

*Artículo de Revisión*

# Methanol Detection in Commercial Sanitizing Gels, During the COVID-19 Pandemic

Detección de metanol en geles desinfectantes comerciales, durante la pandemia COVID-19

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## Abstract

Some antibacterial gels, used for commercial sanitizing, containing ethanol (active) and methanol (toxic) were quantified. The health emergency caused by the COVID-19 epidemic has motivated the production of sanitizing gels to cover higher demand. The analytical composition of 24 commercial gels is reported (15 produced by national and transnational companies, and nine collected from public areas – in use). The chemical analysis results found that only one brand of 15 gels meets the quality requirements regarding 70% (wt./wt.) of ethanol content. Concerning the collected gels, none of them contains the minimum active compound required. The non-compliance of this requirement means that these gels present their sanitizing action diminished. A striking result is that 25% of commercially packaged gels contain methanol - a toxic substance - in alarming amounts, hundreds of times more than the FDA upper limits requirement.

**Keywords:** methanol; ethanol; sanitizer gels; sars Cov-2; Covid-19.

## Resumen

El contenido de sustancias etanol (activo) y metanol (tóxico) se cuantificó para geles desinfectantes comerciales. La emergencia sanitaria provocada por la epidemia de COVID-19 ha motivado la producción de geles desinfectantes para cubrir la mayor demanda. Se reporta la composición analítica de 24 geles comerciales (15 producidos por empresas nacionales y transnacionales, también nueve geles recolectados que estuvieron en uso desde áreas públicas). De los resultados del análisis químico, se encontró que solo una marca de 15 geles cumple con los requisitos de calidad con respecto al 70% (peso/peso) del contenido de etanol. En cuanto a los geles recolectados de zonas públicas, ninguno de ellos contiene el compuesto activo mínimo requerido. El incumplimiento de este requisito hace que estos geles presenten disminuida su acción sanitizante. Un resultado

sorprendente es que el 25% de los geles empacados comercialmente contienen metanol, una sustancia tóxica, en cantidades alarmantes, cientos de veces más que los límites superiores regulados por la FDA.

**Palabras Clave:** metanol; etanol; geles sanitizantes; sars Cov-2; Covid-19.

## 1. Introduction

The ethanol-based sanitizing gels production increased markedly in 2020, mainly caused by the recent COVID-19 pandemic (March 2020). The purpose of its disinfecting action makes this product available in almost all public facilities, such as banks, supermarkets, hospitals, offices, etc. The advantage of this product is its use in some places where there is no access to soap and water, and its sale doesn't require a prescription (Paulson, 1999). Before the present pandemic, this product was in low demand. However, as it became a product promoted by health institutions as a preventive product (Alvarez, 2020), with high antimicrobial efficiency, the people increased its usage considerably, which is why many companies began their mass production. Even part of the people made their formulations based on videos and online tutorials on the websites. This activity generated a problem since there is no precise regulation of established requirements. The production is currently carried out with various chemical compounds, but several of them could be toxic. Some formulations could harm users, starting from a simple dryness or skin irritation, even severe poisoning. Antibacterial gels are defined as liquid disinfectants for applications on hands and surfaces. Its main component must be 60-80% (wt./wt.) Isopropyl alcohol or 70% ethanol. The last one is the most commercially used, due mainly to the fact that being cheaper than Isopropyl alcohol. The 70% ratio is cited by several studies, such as those carried out by Guilhermetti *et al.* (2010), where they used 12 alcohol-based gels produced in Brazil, according to the European standard EN1500. This study concluded that the gels have an effective disinfecting action equal to that obtained using 70% ethanol. Its antiviral activity was demonstrated in the studies carried out by Pandejpong *et al.* (2012).

They determined that there is effective when it is using antibacterial gel to reduce influenza by studying 1,437 preschool children. This evidence showed that the mandatory use of ethanol-based gel as classroom hand disinfection could significantly reduce school absenteeism rates by influenza. The ethanol-based gel is also currently used in hospitals; as mentioned in the studies carried out by Chávez *et al.* (2010), they recommend that hospital staff working in places such as intensive care units (ICUs), neonatal wards, and emergency services. They must have their hand hygiene by carrying out a wash with soap and water, alternating with ethanol and glycerin-based gel to keep their hands moisturized.

