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BRIEF COMMUNICATION

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# A pocket-sized device enables detection of methanol adulteration in alcoholic beverages

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**Alcoholic drinks contaminated, either accidentally or deliberately, by methanol claimed at least 789 lives in 2019, mostly in Asia. Here, a palm-sized, multi-use sensor–smartphone system is presented for on-demand headspace analysis of beverages. The analyser quantified methanol concentrations in 89 pure and methanol-contaminated alcoholic drinks from 6 continents and performed accurately for 107 consecutive days. This device could help consumers, distillers, law-enforcing authorities and healthcare workers to easily screen methanol in alcoholic beverages.**

Alcoholic beverages are often intentionally adulterated with cheap methanol (up to 50 vol%)[1] to increase beverage profit and potency. In 2017–2019, approximately 7,104 intoxicated people and more than 1,888 fatalities were reported in 306 registered methanol poisoning outbreaks, with more than 90% in Asia[2]. Young men are most affected, as was shown in a 2018 case in Iran with 768 victims: 41% were aged 25–36 and 93% of the deaths were male[3]. Also, methanol occurs naturally in most alcoholic beverages, originating from the degradation of pectin during fermentation[4]. Methanol may reach high concentrations during improper distillation, particularly in fruit spirits (up to 2.4 vol%)[5]. In the European Union, the legal limits for distillates from fruit fermentation range from 0.09 to 0.71 vol% (at 36 vol% ethanol)[6].

Chromatography is the 'gold' standard for methanol testing, but it is costly, slow and confined to the laboratory. More compact gas sensors, such as fluorescent silica-gel plates[7] or aluminium-doped nickel oxide nanofibres[8], detect methanol in the container headspace above beverages, but can be unreliable owing to insufficient detection limits (for example, 4 vol%)[7] and an inability to distinguish methanol from ethanol background[8]. Most importantly, they have not been validated under real conditions[7,8], which is a general challenge for sensor science[9]. Inexpensive, simple-to-use and portable methanol detectors are urgently needed by consumers, distributors and authorities (for example, police and customs) to screen such beverages. These detectors would also be valuable for professional and even home distillers to assess product adherence to legal limits and monitor methanol concentrations during distillation and possibly even occupational exposure. Furthermore, such detectors could facilitate screening of methanol intoxication by breath analysis by first responders and emergency room workers[10].

Thus, we introduce a fully integrated, handheld, smartphone-compatible and inexpensive analyser (Fig. 1a) for rapid methanol and ethanol quantification, based on a previously developed[10] separation column (Fig. 1b), with validated performance in real alcoholic beverages. The analyser weighs 94 g and is small ($2\times4\times12\,cm^3$), comparable to commercial breath ethanol detectors (for example, Dräger Alcotest 3820). The separation column consists of Tenax particles that retain ethanol longer than methanol[10] and a highly sensitive chemo-resistive sensor, based on flame-deposited palladium-doped tin dioxide nanoparticles[11], detects both chemicals sequentially and thus selectively[10]. Owing to its low power consumption (~1.1 W), which is reduced by non-continuous operation (the pump is switched on only during sampling, analysis and recovery; Fig. 1c), it can be powered by a battery. This protects the sensor and the column from unnecessary exposure to room air contaminants and reduces fluctuations in baseline resistance (Supplementary Fig. 1). Wireless communication by WiFi to a smartphone controls the device and displays the ethanol and methanol concentrations in real time (Fig. 1d). In the field, the device can be operated also without an external network by direct communication through Bluetooth with the smartphone. The app can be used by Android- or iOS-based systems, and thus, should be compatible with older smartphones as well, which are common in low-income regions where most outbreaks occur. Also, additional functionalities such as text-to-speech features can be implemented flexibly.

