Sniffing methanol in hand sanitizers

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Abstract

The COVID-19 pandemic has increased dramatically the demand for hand sanitizers. A major concern is their adulteration with methanol that caused more than 700 fatalities in Iran and U.S.A. (since Feb. 2020). In response, the U.S. Food and Drug Administration (FDA) has restricted the methanol content in hand sanitizers to 0.063 vol% and blacklisted 194 products (as of Oct. 1, 2020). Here, we present a low-cost, handheld and smartphone-assisted device that detects methanol selectively in hand sanitizers between 0.01 - 100 vol% within two minutes by headspace analysis. It features a nanoporous polymer column that separates methanol from confounders by adsorption (i.e. van-der-Waals forces) rendering it selective. A chemoresistive gas sensor detects the methanol. When tested on seven pure and spiked commercial sanitizers (total 76 samples), methanol was quantified accurately, in excellent (R^2 = 0.99) agreement to “gold standard” gas chromatography. Most importantly, methanol quantification was hardly interfered by different sanitizer compositions (e.g. 2-propanol, ethanol, butanone, glycerin, aloe vera essence, various odorants and colorants) and gel-like viscosity while other potential contaminants (e.g. 1-propanol) were recognized as well. This device meets an urgent need for distributed and on-site methanol screening by authorities (e.g. customs, police), health product distributers and even laymen.

Keywords:

Public health, hazardous material monitoring, disinfectant, chemical detection, SARS-CoV-2.

Introduction

The global health emergency due to the infectious respiratory disease SARS-CoV-2 or COVID-19 (Wu et al., 2020) has caused a rapid increase in hand sanitizer consumption that led temporarily to acute shortages in supply. In response, global production has grown involving also small businesses (e.g. distilleries) and universities (Dicken et al., 2020) that produce and distribute hand sanitizers often locally at small scale. Public awareness about safety issues in hand sanitizers has emerged since the FDA placed a warning for 194 products (by Oct. 1, 2020) (U.S. Food and Drug Administration, 2020a) that contained up to 81 vol% of toxic methanol, drastically exceeding recommended (U.S. Food and Drug Administration, 2020b) limits (0.063 vol%). Similar hand sanitizer concerns have been published by the Canadian government (Government of Canada, 2020). The ingestion of methanol-contaminated sanitizers led already to more than 700 fatalities in Iran (Wambua-Soi, 2020) and the U.S.A. (Fazio, 2020) since Feb. 2020.

Commercial hand sanitizers should contain only ethanol or 2-propanol for antisepsis, according to the World Health Organization (WHO) (World Health Organization, 2010). For instance, after 30 seconds, the viral infectivity of SARS-CoV was reduced by more than 4 or 3 orders of magnitude with 80 vol% ethanol or 70 vol% 2-propanol, respectively. (Kampf et al., 2020) Other substances like glycerol (humectant), hydrogen peroxide (against bacterial spores), odorants and colorants may be contained as well (World Health Organization, 2010). Methanol is colorless and hardly distinguishable by odor from other alcohols like ethanol, so it cannot be recognized easily by human olfaction or vision. Its toxicity is primarily related to its metabolic products formaldehyde and formic acid (Barceloux et al., 2002) that can cause permanent neurologic dysfunctions, ocular morbidity up to blindness or even death (Kraut and Mullins, 2018). Therefore, low-cost and portable methanol detectors are needed to assist distributors, local authorities and even consumers to check product safety. Analytically challenging for such detectors are the required selectivity over other hand sanitizer ingredients, the large methanol detection range (at least 0.063 - 81 vol%), fast response times and, ideally, repeated usability.

