

## Evaluation of Alcohol Content of Cologne Products in the Turkish Market Amid the COVID-19 Pandemic

### COVID-19 Salgını Sürecinde Türkiye Pazarındaki Kolonyaların Alkol İçeriğinin Değerlendirilmesi

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#### ABSTRACT

The World Health Organization and Turkish National Health Authorities advise the public to use an alcohol-based hand sanitizer or wash with soap and water for cleaning against the COVID-19 outbreak whilst Turkey was ready for this new situation from the beginning because of the widespread use of colognes. While the pandemic resulted in stockpiling and absence of related products, the industry responded fast by making fast production, but it has raised concerns about the safety and efficacy of these new products. Alcohol content of the cologne samples purchased from various daily supermarket stores in Turkish market were evaluated with Headspace - Gas Chromatography - Flame Ionization Detector (HS-GC-FID) to check and verify their safety for consumers during the COVID-19 pandemic. The headspace oven, loop, and transfer line temperatures were 130 °C, 135 °C, and 140 °C, respectively. The GC oven temperature program was hold at 50 °C for 10 min, increased at 10 °C/min to 220 °C for 5 min. Helium flow rate was 1 mL/min. Injection and detector temperature were 140 °C, and 250 °C, respectively. Injection volume was 1 µL with the split ratio of 50:1. The ethanol content of the colognes is in a range of 37.9 – 98.9 % (w/w). The alcohol content of some of the products was observed as below the limit of Turkish Guideline for Cosmetic Products to be labelled as cologne. Therefore, the regulatory bodies should check the products more intensively or the regulations on cologne in pandemic can be revisited.

**Key Words:** Cologne, Turkish market, ethanol content, COVID-19 pandemic, safety, regulation

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#### ÖZET

Dünya Sağlık Örgütü ve Türk Ulusal Sağlık Otoriteleri, COVID-19 salgınına karşı halka temizlik için ellerin alkol bazlı el temizleyicileri veya sabun ve su ile yıkama yapılmasını tavsiye ederken, Türkiye bu yeni duruma kolonya kullanımının yaygın olması nedeniyle en baştan beri hazır durumdaydı. Pandemi, ilgili ürünlerin stoklanması ve yokluğuna yol açarken, endüstri hızlı bir şekilde üretim yaparak duruma cevap vermiştir, lakin bu yeni ürünlerin güvenliği ve etkinliği konusunda endişeler ortaya çıkmasına sebep olmuştur. COVID-19 salgını sırasında tüketicilerin güvenliğini kontrol etmek ve doğrulamak için Türkiye pazarındaki çeşitli süpermarket mağazalarından satın alınan kolonya örneklerinin alkol içeriği, Tepe Boşluk- Gaz Kromatografi – Alev İyonlaşma Dedektörü (GC-FID) ile değerlendirilmiştir. Tepe boşluk fırın, döngü ve transfer hattı sıcaklıkları sırasıyla 130 °C, 135 °C ve 140 °C seçildi. GC fırın sıcaklık programı; 50 °C'de 10 dk ısıtılıp, 10 °C/dak artışla 220 °C'ye artırılarak 5 dak ısıtıldı. Helyum akış hızı 1 mL/dak, enjeksiyon ve dedektör sıcaklığı sırasıyla 140 °C ve 250 °C, enjeksiyon hacmi 50:1 bölme oranıyla 1 µL seçildi. Test edilen kolonyaların etanol içeriği %37.9 ila %98.9 (a/a) aralığındadır. Bazı ürünlerin alkol içeriği, Kozmetik Yönetmeliği'nde kolonya olarak etiketlenebilecek limitin altında olduğu görülmüş olup, düzenleyici kurumların ürünleri daha yoğun bir şekilde kontrol edilmesi tavsiye edilebilir veya pandemi döneminde kolonya ile ilgili düzenlemeler yeniden gözden geçirilebilir.