Currently, there is no legal regulation in México for the manufacture and evaluation of these products. The European community uses the UNE EN 1500 standard, which sets the antimicrobial evaluation procedures of sanitizing products. Still, it does not mention the banning of possibly toxic substances in its preparation. Due to the COVID-19 disease pandemic, the US Food and Drug Administration (FDA) issued guidelines to communicate its policy regarding the chemical composition of certain ethanol-based hand sanitizers by pharmacists in establishments licensed by the state or federal facilities. They also published a guide, "Temporary Policy for Manufacture of Alcohol for Incorporation into Alcohol-Based Hand Sanitizer Products during the Public Health

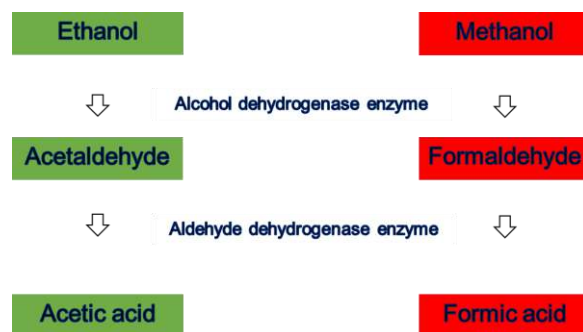
Emergency (COVID-19) Guidance for Industry". This document contains guidelines for using ethyl alcohol as an active pharmaceutical ingredient (API) to prepare and distribute hand sanitizer as a product for public use. This document, issued in March 2020, will be temporarily allowed respect to certain impurities at levels that can be tolerated for a short time, thought out the COVID-19 public health emergency.

**Table 1.** FDA recommended a maximum limit for impurities in ethyl alcohol for sanitizers, in weigh percent (%), and parts per million (ppm).

**Tabla 1.** Límite máximo recomendado por la FDA para las impurezas en el alcohol étlico para desinfectantes, porcentaje en peso (%) y partes por millón (ppm).

Impurities	Maximum limit	
	%	ppm
Methanol	0.063	630
Benzene	0.0002	2
Acetaldehyde	0.005	50
Acetyl (1,1-diethoxyethane)	0.005	50
Sum of other impurities	0.03	300

Values in Table 1 shows methyl alcohol (methanol) as the primary contaminant. Ethanol used to make sanitizers could contain methanol as a contaminant in two ways: the first could be due to the ethanol decomposition by heating. The second is due to a deliberate addition to save costs since methanol is cheap. Methanol is metabolized in the liver, much slower than ethanol, by the enzyme alcohol dehydrogenase activity, producing formaldehyde and formic acid, as shown in Figure 1. Both metabolites cause severe metabolic acidosis and other organ damage. The produced cellular acidosis increases by accumulating lactic acid due to secondary cellular hypoxia (UNAM, 2014).



**Fig 1.** Ethanol and Methanol metabolism diagram. Ethanol produces non-toxic byproducts compared to methanol (UNAM, 2014).

**Fig 1.** Diagrama de metabolismo de etanol y metanol. El etanol produce subproductos no tóxicos en comparación con el metanol (UNAM, 2014).

A Material Safety Data Sheet (MSDS) of methanol indicates that skin contact generates moderate irritation. It can be absorbed through the skin in harmful amounts. Prolonged and or repetitive contact can cause dry skin and dermatitis. Methanol can be absorbed through the skin, producing systemic effects that include visual disturbances (Fisher. 2020).

This work focuses on the qualitative and quantitative composition analysis of commercial and collected sanitizing gels using infrared spectrometry and gas chromatography (CG) to evaluate their ethanol and methanol content percentage for each one.

## **2. Experimental**

### **2.1 Samples**

Fifteen (new and sealed) commercial sanitizing gels produced by national and international companies were purchased in different stores and they made chemical analyses. In addition, nine gels samples were analyzed too; they were collected from public areas such as banks, factories, convenience stores, and shopping centers in Chihuahua City, Mexico, in June 2020. About the public places collected samples; their brands were not recorded because this information was not visible. To analyzed gels acquired in the store, they were opened and shaken for 10 minutes before the analysis. The sealed commercial sanitizing gels were numbered (1 to 15) and, the collected samples, were labeled by letters (A to I); it was made due to the confidential protocols.