Gas or liquid chromatography are most established for methanol detection in complex mixtures, but these are bulky, expensive instruments that require trained personnel, (Kraut and Kurtz, 2008) usually available only in specialized laboratories and unsuitable for on-site analyses. (Kraut and Mullins, 2018) Also optical infrared detectors suffer from similar drawbacks, for instance, the DX4000/DX4015 (Gasmet Technologies) that weighs 15 kg and is rather expensive (tens of thousands of US$ (U.S. Department of Defense, 2020)). Cheaper (Park et al., 2020), more compact (Weber et al., 2020) and less power consuming (Güntner et al., 2020) are chemical gas sensors (e.g. Pt-loaded tungsten nitride (Meng et al., 2020), polymer-coated Si bridges (Guo et al., 2011), electrochemical cells (Ou et al., 2019) or nanoporous Al_2O_3-coated carbon nanotubes (Zhao et al., 2012)) that detect methanol from the headspace of liquids. However, most are interfered by ethanol that is usually present at high content (Table 1) and none has been tested on hand sanitizers. Finally, a colorimetric assay (Alert for Methanol, Neogen Corp., ca. $20 per test) is available for alcoholic beverage analysis, which indicates if methanol is below or above 0.35 vol%, but is insufficient to check FDA adherence. Also, it is single-use, requires cooling (2 – 8 °C) and might be interfered particularly by colorants but also other hand sanitizer ingredients (e.g. 2-propanol, glycerol, odorants) and may fail on gel-like hand sanitizers.

Here, we present an inexpensive and compact device that quantifies hazardous methanol accurately in hand sanitizers by headspace analysis. It comprises a separation column of Tenax

TA particles and a chemoresistive gas sensor of Pd-doped SnO_2 nanoparticles (van den Broek et al., 2019) integrated into a smartphone-assisted analyzer with validated performance for alcoholic drinks (Abegg et al., 2020). Here, we applied it to seven pure and methanol-spiked (0.01 – 90 vol%) commercial hand sanitizers (total 76 samples) with various compositions (Table 1) to assess its resistance to challenging 2-propanol, glycerol, various odorants and gel-like viscosity. Results were compared to established gas chromatography as recommended by FDA (U.S. Food and Drug Administration, 2020b).

Materials and methods

Device design

The handheld detector is shown in Figure 1 and its design elaborated elsewhere (Abegg, et al., 2020). In brief, vapor from the headspace of liquid samples was extracted with a capillary (Sterican, B. Braun, Germany) fixed to a Teflon tube (4 mm inner diameter). This tube contained the sorption material, 150 mg Tenax TA powder (60–80 mesh, ~35 $m^2\ g^{-1}$, poly(2,6-diphenyl-p-phenylene oxide), Sigma Aldrich, Switzerland) (van den Broek, et al., 2019), that was fixed as packed bed with tension springs and silanized glass wool plugs to avoid voids. Note that such separation columns could be miniaturized even further by microfabrication and their loading can be varied flexibly to adjust analyte separation for other analytes (e.g. formaldehyde (van den Broek et al., 2020)). A vane pump (135 FZ 3 V, Schwarz Precision, Germany) provided the flow for sampling and flushing to recover the separation column.

The gas sensor consists of Pd-doped SnO_2 nanoparticles made by flame spray pyrolysis and directly deposited onto micromachined sensor substrate (Güntner et al., 2016) (1.9×1.7 mm^2, MSGS 5000i, Microsens SA, Switzerland) featuring interdigitated electrodes and a heater on a free-standing membrane. This sensor was mounted onto a leadless chip carrier (LCC, Chelsea

Technology Inc., U.S.A.) with high temperature carbon paste (Ted Pella Inc., U.S.A.) and electrically connected through aluminum wires (30 µm in diameter) by bonding (F&K Delvotec, Germany). After placing it on a socket (E-Tec, Switzerland) that was soldered to a printed circuit board (PCB), the sensor was sealed (gas-tight) by an inert Teflon chamber with its design disclosed elsewhere (Abegg, et al., 2020). A microcontroller (Raspberry pi Zero W, U.S.A.) provided the required heating power to operate the sensor at 350 °C (van den Broek, et al., 2019), monitored its resistance and communicated data wirelessly to a smartphone by Bluetooth or Wi-Fi. The smartphone prototype app was made with a free mobile app constructor (Version 2.27.19, Blynk Inc., U.S.A.).

