without the addition of ethyl alcohol) was measured. By the method of successive additions, by adding 1 mL of ethanol (70%), samples A2-A5 were prepared, measuring the IR spectra of the sample, after each addition of the standard. Samples B, C, and D were treated similarly.

IR Spectroscopy: The QUART-S Spectrophotometer was used for measurements. A background scan was initially performed to calibrate the spectrophotometer. One or two drops of sample A were transferred to the IR diamond crystal of the spectrometer. An IR spectrum of the sample was generated, performing 15 scans. The IR range was set at 4000-600 cm^{-1}.

For each sample investigated, IR spectra were measured. From the obtained IR spectra, there was documented the area of the band in the region 1044-1045 cm^{-1}, which corresponds to the C-O bond in the alcohol. Analyzing the changes in intensity in the IR spectrum of the samples, which appeared with each addition of ethyl alcohol, the graph was constructed: $[C]_i \cdot V_s / V_0$] as a function of $I_{(s+x)} \cdot V/V_0$ for the samples A-D, where V_0 – the initial volume of a dilute solution (13 ml); V_s – the volume of added ethanol (standard); V - the total volume of the solution; $I_{(s+x)}$ - the absolute value of the peak area at each addition of the standard (band area); C_i - initial alcohol concentration (standard).

3. Results and discussions

In this study, we presented data on alcohol concentration in four hand sanitizer samples, with different expiration dates (Table 1). The five solutions of each hand sanitizer samples were prepared by dilution and successive addition of standard. Five measurements were performed and the change in the intensity of the C-O band corresponding to the primary alcohols was analyzed. The absolute value of the peak area at each standard addition (C-O band area) was calculated using the LabSolutions IR program and noted in Table 1, Figure 2.

Using the calibration curve obtained by adding the standard (Figure 3) the initial alcohol concentration in hand sanitizers was calculated. The point of the intersection of the line with the **x** - axis, represents the initial concentration $[X]_i$ of the alcohol in each sample of hand sanitizer. The initial sample has the volume of 5 mL. It was diluted with water to reduce its viscosity, the final volume being noted in Table 1. Using equation (1), we can

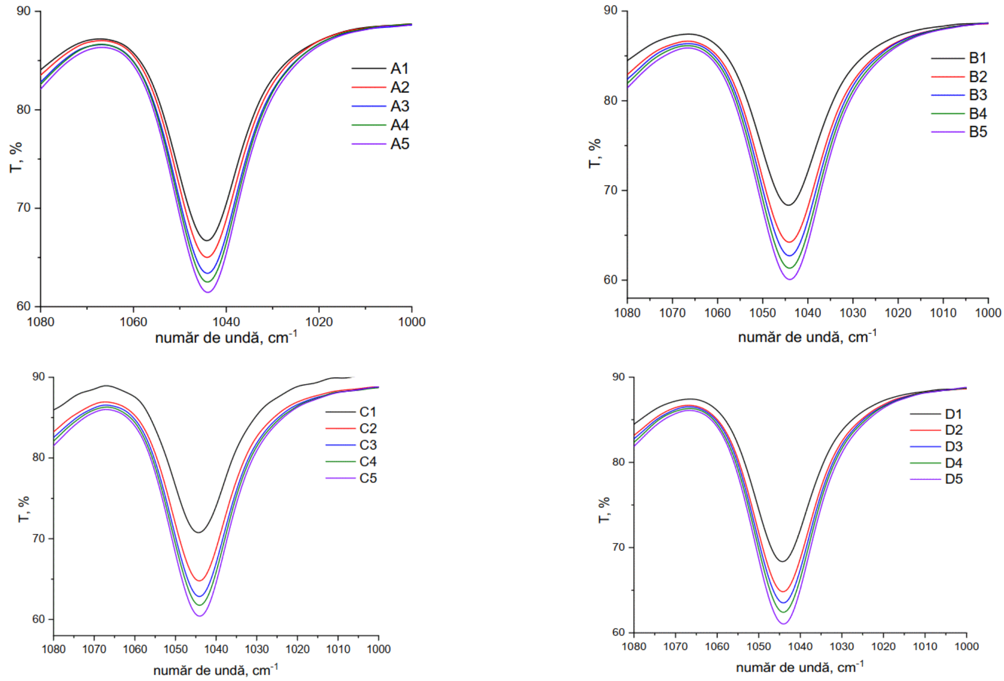

Figure 2. IR spectra of the studied samples A-D, indicating the region of interest, 1080-1000 cm^{-1}

calculate V_e the experimental volume of ethanol in 5 mL of hand sanitizer.

$$V_e = (13 \cdot [X]_i) / (1 + [X]_i) \tag{1}$$

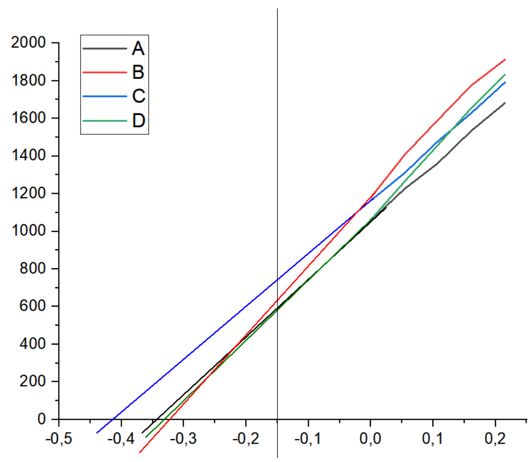

Figure 3. Calibration curve for A-D samples

The calculated volume of alcohol in the investigated hand sanitizers is shown in Table 2.

Table 2. Volume of ethanol determined experimentally for A-D samples

Sample	$[X_i]$ C_2H_5OH in 13 ml sample (%)	% (volume) C_2H_5OH, obtained	% (volume) C_2H_5OH, indicated	Loss of C_2H_5OH, % (volume)
A	0.344	66	70	6
B	0.323	63	73	14
C	0.413	75	75	0
D	0.331	60	70	15

The hand sanitizer ”Sample A” expired two months ago, and the amount of ethanol identified is 66%, which is a loss of about 3% per month. However, the ”Sample A” hand sanitizer remains effective, as the amount of alcohol detected is > 60%. In the hand sanitizers ”Sample B” and ”Sample D”, which have not been yet expired, revealed a loss of volume of ethanol of 14% and 15%, respectively, which allowed us to conclude that they initially had a lower alcohol concentration than indicated on the package. The concentration of alcohol in ”Sample C” proved to be equal to that indicated on the package, so we can conclude that the initial concentration of alcohol in this hand sanitizer was higher than that indicated on the package, taking into account the volume losses in time.

4. Conclusions

Infrared spectroscopy, compared to traditional methods, is one of the most efficient, easy, and inexpensive methods of qualitative and quantitative analysis of pharmaceutical, food, and industrial samples. This study demonstrated the effectiveness of using IR spectroscopy to determine the ethanol concentration in the samples. The alcohol concentration was determined using the calibration curve obtained by adding the standard, considering the matrix effect. While expired ”Sample A” may still be effective, with the minimum threshold for ethanol in hand sanitizers being 60% (volume), ”Sample C” suggests that manufacturers may use a higher percentage of alcohol to create hand sanitizer, thus maintaining the effectiveness and avoiding the loss of the percentage of alcohol over time. Spectroscopic methods are currently used with great success in the preparation and testing of pharmaceuticals, the determination of the content of the main components of food (water, protein, lipids, and carbohydrates), as well as in other fields.

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