### **2.2 Chemical reagents**

High purity methanol (JT Baker 99.8%) and ethanol (JT Baker 99.8%) were used as a reference to instrument calibration and also to corroborate their detection limit furthermore optimal operation of the infrared spectrometer and gas chromatograph.

### **2.3 Fourier Transform Infrared (FTIR) Spectroscopy**

For the FTIR analysis, a Shimadzu model IR Affinity 1S spectrometer was used. The spectra were obtained by reflectance using the accessory called ATR (Total Attenuated Reflectance by its acronym in English), Smiths brand, Quest model, with a single reflection diamond window (bounce) with 20 scans to obtain each spectrum. It was used to qualitatively identify the presence of the alcohol type present in the gels. FTIR spectra were recorded in the interval between 900 and 1200  $\text{cm}^{-1}$ .

### **2.4 Gas Chromatography**

For GC analysis, a Perkin Elmer equipment, model Auto system XL, with a Porapak Q packed column with 6 feet length and 1/8 inch in diameter, was used. The used chromatographic procedure temperature was: injection 220 °C, detector: TCD 220 °C, the carrier gas was helium at 30 mL/min (Praxair 99.99%), the oven program was an initial temperature of 105 °C/min with 10 °C/min ramp up to 200 °C and a holding isothermal of 5 min. The quantification procedure was carried out, preparing calibration curves with a reactive grade of ethanol and methanol. The samples for analysis were injected directly from the container without previous preparation.

## **3. Results and discussion**

In this part, the qualitative analysis by FTIR infrared spectroscopy of the mixtures used for calibration can be noticed. Then, the spectra of the purchased and collected sanitizing gels sets are shown. Finally, the comparative graphs with the quantitative values obtained by gas chromatography are presented.

### 3.1 Qualitative analysis by FTIR spectroscopy

The detection of different alcohols (methanol, isopropanol, and ethanol) contents in the sanitizing gels were determined, comparing with the standard mixtures' spectra. Their fingerprints spectra were taken in the FTIR spectra between 1200 and 900  $\text{cm}^{-1}$ , identifying specific wavenumbers at 1020 and 1115  $\text{cm}^{-1}$  for methanol, at 1046 and 1088  $\text{cm}^{-1}$  for ethanol, at 966, 1015 and 1053  $\text{cm}^{-1}$  for propanol also at 950 and 1129  $\text{cm}^{-1}$  for isopropanol, they were present at Figure 2a. These results are identical to those reported by Coldea *et al.* (2013).

The spectra for sealed commercial sanitizing gels are shown in Figure 2b. This figure shows the comparison among the set of spectra acquired for each sample. Most of them contain ethanol and methanol, but it can be noticed that samples 8, 9, and 13 present methanol in considerable high amounts. Based on this qualitative analysis, some samples contents toxic compound (methanol).