Sample preparation

The applied substances were methanol (> 99.9%, Sigma-Aldrich, Germany), ethanol (> 99.8%, Fisher Chemical, Switzerland), 1-propanol (> 99%, Merck, Germany), 2-propanol (> 99.5%, Sigma Aldrich, Germany), butanone (> 99%, VWR International, France) and Milli-Q water (Milli-Q Synthesis A10, Merck, Germany). Also seven commercial hand sanitizers were tested with their identifiers, producers and compositions, as available, listed in Table 1. Binary, ternary (for calibration) mixtures and methanol-spiked hand sanitizers were obtained by admixing the desired amounts of methanol with high precision pipettes. Each sample was 5 mL prepared in 20 mL glass vials (Vial SCR 20ML, VWR, Germany) leaving sufficient headspace for vapor analysis. The vials were sealed immediately after preparation with caps (polypropylene screw cap with hole 24 mm, Supelco, U.S.A.) containing a septum (Teflon faced silicone septa 22 mm, Supelco, U.S.A.), unless otherwise stated.

Headspace analysis

Right before each sensor measurement, the prepared vials were rigorously shaken (at least 30 s) to afford phase equilibrium in the vial (Abegg, et al., 2020). Next, the capillary of the detector was inserted through the vial septum together with a second capillary for pressure balance. Note that sampling can be done also from the open container (Figure 1), though this is less accurate (Figure S-5) due to higher dilution with surrounding air. Sample was extracted always for 10 s at a sampling rate of 25 mL min^{-1} drawn by the vane pump. Afterwards the capillary was removed from the vial and ambient air was drawn continuously to transport the sample through the separation column and to the sensor. By flushing with ambient air at 65 mL min^{-1}, residual adsorbate was removed from the separation column to facilitate fast detector reusability. After recovery, the flow rate was set to zero to reduce the amount of noise due to ambient air interferants (Abegg, et al., 2020).

The sensor response (S) was defined as:

$$(1) \quad S = \frac{R_b}{R_s} - 1$$

with R_b and R_s being the sensor (i.e. Pd-doped SnO_2 film) resistances at baseline (stabilized in room air) and under sample exposure, respectively. The t_R of an analyte was defined as the time required to reach the response peak, similar to gas chromatography (Geankoplis, 2003). The methanol concentration in pure and spiked hand sanitizers were quantified by comparing the peak response to five-point calibration curves from methanol-ethanol-water mixtures (giving similar methanol responses to mixtures with 2-propanol instead of ethanol, Figure 2c) in the expected concentration range, as elaborated elsewhere (Abegg, et al., 2020).

The methanol content of pure and spiked hand sanitizers #1-6 was determined also by gas chromatography for comparison. Note that gel-type hand sanitizer #7 was not analyzed due to its high viscosity. Measurements were performed on a Varian 3800 (Agilent, U.S.A.) with a column

(Zebron ZB-624, Brechbühler AG, Switzerland) and flame ionization detector operated at 45 and 220 °C, respectively. The sampling volume and pressure were 0.5 μL and 4 psi, respectively and the injector was applied at 210 °C with split ratio 20. Methanol concentrations were obtained by comparing the area under curve of the methanol signal to calibration curves, as evaluated with the software Varian Star Chromatography Workstation (Agilent, U.S.A.). The calibration was done with the above-mentioned standards by mixing the desired amounts with precision graduated and volumetric pipettes (Hirschmann, Germany) in a 100 mL volumetric flask and analyzing the peak response area (McNair et al., 2019).

Results and Discussion

Analytical strategy

The handheld device is shown in Figure 1. For hand sanitizer analysis, headspace vapor is extracted for 10 s through a sampling capillary with a vane pump. When transported through the separation column (i.e. packed bed of non-polar Tenax TA polymer particles), the analytes are separated by sorption (similar to gas chromatography) on the Tenax TA available surface area (van den Broek, et al., 2019) of 35 m^2 g^{-1}. Specifically, larger alcohols (e.g. ethanol, 2-propanol), the main constituents of hand sanitizers (Table 1), are retained longer than methanol due to stronger van-der-Waals adsorption forces (Maier and Fieber, 1988) rendering the device selective. This represents a key challenge for conventional chemical sensors that can hardly distinguish these molecules (Guo, et al., 2011) due to their chemical similarity (i.e. hydroxyl group).

