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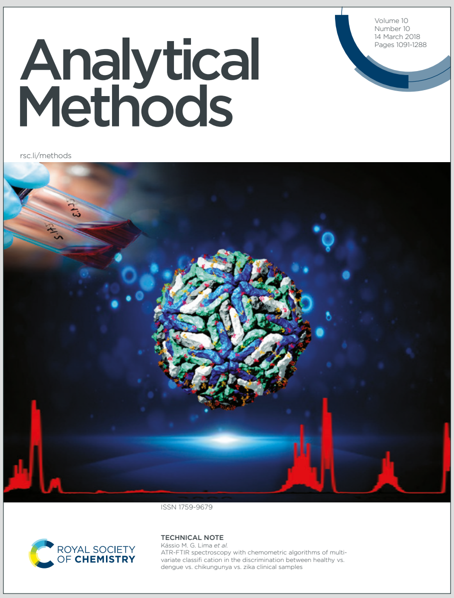

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Data Availability Statement

The data supporting this article have been included as part of the Supplementary Information.

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Handheld Methanol Detector for Beverage Analysis: Interlaboratory Validation

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Abstract

Methanol is a toxic alcohol contained in alcoholic beverages as a natural byproduct of fermentation or added intentionally to counterfeits to increase profit. To ensure consumer safety, many countries and the EU have established strict legislation limits for methanol content. Methanol concentration is mostly detected by laboratory instrumentation since mobile devices for routine on-site testing of beverages in distilleries, at border stations or even at home are not available. Here, we validated a handheld methanol detector for beverage analysis in an ISO 5725 interlaboratory trial: A total of 119 measurements were performed by 17 independent participants (distilleries, universities, authorities, and competence centers) from six countries on samples with relevant methanol (0.1, 1.5 vol%). The detector was based on a microporous separation filter and a nanostructured gas sensor allowing on-site measurement of methanol down to 0.01 vol% (in the liquid) within only 2 min by laymen. The detector showed excellent repeatability (<5.4%), reproducibility (<9.5%) and small bias (<0.012 vol%). Additional measurements on various methanol-spiked alcoholic beverages (whisky, rum, gin, vodka, tequila, port, sherry, liqueur) indicated that the detector is not interfered by environmental temperature and spirit composition, featuring excellent linearity (R^2>0.99) down to methanol concentrations of 0.01 vol%. This device has been recently commercialized *(Alivion Spark M-20)* with comparable accuracy to the gold-standard gas chromatography and can be readily applied for final product inspection, intake control of raw materials or to identify toxic counterfeit products.

Keywords:

chemical sensor, miniaturized gas chromatography, food safety, alcoholic beverages, methanol intoxication, ISO 5725

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Introduction

Methanol is highly toxic and the exposure to only small quantities (as little as 80 mg/kg body mass)[1] can result in blindness, organ failure or even death.[2] However, it is also present in alcoholic beverages being a natural byproduct of fermentation. It is primarily generated from the enzymatic breakdown of pectin,[3] with the quality of raw material (e.g., remainders of leaves, stems, or stones)[4] and storage conditions during fermentation (e.g., temperature, humidity or pH) affecting the final methanol concentration.[5] Methanol can never be fully eliminated in alcoholic beverages,[6] thus it represents an omnipresent risk.

Most countries impose strict legal regulations on the methanol content in alcoholic beverages. In the EU, the maximum methanol concentration ranges from 50 mg/L AA (absolute alcohol) for London gin to 15,000 mg/L AA for fruit marc spirit.[7] Similar regulations exist in China,[8] the US,[9] Mexico,[10] Australia and New Zealand,[11] and many other countries/regions worldwide. To avoid economic and reputational damage as well as legal consequences from exceeding these limits, producers have a need for equipment that allows easy, reliable and fast methanol measurement.

The gold-standard gas chromatography with flame ionization detector (GC-FID)[12] is an expensive equipment (>$30k[13]) that requires long measurement time (~40 min[12]) and, most importantly, can be operated only by trained personnel (Table 1). Thus, medium- to small-sized distillers typically do not possess GCs, but may send their samples to external analytical laboratories for analysis. This is costly ($100–300 per sample[14]) and the results are only available after several days to weeks. Needed is a handheld methanol detector for easy, fast and on-site inspection of final products and intake control of raw materials (e.g., mash, neutral spirit, wine). Beyond, such a device could enable new applications such as better process control by testing methanol already during distillation or in the mash during

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fermentation. Further, such equipment could be used by distributors and authorities for the identification of counterfeit products[15] with possible toxic concentrations of methanol.