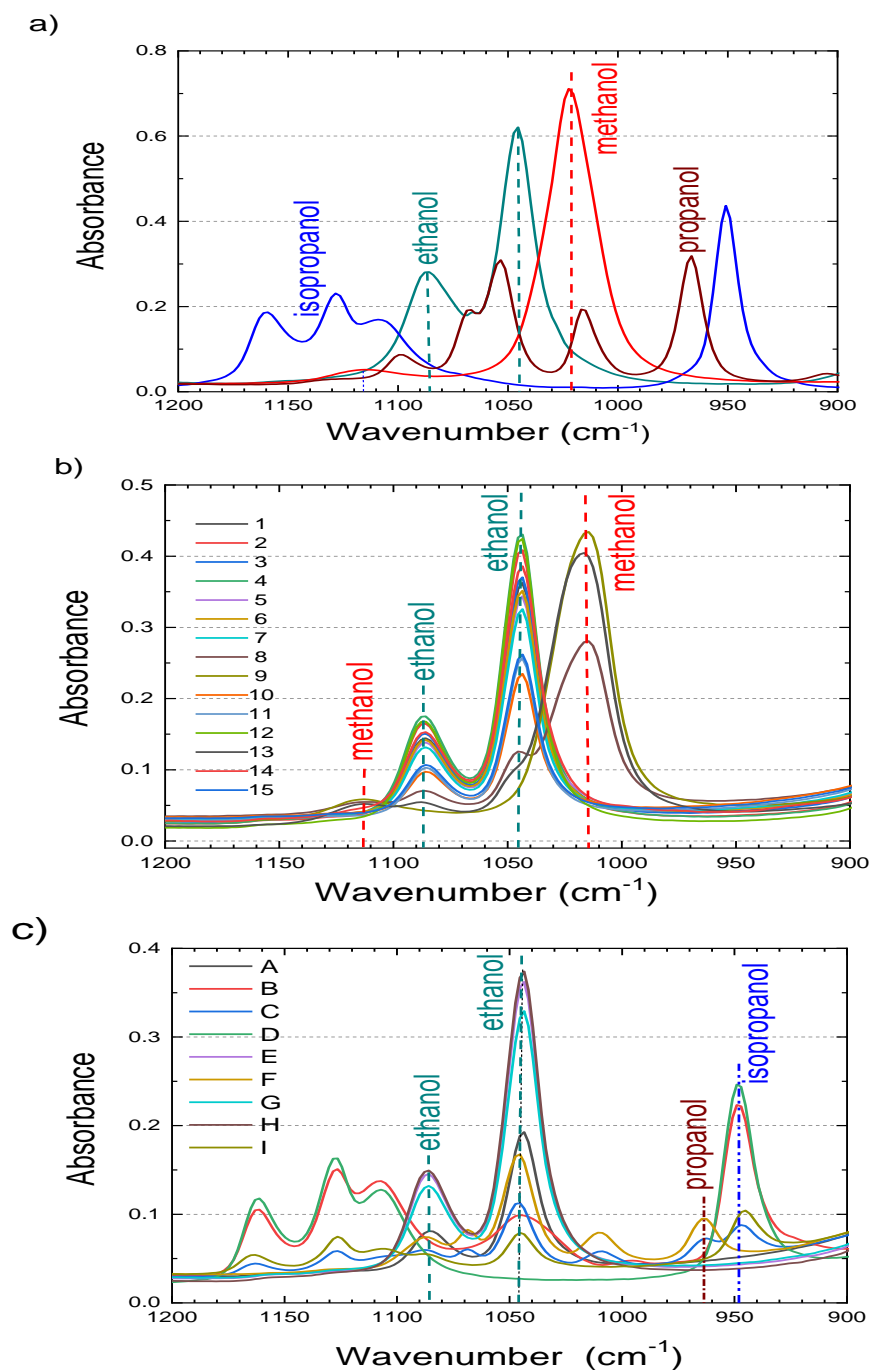
The spectra for collected sanitized gels samples are shown in Figure 2c. These spectra show evident the presence of the different types of alcohols. For the set, there is no methanol presence, it does not appear, but other types of alcohols such as propanol and isopropanol were detected. In this case, these alcohols are allowed for disinfecting purposes too.

With the FTIR technique, their qualitative identification was carried out. It is also possible to make a rough quantification by detecting the intensities variation because the intensity of the signals is proportional to the content (but the precision has low accuracy).

### 3.2 Quantitative analysis by GC

Through this analytical technique, ethanol, methanol, isopropanol, propanol, and water were determined quantitatively (in weight percent). Table 2 shows the quantified values for the 15 sealed commercial samples. It is noticeable that only one trademark meets the minimum requirement of ethanol content (70 %) and another one is close, as indicated on its labels and the guidelines established by the FDA. The implication of these results is; if commercial products do not contain the minimum active ingredient (ethanol or isopropanol), the required antimicrobial function will be diminished with the consequent increase of infected people. It can be noticed; approximately 47% of studied products (7 samples) do not even meet 50% of ethanol content (in contrast with 70% required). In the most severe cases, some commercial brands replaced ethanol with methanol, with the consequent harmful absorption problem in the skin and its possible health consequences mentioned above (intoxication). In addition, these products do not have a disinfectant function, but they cause the spread of the virus.

In the case of quantification for collected sanitizers (Table 3), methanol was not found, but it was found in the commercial gels; none met the optimal ethanol content. For gels that don't meet the concentration standards, they accelerate the virus spread, which has severe consequences for public health by increasing the spread of COVID-19.