A chemoresistive micro-gas sensor upstream the separation column detects and quantifies the methanol content. It is based on a porous film, self-assembled by flame-aerosol deposition of SnO_2 nanoparticles (grain size 16 nm (Abegg, et al., 2020)) containing lattice-incorporated and surface-loaded Pd (Pineau et al., 2020) that feature high sensitivity to various volatile organics (e.g. down to 3 ppb formaldehyde at 90% relative humidity (Güntner, et al., 2016)). Methanol is adsorbed on these nanoparticles (Ouyang et al., 2000) and converted by chemical reaction with oxygen- and hydroxyl-related species (Cheong and Lee, 2006). The associated release of electrons into the n-type semiconducting SnO_2 results in a measurable signal (i.e. film resistance change) (Ogawa et al., 1982) that is proportional to methanol concentration. All other parts of the device in contact with analytes (e.g. tubing, sensor housing, etc.) are made of inert Teflon to minimize adsorption and contamination. After flushing the column and sensor with ambient air to remove residual adsorbate, it can be reused after 15 min and provides stable results tested during more than three months (Abegg, et al., 2020).

Selective methanol detection over other alcohols

Figure 2a shows the sensor response curves for 0 – 100 vol% methanol in ethanol. Methanol passes through the separation column first with retention times (t_R) between 1.5 – 0.8 min for 0.01 – 100 vol%, respectively, in agreement with literature (i.e. 1.25 min for 10 vol% methanol in 80 vol% ethanol and water (Abegg, et al., 2020)). Note that shorter retention times with increasing methanol levels are due to an overloading of the column, as with gas chromatography (Yabumoto et al., 1980), but this does not affect methanol quantification, as shown below. Most importantly, ethanol elutes later (t_R = 2 min for pure ethanol, Figure S-1) without interfering the methanol measurement. Similarly, 2-propanol (Figure 2b) passes the separation column even later (t_R = 2.8 min for pure 2-propanol, Figure S-1) with rather small response. As a result, methanol is detected selectively over all alcohols overcoming a major bottleneck in chemical sensing.

Another challenge is the quantification of methanol over a large concentration range: at least from 0.063 vol% (U.S. Food and Drug Administration, 2020b) (FDA limit) to 81 vol% (max. content found in adulterated sanitizers (U.S. Food and Drug Administration, 2020a)). This is met by the device that detects methanol over four orders of magnitude (0.01 – 100 vol%, Figure 2c) with almost identical responses (average deviation 4%, $R^2 = 0.99$) in ethanol (squares) and 2-propanol (circles), highlighting again its excellent selectivity. Remarkably, even lowest 0.01 vol% (Insets, Figure 2a and Figure 2b) are detected with high signal-to-noise (SNR > 300) within 2 min at very high alcohol background (i.e. > 99 vol%). The recognition of such low methanol concentrations is superior to state-the-art sensors featuring higher detection limits, for instance, electrochemical cells (Ou, et al., 2019) (0.15 vol%) or fluorescent sensors (Huang et al., 2018) (4 vol%). Also close to the FDA limit, methanol concentrations are distinguished clearly, as demonstrated for 0.05, 0.06 and 0.07 vol% (Insets, Figure 2a and Figure 2b). Please note that the t_R at such low methanol concentrations are slightly higher (e.g. 1.6 vs. 1.5 min at 0.06 vol%) in 2-propanol than ethanol, probably due to competitive adsorption (Comes et al., 1993) on the Tenax TA and the higher vapor pressure of ethanol.

Hand sanitizers

Hand sanitizers are typically more complex mixtures containing also humectants, odorants, denaturants and colorants. Thus, the device was evaluated (Figure 3a) on six commercially available hand sanitizers with different compositions (Table 1), as characterized also by gas chromatography (Figure S-2). Sanitizers #1 – 5 are ethanol-based, as correctly recognized by the device. On the other hand, hand sanitizer #6 contains mainly 2- (49 vol%) and 1-propanol (32 vol%) with both compounds being identified by the sensor (Figure S-3). It should be noted that the FDA considers 1-propanol toxic (U.S. Food and Drug Administration, 2020b) and has limited its content also to 0.1 vol% while it is recommended as active substance in biocidal products in the E.U. (European Chemical Agency, 2020).

Only sample #2 contained methanol, as detected by the device with a response of 2.2 at (t_R) 1.4 min and confirmed by gas chromatography (0.19 vol%, Figure S-2). This hand sanitizer is based on fruit-derived distillates where methanol is formed naturally during fermentation (from pectin degradation (Bindler et al., 1988)). Please note that its methanol content, however, is below the E.U. limit (i.e. 0.9 vol% at that ethanol content (European Parliament and Council, 2019)) for fruit distillates.