**Anahtar Sözcükler:** Kolonya, Türkiye pazarı, etanol içeriği, COVID-19 salgını, güvenlik, düzenleme

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## INTRODUCTION

The new infectious disease COVID-19 caused by a novel coronavirus (SARS-CoV-2) has rapidly spread around the World with alarming levels of severity, which was declared as a pandemic by the World Health Organization (WHO) in 11 March 2020 (1). As of 1th July 2020, over ten million people have contracted the disease, and over 500 thousand deaths have been attributed to COVID-19 globally (2).

Decontamination using hand hygiene is well known as one of the most important and effective methods for reducing healthcare-associated infections and cross-infection between patients, but with the COVID-19 pandemic, it has been demonstrated that effectively applied hand hygiene is a vital intervention that can be used to prevent the spread of the disease (3). As disease progress, from the very first moments of the situation, WHO and also national health authorities give information to public in order to reduce the chances of being infected or to reduce the spread of COVID-19 by taking some simple precautions

such as regularly and thoroughly cleaning hands with an alcohol-based hand rub or washing them with soap and water (4).

Turkey is totally ready for this simple protection action as the cologne is very popular and known to be used as an alcohol based cosmetic product and a hand sanitizer, and it is already widely available in Turkish markets and Turkish households (5). However, the outbreak has triggered stockpiling of emergency, protection and cleaning supplies all around the world. Among these supplies, stocks of cologne have rapidly vanished from some markets, as soon as the frequent handwashing and sanitization was recommended by the public health agencies across the world. Well-known internet search engine Google deploys "Google Trends" tool, which analyzes and compares the search volume of given keywords on their search engine, which enables understanding the magnitude of the emergent interests of the general public. For the cologne as a hand sanitizer, a constant volume of Google searches on this topic was shown until March 2020, then a massive spike of 50-fold increase in interest appeared (6).

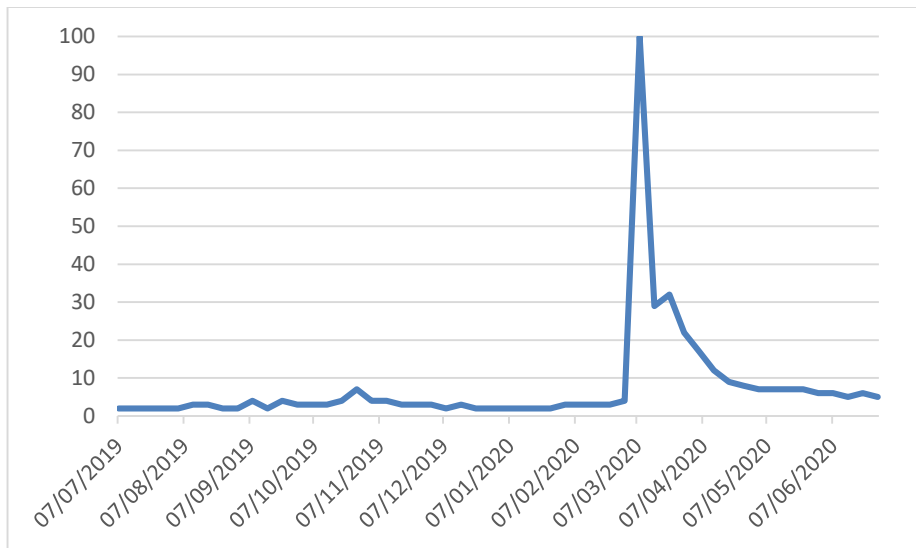


Figure 1: Trends in search of the word "colonge" amid COVID-19 in Turkey, extracted from Google Trends on the 1th of July 2020 (6).

To respond to the stockpiling and shortage, government authorities and chemical industries reacted very fast and have started to produce large amounts of cologne products, for unprecedented demand of hand sanitizer market in Turkey (7, 8).