The device works by drawing a vapour/gas sample from the container headspace (Fig. 1) into the Tenax column. There, methanol and ethanol are retained temporarily. Methanol elutes first and peaks at 1.5 min while ethanol starts to elute later (that is, 1.9 min for Stroh rum and 3.8 min for beer), enabling the selective and quantitative detection of both (Fig. 2a). The simultaneous quantification of methanol and ethanol is critical as the legally allowed methanol content depends on ethanol concentration[6]. The present device offers a lower methanol detection limit (0.01 vol%) than previous sensors, as demonstrated in the relevant ethanol (5–80 vol%) concentration range (Supplementary Figs. 2 and 3) and compared in the Supplementary Information. Alcoholic beverages are complex mixtures including flavouring additives that may interfere with the sensor. However, no additional peaks are observed as these compounds are present at much lower concentrations (for example, 0.0015 vol% ethyl acetate[12]) or retained longer (for example, 1-propanol 29 times longer than ethanol[13]) (Supplementary Fig. 4).

The device was evaluated on 89 pure and methanol-contaminated samples of beer, sake, wine (from five continents; Supplementary Fig. 5), Baileys, arrack, Stroh rum, and pear and cherry spirits (Fig. 2b). The ethanol concentrations are quantified accurately with a high $R^2$ (0.96) and low relative error ($\varepsilon_{rel}=12.9\%$) (Fig. 2c). Pear spirit errors are discussed in the Supplementary Information. The device accurately detects methanol concentrations over three orders of magnitude (0.01–10 vol%) with $R^2=0.94$ and 19.5% error (Fig. 2d). This includes the correct quantification of 0.39 and 0.54 vol% methanol in pure home-made pear and local cherry

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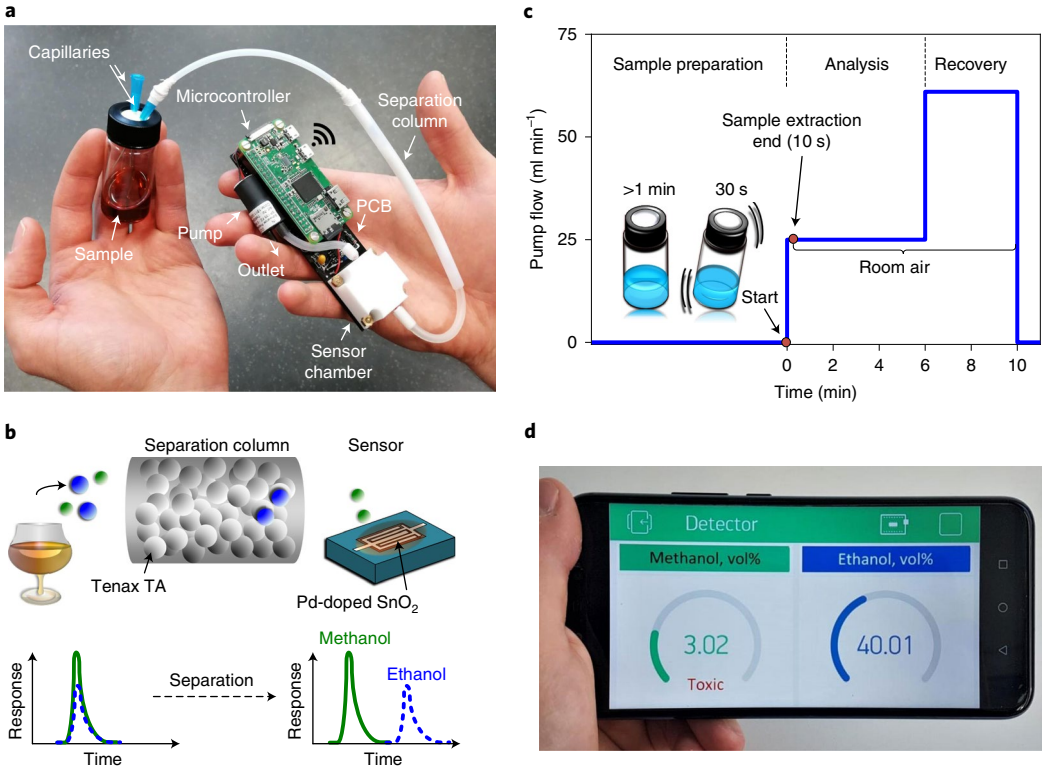


**Fig. 1 | Analyser design. a**, The handheld analyser during measurement. **b**, A schematic of the detection concept. **c**, The sampling and analysis procedure. **d**, The tailor-made app to visualize results on a smartphone transmitted through a wireless local area network. PCB, printed circuit board; Pd, palladium.

spirits, just below the EU legal limit[6]. Harmful concentrations of 3 and 10 vol% methanol, above the recommended limit (2 vol%; dashed line)[14], are recognized.