Next, these hand sanitizers were spiked with 0.01 – 90 vol% methanol (total 66 samples) to simulate the entire range of typical contamination/adulteration. Figure 3b shows the sensor response exemplarily for sample #5 that contains 81 vol% ethanol (Table 1) but also glycerol, panthenol, cyclopentasiloxane, cyclohexasiloxane, isotrideceth-8, 2-propanol, and didecyldimethylammoniumchloride (please see Figure S-4 for sample #3). Remarkably, these compounds do not interfere the measurement. In fact, methanol elutes at comparable t_R to the binary mixtures with ethanol (Figure 2a) and is quantified with similar response (1.5 vs. 1.7 for 0.1 vol% methanol). We confirmed this also through experiments with pure substances (Figure S-1) where other compounds were detected only after 2 min being higher than the methanol t_R for lowest 0.01 vol% (i.e. 1.5 min).

Figure 3c shows the methanol concentrations of pure and spiked hand sanitizers, as measured by our detector and “gold standard” gas chromatography. The detector quantifies methanol accurately over four orders of magnitude with high R^2 of 0.99. The error is fairly small (95% confidence interval: -18.5 to 16.4%, dashed lines in Figure 3b) and stays rather constant over the entire measurement range, as revealed by Bland-Altman analysis (Martin Bland and

Altman, 1986). In other words, methanol concentrations at the FDA limit (0.063 vol%) will be determined between 0.051 – 0.073 vol%, which should be sufficiently accurate for screening hand sanitizers. Consequently, methanol is detected reliably in the commercial hand sanitizers #1-6 despite their different compositions (Table 1). Also colorants (e.g. #6 contains patent blue V) do not interfere the measurement (Figure 3c, inverse triangles), that may be quite problematic for colorimetric tests (e.g. Alert for Methanol).

Finally, we tested also the gel-like hand sanitizer #7 (Figure 4) to assess viscosity effects. Most importantly, the spiked methanol concentrations were recognized well with high R^2 (0.99), consistent to the less viscous samples #1 - 6 (Figure 3c). This highlights the robustness of present headspace analysis even for highly viscous samples where commercial colorimetric assays might fail, as indicator solutions do not mix well with such fluids.

We anticipate this device to be helpful to police, customs, distributors and consumers to check product safety. It is compact (2×4×12 cm^3, Figure 1), weighs only 94 g and offers low power consumption (ca. 1.1 W during analysis) enabling battery-driven operation(Abegg, et al., 2020). The operation and data display are user-friendly by providing wireless communication by Wi-Fi or Bluetooth, functioning even if no external network is available. When combined with a breath sampler, this device is even applicable for medical screening of methanol poisoning by breath analysis (van den Broek, et al., 2019), as established for ethanol by law enforcement (Güntner et al., 2019).

Conclusions

We presented a handheld and readily applicable detector for distributed and on-site screening of sanitizers for toxic methanol. It quantifies methanol within two minutes selectively over four orders of magnitude (0.01 – 100 vol%) and meets even newest national guidelines (e.g. FDA), as validated by gas chromatography. Typical hand sanitizer constituents and gel-like viscosity do not interfere the measurement while other potential contaminants (e.g. 1-propanol) are recognized as well. The device operation and data analysis is user-friendly, providing results on smartphones where further communication to data clouds for remote analysis is possible. The device contains mostly commercially available components, thus can be produced at low cost and large numbers. It addresses an urgent need during the COVID-19 health crisis where widespread access to safe sanitizers is crucial to mitigate disease propagation.

CRediT authorship contribution statement

Andreas T. Güntner: Conceptualization, Methodology, Investigation, Visualization, Writing – Original Draft, Project administration, Funding acquisition. **Leandro Magro:** Conceptualization, Methodology, Investigation, Writing – Review & Editing. **Jan van den Broek:** Conceptualization, Methodology, Investigation, Writing – Review & Editing. **Sotiris E. Pratsinis:** Conceptualization, Writing – Review & Editing, Project administration, Funding acquisition.

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Declaration of Competing Interests

A patent application for this methanol detector has been submitted by ETH Zürich.