As the SARS-CoV-2 is an enveloped virus, its viral core is protected by a lipid layer, and alcohol based products can easily disintegrate the protective lipid of the virus (9). Ethanol has been shown to be effective against various enveloped viruses, while beginning at a concentration of 42.6% (w/w) it is also listed to be effective within 30 seconds against SARS coronavirus, MERS coronavirus (10). It can be easily predicted that the hand sanitization will remain at the forefront of infection prevention measures, and the cologne, in a base of dilute ethanol (70-90%), will serve as a great tool for the "new normal" for an extended period of time. The most important factor in determining the efficacy of a hand sanitizer and also for the cologne would be indeed the alcoholic content. According to Turkish Regulation on cosmetic products, colognes should contain 60% (v/v) alcohol content while lemon colognes should be over 70% (v/v), definitely ethyl alcohol (11). With this high demand, as most of them might not be regulated affectively, sub-standard products, which may contain low or unknown alcoholic content, might be available in market. Methanol may be used instead of ethanol in alcohol production since it is less expensive compared to ethanol, which is a major health concern (12). In addition, following inhalation, ingestion or cutaneous exposure, methanol is well absorbed and metabolized to formaldehyde, then to formic acid while these metabolic products can produce a syndrome of delayed-onset acidosis, obtundation, visual disturbance and death (13). Safety of cheap priced and rushed production colognes may jeopardize consumer health because of possible ineffectiveness or potential toxicity. In this study, we assessed the alcohol content of different types and price range of cologne samples that were purchased from various daily supermarket stores in Turkish market to check and verify their safety for consumers.

## MATERIALS and METHODS

*Samples and Reagents*

For our study, 19 different brands and types (lemon cologne or other scented types) of colognes were deployed from the local stores in Ankara, Turkey in 2020. Price range categorization is not possible and feasible as the surplus of product, volume of product and availability of products are not constant at as this time of pandemic; although all the colognes deployed were bought from supermarkets, which are easily accessible and have affordable price ranges for the population. The samples were stored at +4 °C before the analysis.

*Instrumentation*

Ethanol was determined in colognes using a Gas Chromatography Flame Ionization Detector GC-FID) (7890A GC System, Agilent Technologies, Santa Clara) equipped with Headspace Sampler (7697A Headspace Sampler, Agilent Technologies, USA), and HP-20M (Carbowax® 20M) polyethylene glycol capillary column (50 m × 0.32 mm ID × 0.3 µm film thickness, Agilent Technologies, US). All chemicals were gas chromatographic quality. Absolute ethanol and methanol were obtained from Merck, Darmstadt, Germany. High purity helium, hydrogen, and dried air gases (for gas chromatography, ≥99.999%) were purchased from Oksan Co., Ltd. Ankara, Turkey. Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Hdspc vial (20 mL) and Hdspc Al crmp cap, PTFE/Si sep (Agilent Technologies Inc., US) were used to prepare all solutions.

**Chromatographic conditions**

The GC-FID analysis was performed on an Agilent Technologies 7890A GC System equipped with headspace sampler and HP-20M (Carbowax® 20M) capillary column. The headspace sampler temperature program was as follow; oven, loop, and transfer line temperatures were 130 °C, 135 °C, and 140 °C, respectively. Headspace vial equilibration and injection duration time were 2 min and 0.2 min, respectively. The GC oven temperature program was as follows; hold at 50 °C for 10 min, increase at 10 °C/min to 220 °C, then hold for 5 min. High purity helium at a constant flow rate of 1 mL/min was used as the column carrier gas. Injection and detector temperature were 140 °C, and 250 °C, respectively. Injection volume was 1 µL with the split ratio of 50:1. Hydrogen (30 mL/min) and dried air gases (400 mL/min) were used as flame gases (14).