Various chemoresistive (e.g., Pt/WN particles,[16] MoS_2/TiO_2[17]) and optical (e.g., cholesteric liquid crystals,[18] perovskites[19]) sensors were reported for the selective measurement of methanol in alcoholic beverages. However, none of these technologies has been validated in real applications nor made commercially available yet. A system that was rigorously validated in various applications combines a chemoresistive metal-oxide gas sensor with a separation column.[20] As in GC, methanol is separated from confounders and detected without interference by the sensor, which has allowed successful quantification of methanol in various spirits & wines,[21] hand sanitizers,[22] during distillation,[23] and even in human breath for intoxication screening.[24] This technology was recently made commercially available[25] as a handheld device (*Spark M-20*, see Figure 1) by Alivion AG. Primarily targeted at distillers of fruit-based spirits to confirm their products' adherence to legal limits, it can be used also for quality assurance of other alcoholic beverages (e.g., whisky, vodka, gin, port wine) or to screen beverages for toxic adulterations.

In recent years, portable sensor technologies for other analytes have become commercially available, but have not been validated sufficiently under real-world conditions and failed to meet the requirements (e.g. in air quality monitoring[26]). Sources of error have included high device-to-device variability, non-ideal and variable measurement conditions (e.g., sample composition or ambient temperature).[27] Therefore, it is crucial to prove the performance of a new device following established standards with multiple devices to establish research-based sensor technology as a product in industry.

Here, we validate the *Alivion Spark M-20* in an interlaboratory trial following ISO 5725 — a standardized method to assess the accuracy of new measurement technology.[28] Samples with realistic concentration levels of methanol and ethanol were analyzed by 17 independent

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participants from six different countries to determine device precision and bias. Further, we tested the robustness of the device to temperature variation and matrix effects with twelve different alcoholic beverages.

Experimental

Detector design

All tests were performed with the handheld methanol detector *Spark M-20* (Figure 1, Alivion AG, Switzerland). The core detector comprises a column of Tenax TA particles to separate methanol from other analytes (e.g., ethanol), that is combined with a chemoresistive gas sensor to quantify methanol. This concept has been described[20] and characterized[21] under laboratory conditions elaborately elsewhere. The sample preparation and analysis process is illustrated in Figure 2. For a measurement, 2 mL of sample liquid are dripped into a sampling vial with a pipette, both provided as consumables by Alivion AG. The sample is dispersed on the adsorbent within the vials facilitating fast generation of a gaseous headspace sample through its large surface area. The vial is screwed into the bottom of the device and a headspace sample is withdrawn by the pump. The user unscrews the vial after which the device automatically performs the measurement within two minutes. Room air serves as carrier gas and flushing agent to fully regenerate the separation column and gas sensor within a few minutes after analysis. The detector hosts additional sensors to monitor environment and device parameters, that serve as input for correction algorithms (e.g., for ambient temperature). Methanol is quantified based on an internal two-point calibration that users can perform themselves with provided calibration standards (Figure 1). The device further features a rechargeable Li-ion battery, color display, haptic keyboard navigation and storage space for up to 1,000 measurements that can be exported to a PC.

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Sample preparation

The two sample liquids were prepared by volumetric mixing of deionized water, methanol (Sigma-Aldrich, ≥99.9%) and ethanol (Thommen-Furler, absolute, ≥99.8%). First, a mother solution of 40 vol% ethanol in water was prepared by addition of water to 2 L of ethanol using measuring cylinders to achieve a total volume of 5 L. Next, 30 and 2 mL of methanol was added to 1970 and 1998 mL of the mother solution, respectively, using volumetric pipettes to achieve the final water-ethanol-methanol sample liquids. Sample liquids were filled into 20 mL glass vials with foamed polyethylene lined screw caps. All participants received identical sample liquids prepared from the same batch.

Study design

The interlaboratory study was planned and conducted following ISO 5725, as illustrated in Figure 3. Detectors (different devices for all participants), all necessary consumables for the measurements and prepared samples were provided by Alivion to the participants. Participants included distillers, universities and competence centers for spirits. The participants performed the measurements independently, without receiving any financial remuneration or other incentives, following the manufacturer instructions. The measurement results were reported to Alivion, who performed the statistical analysis.