Supporting Information

Sensor responses to sanitizer-related pure substances (Figure S-1); gas chromatograms of pure commercial hand sanitizers and reference substances (Figure S-2); full sensor response to pure sanitizer #6 (Figure S-3); sensor responses of pure and methanol-spiked sanitizer #3 (Figure S-4); detector sampling with sealed and open vials (Figure S-5).

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Tables, Figures & Captions

Table 1. Analyzed commercial hand sanitizers and their composition, as indicated by supplier. Contents by volume are indicated in brackets, if available.

Brand	Sample	Composition (vol %)
B. Braun Medical	#1	Ethanol (85), glycerol (0.7), butanone (<3)
*WHO	#2	Ethanol (72), glycerol (1.45), hydrogen peroxide (0.125), rest water
Martec Desinfektion	#3	Ethanol (82)
Lactipar Desin Händedesinfektion	#4	Ethanol (>80), butanone (<5.3)
Conviva Händedesinfektionsmittel	#5	Alcohol denat. (81), water, glycerol, panthenol, cyclopentasiloxane, cyclohexasiloxane, isotrideceth-8, 2-propanol, didecyldimethylammoniumchloride (0.05 vol%)
Sterillium	#6	2-propanol (49), 1-propanol (32) mecetroniumetilsulfat (0.2), glycerol, tertradecanol, odorants, patent blue V, water
Martec Hand-Desinfektion Gel	#7 (gel)	Ethanol (71.5), aloe vera essence

*Mixed according to WHO hand rub formulation (World Health Organization, 2010) but with fruit spirit-derived ethanol.

Figure 1. Handheld methanol detector for screening hand sanitizers. Key components are the capillary for vapor sampling, separation column, gas sensor (sealed by chamber), pump and micro-controller. Data is communicated wirelessly to a smartphone and an exemplary user-interface is shown.