**Preparation of standard ethanol solutions**

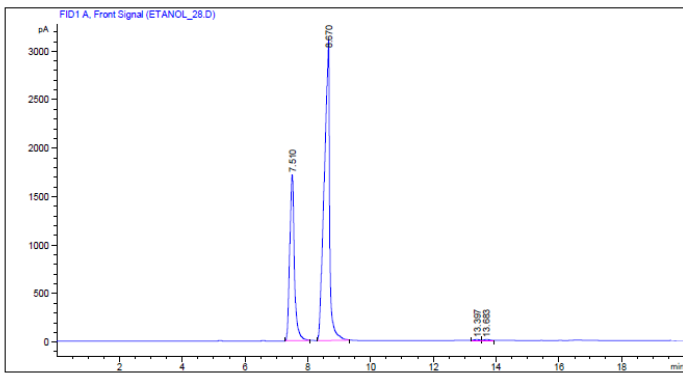
Fifty, 100, 150, 200, and 250 µL of absolute ethanol (99.5%, w/w) were diluted to 10.0 mL with deionized water. Then 2.0 mL of diluted solutions were transferred to 20 mL of headspace vial separately, and Hdspc Al crmp. cap, PTFE/Si sep. closed immediately. As a consequence, 0.5, 1.0, 1.5, 2.0, and 2.5% (w/w) standard ethanol solutions were analyzed with Headspace-Gas Chromatography-Flame Ionization Detector (HS-GC-FID).

**Preparation of sample solutions**

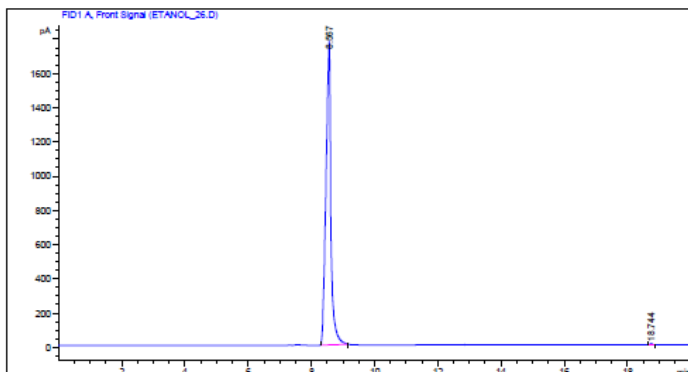
The cologne samples were stored at +4 °C before the analysis. 200 µL of each sample was diluted to 10.0 mL with deionized water. Then 2.0 mL of diluted solutions were transferred to 20 mL of headspace vial separately, and Hdspc Al crmp. cap, PTFE/Si sep. closed immediately. Then, ethanol in the cologne samples were analyzed with HS-GC-FID.

**Qualitative and quantitative analysis**

Identification of the methanol and ethanol in sample were performed based on comparison of their retention times ( $t_R$ ) with a pure standard of ethanol and methanol (Figure 2) under the same Headspace-Gas Chromatography-Flame Ionization Detector (HS-GC-FID) analysis program as applied to the sample (Figure 3)

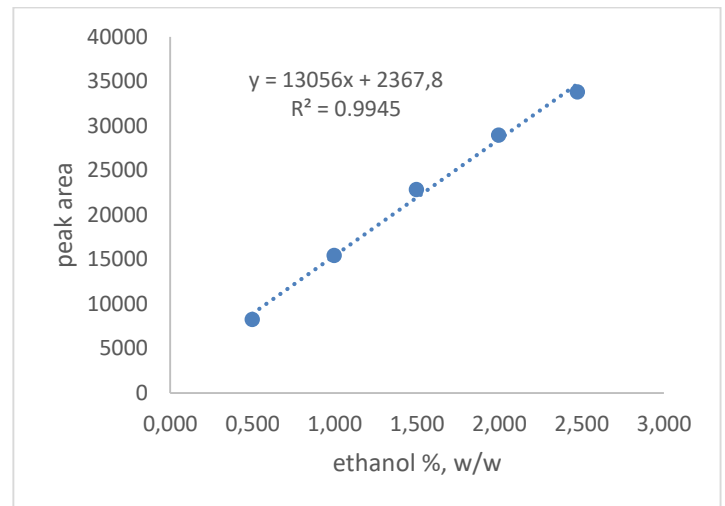


**Figure 2:** HS-GC-FID chromatogram of standard 2.0% (w/w) methanol and 2.0% (w/w) ethanol ( $t_R$ , methanol = 7.51 min,  $t_R$ , ethanol = 8.67 min)



**Figure 3:** HS-GC-FID chromatogram of cologne sample #18

The peak areas were used for the quantitative analysis of ethanol. Ethanol was quantified by using an external calibration curve. Calibration curve was drawn against the percentage of the ethanol concentration (0.5, 1.0, 1.5, 2.0, and 2.5%) versus GC peak area. Calibration equation was calculated as  $y = 13056x + 2367.8$ ,  $R^2 = 0.9945$  ( $y$  is the peak area,  $x$  is the ethanol %, w/w) (Figure 4).