Following ISO 5725, performance parameters were determined independently for different methanol concentration levels. To keep the time investment for participants manageable, two methanol compositions were selected as samples with concentrations covering the full range found in spirits: 1.5 and 0.1 vol% of methanol in 40 vol% water-ethanol mixtures (labeled 1.5/40 and 0.1/40, respectively). These correspond to 29,700 and 1,980 mg/L AA encompassing legal limits of all fruit based spirits in Europe.[7] The samples were measured under repeatability conditions, as outlined in ISO 5725 (i.e., within a short time frame, by the same operator and device, in the same environment and at constant

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ambient conditions). For this, each sample liquid was measured four times in series after a preceding calibration. Participants performed individual measurements and calibrations according to the instruction manual provided with the detector and the standard measurement method (see Supplementary Information). For all measurements, only consumables provided by Alivion (Figure 1: sample vials, sample pipettes, calibration solutions) were used.

Statistical evaluation

Grubbs and Cochran tests were performed on the mean and variance of individual participants to identify mean and variance outliers, respectively. ISO 5725 describes the accuracy of a measurement method by its trueness and precision. Trueness is typically and throughout this work expressed as bias. Bias is a measure of the systematic measurement error and is calculated as the difference between the mean of the test results and the reference value. Precision is defined as the closeness of agreement between test results. It is typically expressed as the standard deviation between test results measured under repeatability and reproducibility conditions. To better compare the performance parameters obtained from the different samples, relative bias and relative repeatability/reproducibility standard deviations were calculated by dividing them by the mean.

Temperature influence, matrix effects and measurement linearity

Additional tests to characterize device robustness were performed by the Scotch Whisky Research Institute, Edinburgh, UK. For all tests, real liquors were spiked with methanol (99.7%, Greyhound Chromatography and Allied Chemicals Ltd, England, UK). The concentration was determined by gravimetric method through weighing the methanol added to samples with a precision scale (Mettler Toledo AT261, England, UK). Temperature influence was tested with a real sample of a whisky-blend (Scotland, UK) spiked with 1.55 vol% methanol. After performing a two-point calibration with the detector at 23 °C, measurements of the spiked whisky-blend sample were performed by equilibrating the

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samples at different room temperatures of 19, 23, 29 and 33 °C. The influence of the sample matrix was tested with samples of whisky–blend (Scotland, UK), whisky–malt (Scotland, UK), whiskey–Irish (Ireland, UK), low wines (Scotland, UK), tequila (Mexico), sherry (Spain), rum (Puerto Rico), port (Portugal), gin (England, UK), new make spirit (Scotland, UK), liqueur (Netherlands), and vodka (England, UK) spiked with methanol concentrations in the range 1.40–1.80 vol%. All samples were tested in series by the detector after calibration. To test detector linearity, whisky–blend samples spiked with 0.01, 0.03, 0.1, 0.3 and 1.0 vol% of methanol were measured sequentially after a two-point calibration, in addition to the 1.55 vol% methanol spiked sample. Linearity was evaluated through the coefficient of determination (R^2).

Results & discussion

Study characteristics

Seventeen participants agreed to contribute to this trial, covering a wide cross-section of possible device users including different industry, public and educational backgrounds (e.g., laymen, analytical chemists) (Figure 4a) and countries (Figure 4b). The institutions, types, countries and number of operators are specified in Table S1. In total, 119 individual measurements were performed and their data are shown in Tables S2-S3. Measurements of sample 1.5/40 from participants #4 and #9 as well as all the data from participant #13 were not considered, as measurements were not performed under repeatability conditions according to ISO 5725.

All study participants were able to complete the required measurements using only the provided device documentation (i.e., manual & quick start guide) and their feedback confirmed the simple operation of the device. Analysis of the measurement results further revealed no difference between experienced and new users as well as between users with different backgrounds with analytical methods (e.g., students vs. experienced distillers). In contrast to GC, the detector thus offers a simple and fast alternative to measure methanol by laymen.