The repeatability and stability were evaluated on laboratory mixtures containing 1 vol% methanol and 40 vol% ethanol in water. During 3 consecutive exposures (Fig. 2e), the peak methanol response and retention time, $t_R$, of ethanol vary by 4% and 3%, respectively, indicating reliable repeatability. The device provided stable results for 107 consecutive days, once per day for freshly prepared samples (Fig. 2f), with errors of 17 and 19% for methanol and ethanol, respectively. No deterioration was observed, meaning the recovery methodology (Fig. 1c) suffices to maintain the sensor's performance. Variations may be related to altered humidity (27.1–48.2%) and/or temperature (22.5–26.0 °C) during these 107 days—the response of chemo-resistive sensors is affected by humidity[11] and the $t_R$ of the separation column changes with temperature, as shown previously[10]. Nevertheless, the accuracy of the detector is sufficient to distinguish harmful from harmless methanol concentrations in alcoholic beverages (Fig. 2d). If higher accuracies are required, this can be corrected with co-located temperature and humidity sensors[15].

In conclusion, we present a handheld, low-cost, simple-to-use and reliable methanol detector that can be readily used by beverage consumers, distillers, healthcare workers and law-enforcing authorities for easy methanol screening of alcoholic beverages and possibly even in the breath of intoxicated people. This modular design could be applied also for detection of other food contaminants, such as formaldehyde[16], or food freshness markers, such as ammonia from spoiling seafood[17]. Concepts for selective analyte sensing exist, including zeolite membranes (formaldehyde)[11] or porous CuBr (ammonia)[18], which can be incorporated into the present device. Affordable detectors are particularly attractive for widely distributed use, especially in low-income economies where food safety is a concern.

## Methods

The stand-alone analyser is shown in Fig. 1a. It consists of a capillary (Sterican, B. Braun AG) to sample the headspace, a separation column to pre-separate the gas mixture, a sensor for analyte detection, a vane pump (135 FZ 3 V, Schwarz Precision) providing the required flow of 25 ml min$^{-1}$ and a microcontroller (Raspberry Pi Zero W) to control the sensor and pump, extract the data and communicate wirelessly with a computer or smartphone. The components are integrated onto a PCB and powered by the microcontroller's micro-USB port using a power adapter. The separation column, palladium-doped tin dioxide sensor and PCB are described in the Supplementary Information. The device is inexpensive, consisting mostly of standard components.

The sensing film resistance is determined in the relevant range of 1–30 MΩ with an accuracy of 99.79%, as described in the Supplementary Information. The sensor response $S$ is defined as:

$$S = R_b/R_s - 1 \quad (1)$$

Therein, $R_s$ and $R_b$ are the resistances during sampling and after overnight stabilization (without flow), respectively. The retention time $t_R$ is defined as the time needed to reach the peak response, analogous to gas chromatography[19]. The breakthrough time $t_B$ is extrapolated from a tangent to the ethanol peak[20]. Examples for the definition of $t_R$ and $t_B$ are shown in Supplementary Fig. 6. All signals are continuously processed and stored by the microcontroller. Methanol and ethanol concentrations are determined by comparison of the methanol peak response and ethanol $t_R$ to calibration curves (Supplementary Fig. 3), which is more accurate than if the $t_R$ of methanol and ethanol peak response are used, respectively (Supplementary Fig. 7). The microcontroller communicates wirelessly to a smartphone or computer to control its operation and display the results. The smartphone app was designed using the free mobile app constructor Blynk (Version 2.27.9, Blynk Inc., United States).