**Figure 4:** Calibration curve of ethanol

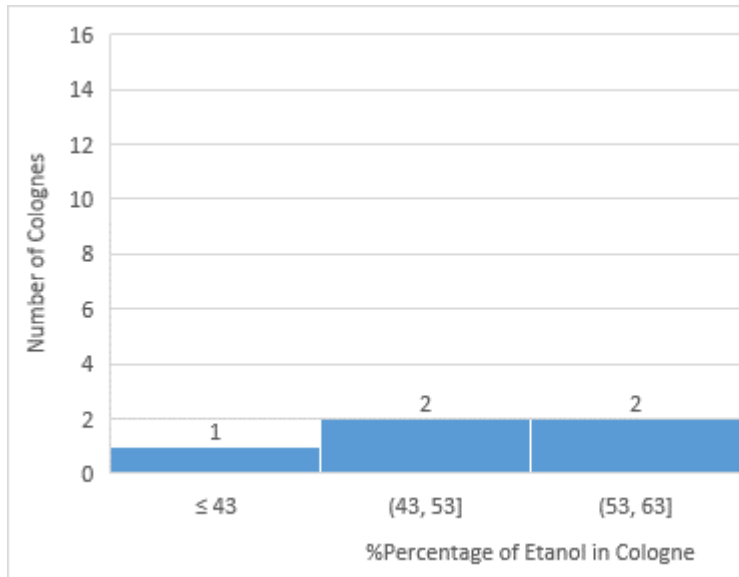
**RESULTS**

All the data were the mean of double replicates. The percentage of ethanol contents and their distribution ranges among the 19 cologne samples are shown in Table 1. The ethanol content of the colognes is in a range of 37.9 – 98.9% (w/w). 3 of the tested 19 colognes have ethanol content lower than 53%. All of the samples are based on ethanol only as the alcoholic content.

**Table 1:** Percentage (w/w) of ethanol in cologne samples.

Sample no:	Ethanol %, (w/w)	± sd*
1	56.7	2.6
2	39.3	2.0
3	49.9	3.2
4	77.8	3.2
5	79.7	5.1
6	43.8	0.3
7	72.5	0.4
8	87.3	1.6
9	75.9	0.5
10	64.7	1.9
11	81.1	2.2
12	73.2	2.3
13	99.8	1.3
14	75.3	2.2
15	67.1	1.8
16	63.2	2.0
17	60.5	1.3
18	66.8	2.3
19	77.8	2.8

\*sd: standard deviation



**Figure 2:** Distributions of colognes by ethanol % (w/w) contents. Note that <43% might not be effective against corona viruses, if only >53% can be referred as cologne and if only >63% can be referred to be lemon cologne.

Recovery experiments were done to evaluate the accuracy of the HS-GC-MS method. Three concentration levels of ethanol standards were spiked into cologne sample solutions and analyzed for accuracy tests. The results are shown in Table 2.

**Table 2:** Recovery experimental results

Ethanol % in Sample 4	Spiked ethanol concentration, %	Detected concentration, %	RSD %	Recovery, %
1.40	0.25	1.62	0.62	101.8
1.36	0.50	1.82	2.20	102.2
1.26	0.75	2.02	1.24	99.5

The recovery corresponding to the detected concentration was 99.5–102.2%, and the percentage relative standard deviation (RSD%) were less than 5%, proving the accuracy of the method. The percentage relative standard deviation (RSD%) of peak area of sample 4 obtained from 5 replicate solutions and injections was used to confirm the system precision. RSD% value was found as 7.6%, which is within the acceptable limits.