Precision and bias

Figure 5a shows the boxplot of methanol concentrations measured from the samples with 1.5 vol% methanol in 40 vol% ethanol. This methanol content corresponds to the upper limit in distilled spirits (EU: ~0.8 vol% methanol at 40% ethanol in pomace spirit, i.e. 15,000 mg/L AA[7]) and approaches the concentration where methanol poisoning can occur.[29] The ethanol level corresponds to a concentration typically found in final products of liquors (~40 vol%). The detector shows negligible bias of 0.005 vol% (i.e., 0.3%) and excellent repeatability of 0.051 vol% (3.4%, Table 2) without any memory effect from previous measurements (Figure S1a). A challenge for portable detectors is consistent performance for different devices and when testing in different environments. This is captured by the reproducibility, which is with 0.081 vol% (5.4%) only slightly higher than the repeatability, but includes these additional sources of error (16 different devices and testing environments each).

Most importantly, this performance is comparable to gold-standard GC (e.g., reproducibility of up to 11.3%[30]) or other analytical detection methods (e.g., portable Raman spectroscopy with repeatability of up to 10%[31]), despite a more compact and inexpensive design (Table 1). Since the detector is handheld and battery-driven (Figure 1), methanol concentration can be monitored accurately on-site even during distillation, as demonstrated already with an early prototype of this device.[23]

To cover also the lower limit of methanol levels in fruit spirits, the detector was further tested for 0.1 vol% methanol in 40 vol% ethanol (Figure 5b). This corresponds to 1,980 mg/L AA, that is close to the lowest EU limit (for fruit based spirits) of 2,000 mg/L AA for brandy[7]. In this case, the detector shows a small bias of 0.012 vol% (11.7%), which

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corresponds to the device resolution (0.01 vol%). The relative repeatability (5.4%) and reproducibility (9.5%) are slightly higher at these lower concentrations than for the samples with 1.5 vol% methanol, which is typical for analytical measurements.[32] Importantly, these values are comparable to GC.[30] Note that due to the measurement resolution of the device, the lower whisker of the box plot in Figure 5b are not visible, as it coincides with the median and 1st quartile, respectively.

An analytical instrument must also be linear over the full measurement range to provide accurate results for intermediate concentrations. We thus performed additional tests on whisky-blend samples spiked with methanol concentrations between 0.01 and 1.55 vol%. Figure 6 shows the correlation between the true concentrations versus the ones measured by the detector. The device accurately quantifies the entire range of concentrations down to 0.01 vol% with excellent linearity ($R^2 > 0.99$). Note that London gin and Vodka feature maximum methanol concentrations of 0.0025 and 0.005 vol% (at 40% ethanol, respectively, in the EU[7] that are below the detection limit of the device.

Temperature correction

The detector can be operated between 10 – 35 °C by correcting for the strong temperature dependance of headspace concentrations, as described by the van 't Hoff's law.[33] Figure 7 shows the measured methanol concentration between 19 and 33 °C without (blue squares) and with (orange circles) temperature correction, after calibrating the device at 23 °C. Without temperature correction, measured concentrations strongly increase with increasing temperature and lead to errors >200% for a temperature change of 10 °C. Most importantly, the device always predicts the same concentration (error <2%) when varying ambient temperature. As a result, the device can be operated in a variety of different settings (e.g., in a cellar or a distillery). This is also confirmed by the results of the interlaboratory trial, where no influence of measurement temperature was found (Figure S1b).

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Matrix effects

Real spirits contain hundreds of different volatiles including other alcohols (e.g., 1-propanol, 2-methyl-1-propanol, 3-methylbutan-1-ol), aldehydes (e.g., acetaldehyde, vanillin), acetates (methyl acetate, ethyl acetate), ketones, esters, carboxylic acids, tannins, terpenes, and many more.[23, 34] These and other additives (especially sugar)[35] might influence the measurement result of the device. To test the robustness of the detector to a large number of different combination of such matrix effects, it was tested on a variety of different alcoholic beverages (low wines, tequila, sherry, rum, port, gin, new make spirit, liqueur, whiskies, vodka) spiked with different methanol contents (1.42–1.85 vol%). Figure 8 shows the methanol concentration added to samples (blue) in comparison to the concentration measured by the detector (orange) together with corresponding recovery percentages. The concentrations measured by the detector match the true concentrations quite closely with recovery values between 96 and 111% (104% on average) and follow the same trend for different samples. This indicates that the measurements of the detector are not influenced by the type of sample being tested, as shown also in earlier studies on early prototypes based on the same technology.[21] Please note that high sugar concentrations (>50 g/L, here port and liqueur) increase the methanol concentration in the headspace.[36] Results from the detector devices must thus be corrected using the sugar correction table provided by Alivion that is, however, more convenient than distilling samples prior to analysis as needed for GC.