Sample preparation of laboratory mixtures and real beverages are described in the Supplementary Information. The detector is exposed to an air flow only during sampling, analysis and recovery (that is, non-continuous operation; Fig. 1c). Before measurement, the prepared vials are at rest for at least 1 min and then shaken for 30 s to facilitate rapid phase equilibrium between the liquid and the headspace. To perform a measurement, the pump is turned on (25 ml min$^{-1}$) and the headspace above the liquid is sampled for 10 s, resulting in a total sample volume of about 4.17 ml. A second capillary compensates the pressure in the vial (Fig. 1a). Afterwards, the capillaries are removed from the vial and room air is sampled to carry the headspace sample through the separation column to the sensor. During analysis ($0 \leq t \leq 6$ min), the headspace sample containing methanol and ethanol

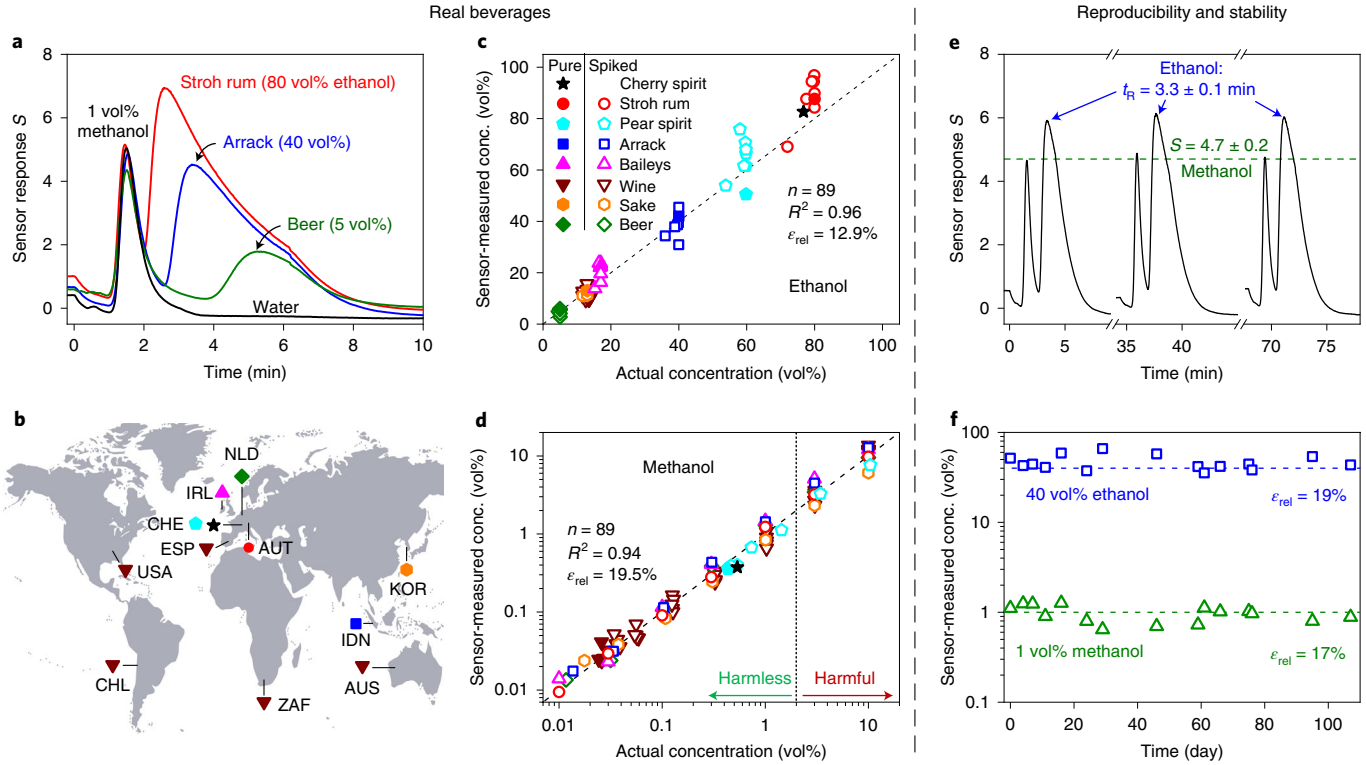


**Fig. 2 | Performance in real beverages and laboratory samples. a**, The sensor response for water, beer, arrack and Stroh rum contaminated with 1 vol% methanol. **b**, The origin of the tested alcoholic beverages indicated by country codes (ISO 3166). **c**,**d**, The corresponding actual and sensor-measured ethanol (**c**) and methanol (**d**) concentrations in pure (filled symbols) and 0.01, 0.03, 0.1, 0.3, 1, 3 and 10 vol% methanol-contaminated or -spiked (open symbols) cherry spirit (star), Stroh rum (circles), pear spirit (pentagons), arrack (squares), Baileys (up triangles), wines (down triangles), sake (hexagons) and beer (diamonds) ($n = 89$ independent samples). The methanol concentrations of pure beer, sake, Baileys, arrack and Stroh rum were below the sensor's detection limit (that is, <0.01 vol%) and thus are not included. The dashed line indicates the recommended limit (that is, 2 vol% (ref. [14])). **e**, Sensor responses to three consecutive headspace samples with 1 vol% methanol and 40 vol% ethanol in water. Methanol responses and ethanol $t_R$ are indicated as mean ± s.d. **f**, Methanol (triangles) and ethanol (squares) concentrations measured for 107 days. The dashed lines show the actual alcohol concentrations. IRL, Ireland; NLD, Netherlands; CHE, Switzerland; ESP, Spain; AUT, Austria; USA, United States; KOR, South Korea; IDN, Indonesia, CHL, Chile; ZAF, South Africa; AUS, Australia. Credit: world map in **b** from https://www.pixabay.com.

passes the column and is analysed by the sensor. Thereafter ($6 < t \leq 10$ min), the flow is maximized (~60 ml min$^{-1}$), to quickly remove analyte residues from the column, refresh the sensor chamber and prepare the device for rapid reuse.

**Reporting Summary.** Further information on research design is available in the Nature Research Reporting Summary linked to this article.

## Data availability

The data that support the findings of this study are available as source data or can be requested from the corresponding author.

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## Author contributions