## DISCUSSION

The world is facing a medical crisis amid the COVID-19 pandemic, and the role of adequate hand hygiene has become inevitable for controlling the spread of the infection. How long SARS-CoV-2 remains active on a surface and can start/spread disease is not definitively known. Previous studies with similar type corona viruses show that virus can persist on hard surfaces like glass, metal or plastic for up to 9 days (15). Van Dorelamm et al. reported that SARS-CoV-2 remains stable on plastic and stainless steel up to 72 hours (16). Cleaning of touchable surfaces of all-things, or even the shopping bags, package goods and etc. regularly with sanitizers also becomes the new normal for protecting ourselves from COVID-19 while cologne is one of the handiest tools for this purpose, too. As the surface area is larger, more cologne may have to be used, the evaporated and exposure amount also gets higher. Exposure to unknown alcohols or even toxic ones such as methanol would be an important emerging issue to concern.

There are many reports of methanol poisoning due to suicidal or accidental ingestion, or even reports of transdermal absorption (17), Kalkan et al.'s study identified the profile of acute methanol exposures reported to Drug and Poison Information Center (DPIC) in Izmir, Turkey, from 1993 to 2002, and it showed that over the 72% methanol poisonings/toxicities mainly resulted from colognes as a source, and they concluded that "methanol for producing cheap "eu de colognes" in Turkey is the principal reason for severe poisoning and deaths" (18). In our study, all cologne samples were also analyzed to discriminate alcohol content, but it was seen that that all colognes were ethanol based.

There has been a great surge in demand for cologne products in Turkey as a sanitization product in pandemic, and this has led to shortages in their supply. WHO and Association of Turkish Pharmacist recommended handrub formulations with ethanol as an active component. These in-house-local production are also formulated to produce final concentrations of ethanol 73.48% (w/w) or 80.0% (v/v) (19-21). These handrub formulations recommended to be used both for hygienic hand antisepsis and for presurgical hand preparation by WHO, and the concentration can be expected to be changed at  $\pm 5\%$ . Our study shows that only half of the tested colognes have over this amount of alcohol, and colognes should not be expected to be a routine hand antisepsis in most clinical situations. On the other hand, Kampf shows that ethanol has been effective against various enveloped viruses, with the minimum concentration of 42.6% (w/w), including the similar SARS coronavirus, MERS coronavirus (10). Our study shows that only one of the tested colognes is below this effective concentration with 39.3% (w/w). All the other samples have over 43% (w/w) ethanol content and should be expected to be effective against novel coronavirus to help control the spread of disease.

According to Turkish Regulation on cosmetic products, colognes should contain ethyl alcohol 60% (v/v) (which is equal to 52.09% (w/w)) while lemon colognes should be over 70% (v/v) (which is equal to 62.39% (w/w)) (11). Our study shows that 3 of the tested 19 colognes have ethyl alcohol content lower than 52%, as they should not be marketed as cologne. Except these 3 colognes, all the colognes including the lemon labeled (higher concentration) are compatible with the regulation. At high demand times, counterfeit products may have find place in shelves, but as the surge and demand are balanced again, this undesirable situation would vanish as the regulatory bodies control mechanisms could determine these counterfeit products more easily.

It is worth to mention that ethanol has a density of 0.7893 g/cm<sup>3</sup>, as the colognes content is mainly ethanol and water, and the percentages of ethanol in water can be significantly different by weight (w/w) and by volume (v/v). Therefore, authors of this study think that this must be specified on the labels more clearly.

## CONCLUSION

The findings of this study show that at the time of pandemic, there has been a stockpiling and shortage of the products, but industry responded fast with a production of colognes. These colognes are now reachable and affordable in everyday supermarkets, and most of them are effective enough to be used against the COVID-19 in daily life. Careful selection of the raw material improves the quality and safety of these products, while no unknown content of alcohol has been detected. Although the alcohol content of some of the products is below the limit of Turkish Guideline for Cosmetic Products to be labelled as cologne, the regulatory bodies should check the products more intensively or the regulations on cologne in pandemic can be revisited.

## Conflict of interest

No conflict of interest was declared by the authors.

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