Conclusions

We evaluated a handheld methanol detector for beverage analysis (*Alivion Spark M-20*) in an interlaboratory trial following ISO 5725 with 17 independent participants. The device, based on university research and recently commercialized, featured small absolute bias <0.012 vol%, excellent repeatability (<5.4%) and reproducibility (<9.5%), that is comparable

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to bench-top GC. Further tests demonstrate the efficient correction of ambient temperature and robustness to sample composition with accurate methanol quantification down to 0.01 vol%. This technology can be readily applied by producers for immediate and on-site product inspection, or to optimize their production process. Also, for authorities, it is an attractive addition to classical GC, as it allows quick screening in the field.

Author contributions

Jan van den Broek: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Sebastian D. Keller:** Conceptualization, Methodology, Resources, Supervision, Writing – review & editing. **Ian Goodall:** Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing. **Katie Parish-Virtue:** Conceptualization, Investigation, Resources, Validation, Writing – review & editing. **Claudia Bauer-Christoph, Johannes Fuchs, Despina Tsipi, Andreas T. Güntner, Thomas Blum, Jean-Charles Mathurin, Matthias G. Steiger, Roghayeh Shirvani, Manfred Gössinger, Monika Graf, Peter Anderhub, Daniel Z'graggen, Claudio Hüsser, Benjamin Faigle, Agapiou Agapios:** Investigation, Writing – review & editing.

Conflicts of interest

Alivion AG is a spin-off of ETH Zürich. A patent application has been submitted by ETH Zürich that covers the concept of selective methanol detection. JB, SK & AG are shareholders of Alivion AG.

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Table 1 Comparison between established GC methods and the *Alivion Spark M-20* for methanol detection in alcoholic beverages.

Method	Price instrument, €	Price per analysis, €	Measurement time	Detection limit, vol%	Mobile	Useable/accessible by laymen
GC-FID (in house analytical laboratory)[a]	>30,000 [13]	<1[b]	40 min [12]	~0.001	×	×
GC-FID (external)	-	100–300 [14]	Days to weeks	~0.001	×	✓
Alivion Spark M-20	3,200	1.5[b]	2 min	0.01	✓	✓

[a] Sugar-containing products must be distilled before analysis.
[b] Excl. costs for personnel and consumables for calibration.

Fig. 1 The *Spark M-20* with calibration standards, sampling vials, pipettes and carry case.

Fig. 2 Measurement process with the *Alivion Spark M-20*. (a) Pipetting 2 mL of sample liquid into a sample vial consumable. (b) Screwing the vial into the bottom of the device for sample headspace extraction (~10 s). The analysis starts after unscrewing the vial. (c) The device performs the analysis automatically and displays the result within 2 min.

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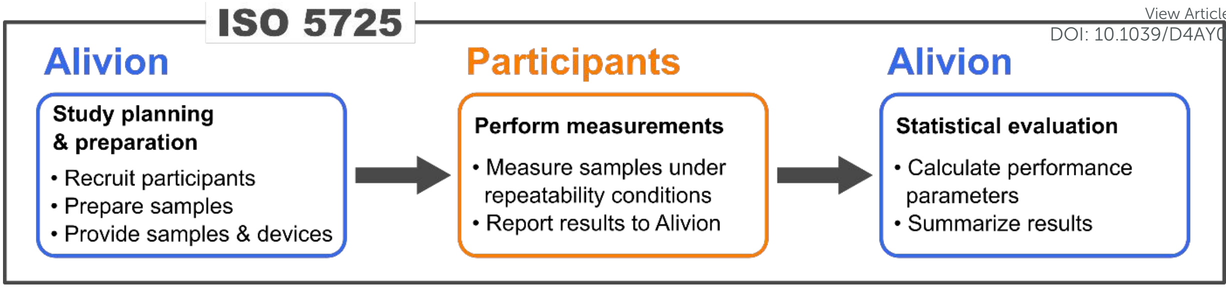

Fig. 3 Study design of the interlaboratory trial following ISO 5725 standard.