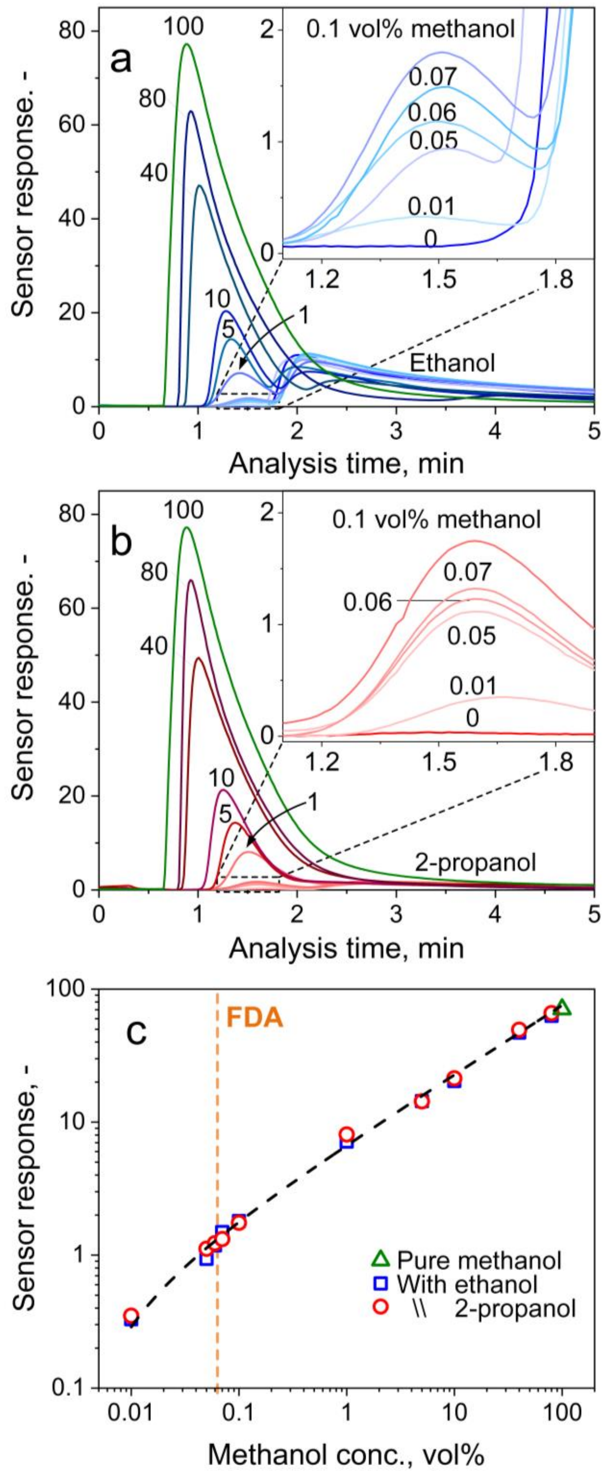

Figure 2. Sensor response to 0 – 100 vol% methanol in ethanol **(a)** or 2-propanol **(b)**. Insets magnify 0 – 0.1 vol% methanol. **(c)** Sensor response peak values for pure methanol (triangle) and with ethanol (squares) or 2-propanol (circles). Indicated is also the FDA recommended limit (i.e. 0.063 vol%, vertical dashed line) and best fit (black dashed line).