**Fig. 2** FTIR spectra for a) reagent grade ethanol, methanol, isopropanol, and propanol - calibration samples, b) sealed commercial sanitizing gels, and c) collected sanitizing gels (from public facilities places).

**Fig. 2** Espectros FTIR para a) etanol, metanol, isopropanol y propanol de grado reactivo - muestras de calibración, b) geles desinfectantes comerciales sellados y c) geles desinfectantes colectados (desde instalaciones públicas).

**Table 2.** Summary chart with ethanol, water, and methanol content determinate by GC in sealed commercial sanitizers (in weight percent).

**Tabla 2.** Resumen del contenido de etanol, agua y metanol determinado por GC en desinfectantes comerciales sellados (en porcentaje en peso).

Sample	Ethanol	Water	Methanol
1	55.3*	44.7	ND
2	64.4*	35.6	ND
3	56.2*	43.8	ND
4	68.7*	31.3	ND
5	51.2*	48.1	0.6**
6	52.8*	47.2	ND
7	48.8*	51.2	ND
8	14.6*	55.1	30.3**
9	0.8*	40.3	58.9**
10	32.0*	67.7	0.3**
11	36.0*	64.0	ND
12	70.0	30.0	ND
13	12.6*	35.6	51.8**
14	57.7*	42.3	ND
15	38.1*	61.9	ND

\* Does not meet to 70% ethanol specification

\*\* Methanol content is higher than the maximum allowed by the FDA and ND means not detected.

**Table 3.** Summary chart with ethanol, water, isopropanol, and propanol quantitative determination in collected sanitizers (in weight percent).

**Tabla 3.** Cuadro resumen con determinación cuantitativa de etanol, agua, isopropanol y propanol en desinfectantes recolectados (en porcentaje en peso).

Sample	Ethanol	Water	Isopropanol	Propanol
A	59.7*	40.2	0.1	ND
B	59.1*	40.9	ND	ND
C	55.7*	44.3	ND	ND
D	54.9*	45.1	ND	ND
E	49.6*	50.4	ND	ND
F	25.3*	74.7	ND	ND
G	16.0*	64.6	19.4	ND
H	9.5*	69.0	10.7	10.8
I	6.5*	75.7	ND	17.7

Does not meet 70% ethanol specification and ND means not detected.