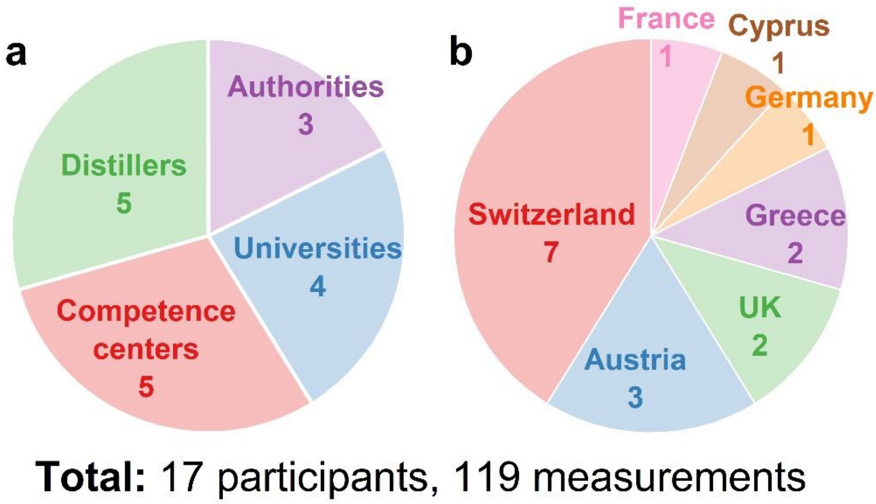

Fig. 4 Participants of the interlaboratory trial categorized by (a) type and (b) country.

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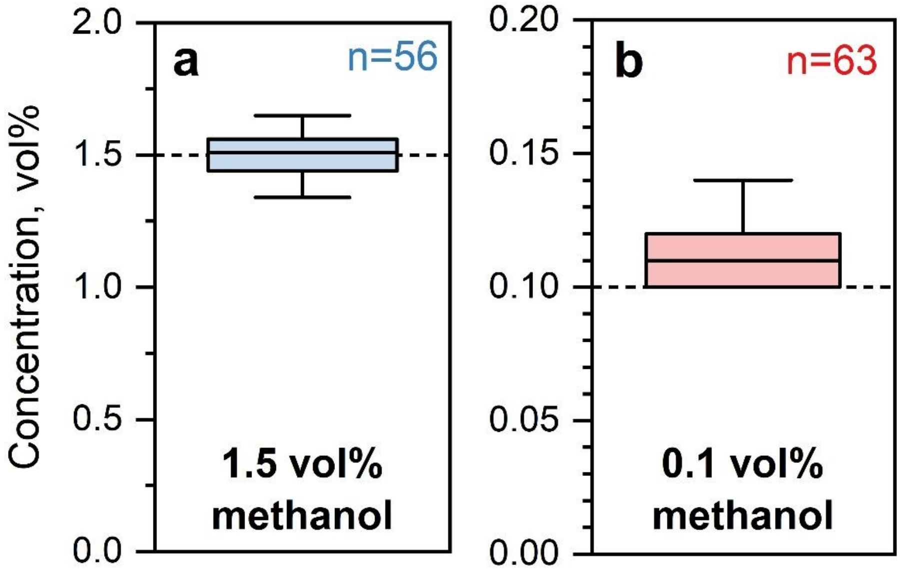

Fig. 5 Concentrations measured by the methanol detector of the samples containing 40 vol% ethanol with (a) 1.5 vol% and (b) 0.1 vol% methanol. Boxes represent median, 25 and 75% quartiles. Whiskers indicate 1.5-times interquartile distance. (Note that in (b) the whisker at low concentration is not visible as it coincide with the median and 1st quartile, respectively.)