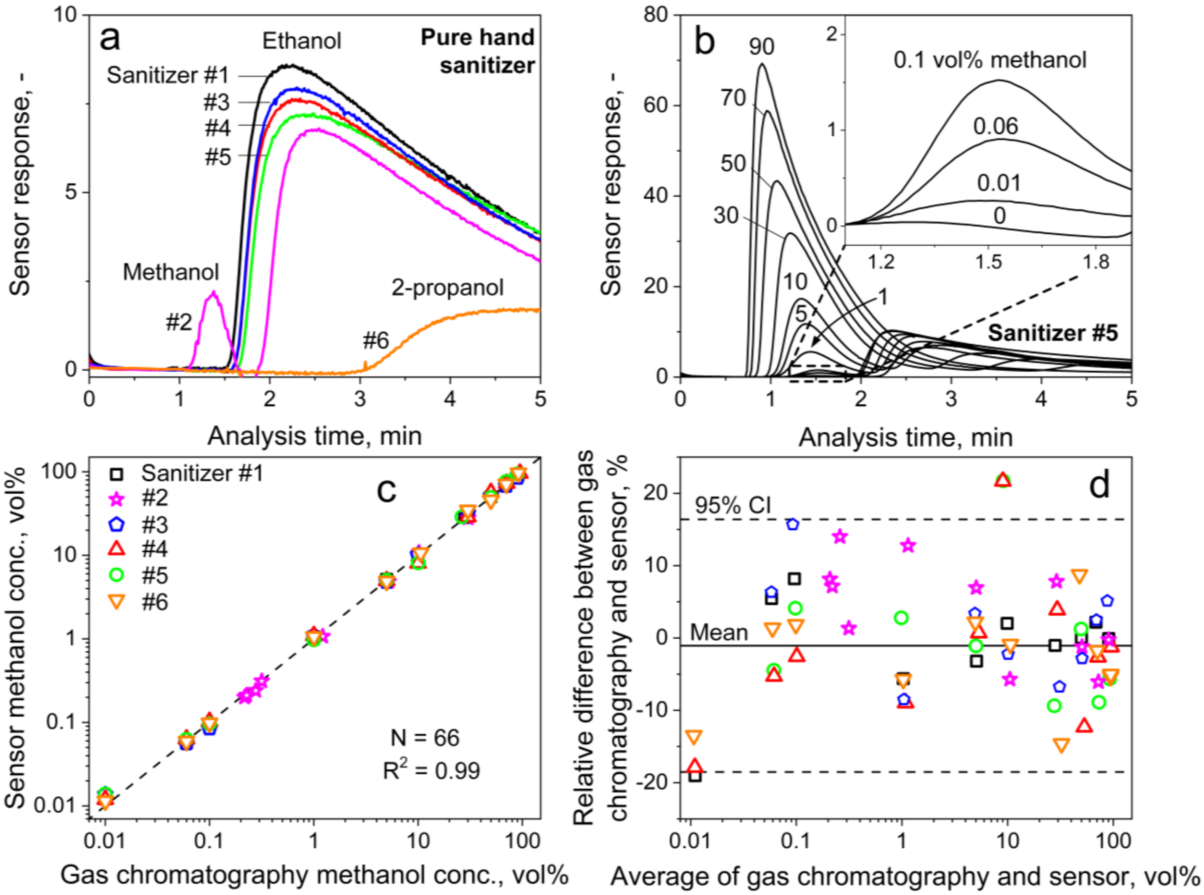

Figure 3. Commercial hand sanitizers #1-6 (pure and methanol-spiked) evaluated by sensor and gas chromatography: **(a)** Sensor response to the commercial hand sanitizers with different compositions (Table 1). Associated peaks for methanol, ethanol and 2-propanol are indicated. **(b)** Response to 0 – 90 vol% methanol-spiked samples of sanitizer #5 that contains 81 vol% ethanol, water, glycerol, panthenol, cyclopentasiloxane, cyclohexasiloxane, isotrideceth-8, 2-propanol and didecyldimethylammoniumchloride (Table 1). Inset shows magnification of 0 – 0.1 vol% methanol content. **(c)** Scatter plot (66 samples) indicating the methanol content in pure and spiked hand sanitizers, as measured by sensor and gas chromatography. **(d)** Corresponding Bland-Altman analysis indicating the relative error of the measured methanol concentrations vs. the average concentration measured by both instruments. Mean and limits of agreement (95% confidence intervals, CI) are provided as solid and dashed lines, respectively.

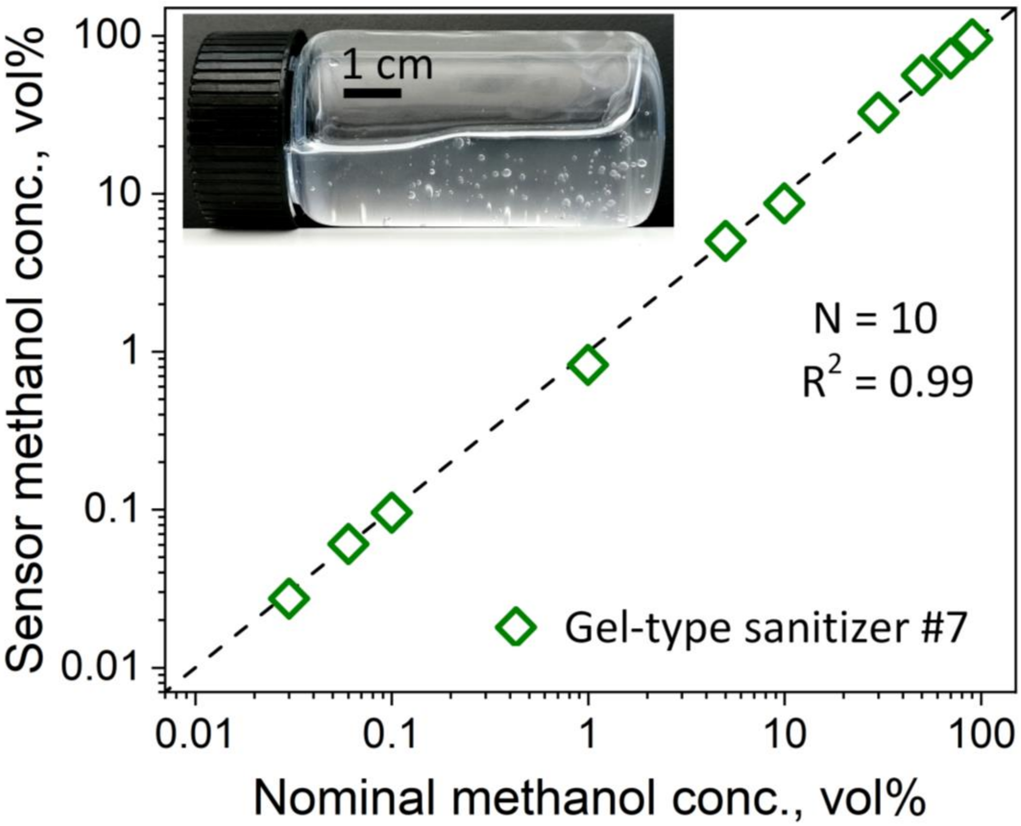

Figure 4. Methanol concentration measured by the sensor in gel-like hand sanitizer #7 (methanol-spiked). Note that direct analysis by gas chromatography was not feasible due to the sanitizer's high viscosity. Inset shows the sample.