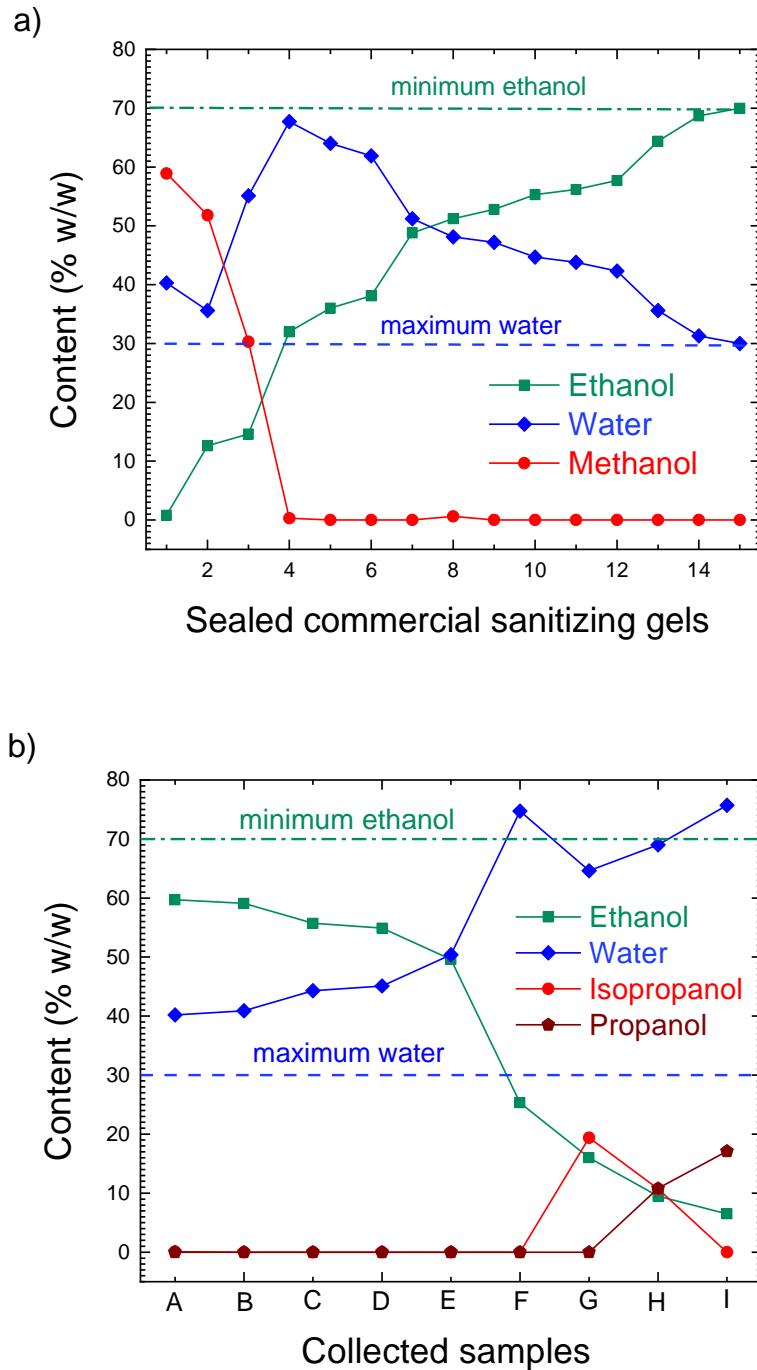
To notice better the comparison between both sets of samples, data from Tables 2 and 3 were plotted. Figure 3a shows the values plotted for sealed commercial sanitizers. This figure clearly shows the variation in the quantitative compositional content. The presence of the toxic substance (methanol) is seen in three brands in alarming amounts (30 to 60%), with a complement of water as the missing percentage, for sanitizers that contain ethanol but do not meet the proper amount (the remainder is water). Thus, these gels do not fulfill their prevention effectiveness; these products play the role of spreading the virus further. Hence, this is important that these products must meet the appropriate requirements. On the other hand, samples 5 and 10 also contain 0.6 and 0.3% methanol, respectively; they do not visualize on their FTIR spectra, this technique is not suitable to determine amounts lesser than 10% (wt./wt.)

Figure 3b shows the graphed values for the sanitizers collected from public places. As can be seen, the presence of propanol and isopropanol does not agree with the minimum recommended content that must have to avoid the virus spread. Consequently, these gels would also be spreading the virus because they do not fulfill the requirements to inhibit the spread. These are even more dangerous since they are being used in public places, where traffic of people is higher.

#### 4. Conclusions

The gas chromatography technique is a valuable tool to perform analytical quantification for quality purposes in sanitizing gels by quantifying the alcohol content quickly and accurately. Appropriate ethanol or isopropanol content is essential for correct hand sanitization purpose. The analyzes carried out show a severe flaw in the formulation of the sealed commercial gels and those collected from public facilities because they do not meet the minimum ethanol content (14 samples of 15) and (9 samples of 9), respectively. Even when they mark an active content of 70% on their labels, this creates false confidence in the consumer, causing them to become infected by not complying with the appropriate sanitizing action of the gel. Analytical techniques also showed that 25% of the studied gels contain methanol in amounts that could cause public health problems. The COVID-19 pandemic has regulatory agencies out of work, creating this type of adulterations in sanitizing gels. Thus, the implicated companies should self-regulate for social good in a state of sanitary emergency. It is clear that during this health crisis, these products will continue to be used regularly, so it is a priority to establish norms and guidelines on their composition.





**Fig. 3** Graph with the content distribution of components in a) sealed commercial sanitizing gels and b) collected samples from public places. They were ordered from the lowest to highest content of ethanol and isopropanol, respectively.

**Fig. 3** Gráfica con la distribución del contenido de componentes en a) geles desinfectantes comerciales sellados y b) muestras recolectadas de lugares públicos. Se ordenaron del menor al mayor contenido de etanol e isopropanol, respectivamente.

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