S.A., S.E.P. and A.T.G. conceived the concept and experiments. S.A. and L.M. performed the experiments and the data evaluation. J.v.d.B. designed and provided the separation column and contributed to the experimental design. S.E.P. and A.T.G. were in charge and advised on all parts of the project. S.A., L.M., J.v.d.B., S.E.P. and A.T.G. co-wrote the paper. All authors gave final approval to the manuscript.

## Competing interests

A patent application has been submitted that covers the concept of selective methanol detection. Applicant: ETH Zürich; inventors: S.A., J.v.d.B., S.E.P. and A.T.G.; application number: DE2019011109582800; status: pending.

## Additional information

**Supplementary information** is available for this paper at https://doi.org/10.1038/s43016-020-0095-9.

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## Software and code

Policy information about availability of computer code

| | |
|---|---|
| Data collection | Excel 2016 (Microsoft)<br>Python (version 3) |
| Data analysis | OriginPro 2018G (OriginLab Corporation)<br>Excel 2016 (Microsoft) |

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The data that support the findings of this study are available from the corresponding author upon request.

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# Life sciences study design

All studies must disclose on these points even when the disclosure is negative.

| | |
|---|---|
| Sample size | Sample size was chosen to cover the range of relevant methanol & ethanol concentrations and includes typical beverages. |
| Data exclusions | No data was excluded. |
| Replication | Reproducibility was performed by subsequent measurement of the same sample (intrasample variability) and of different samples with same concentration/composition (intersample variability). Tests were performed over 107 days to assess measurement stability. Reproducibility was successful. Detector performance was validated with state-of-the-art liquid chromatography. |
| Randomization | Calibration and validation datasets were independent, i.e. calibration was performed with analytical grade methanol/ethanol/water mixtures, while validation was performed on real beverage samples spiked with methanol. The order in which samples were measured was random. |
| Blinding | Blinding was not possible in this study, as calibration and validation datasets were clearly separated to ensure a throrough analysis of the device performance. It was additionally not possible since the color and smell of beverages were indicative of the beverage type in the validation dataset. |

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| ☒ | ☐ Eukaryotic cell lines |
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| ☒ | ☐ Animals and other organisms |
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| ☒ | ☐ Clinical data |

## Methods

| n/a | Involved in the study |
|---|---|
| ☒ | ☐ ChIP-seq |
| ☒ | ☐ Flow cytometry |
| ☒ | ☐ MRI-based neuroimaging |