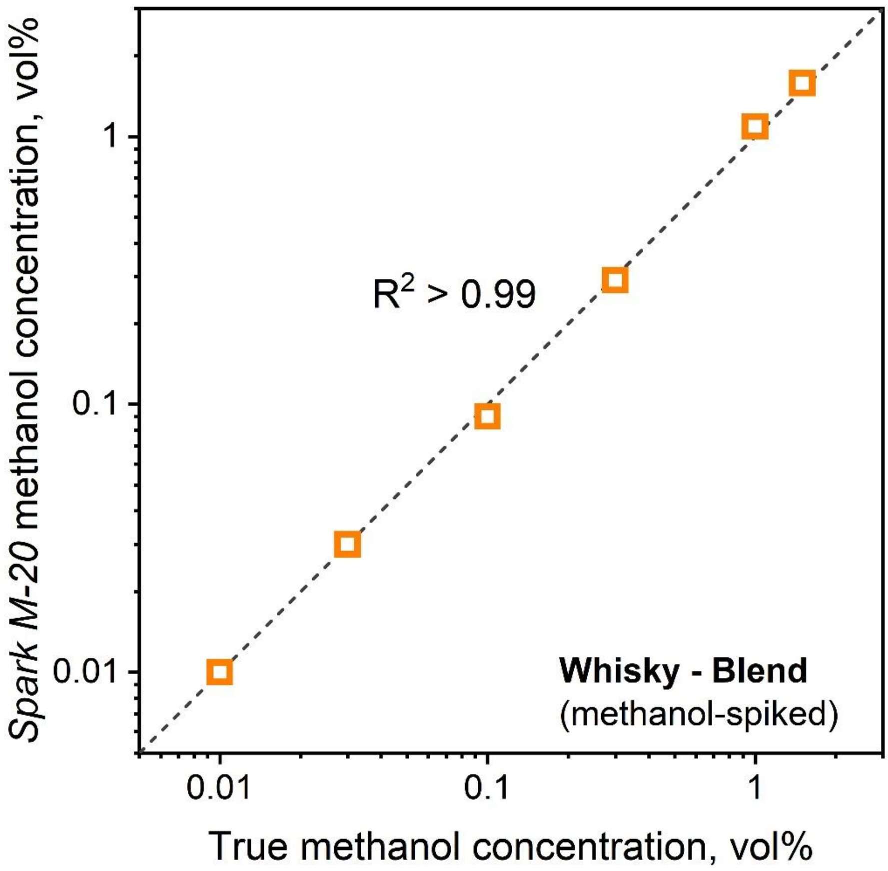

Fig. 6 Methanol concentration in spiked whisky-blend samples, as measured by the detector.

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Table 2 Repeatability, reproducibility and bias of the detector. Results are given both in absolute (vol% methanol) and relative values (% of the mean).

Sample	1.5/40	0.1/40
Repeatability std, vol%	0.051	0.006
Rel. Repeatability std, %	3.4	5.4
Reproducibility std, vol%	0.081	0.011
Rel. Reproducibility std, %	5.4	9.5
Bias, vol%	0.005	0.012
Rel. Bias, %	0.3	11.7

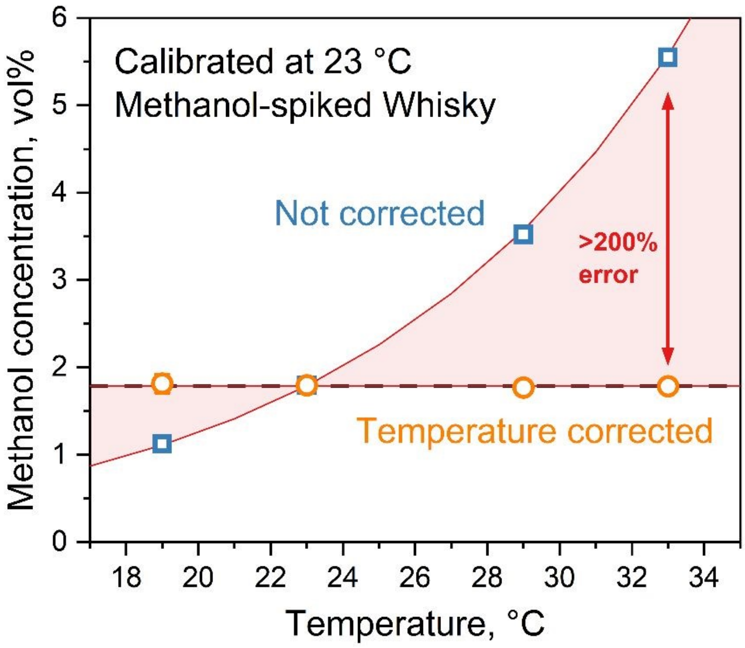

Fig. 7 Methanol concentration measured by the detector of a methanol-spiked whisky–blend at different ambient temperatures without (blue squares) and with (orange circles) temperature correction.

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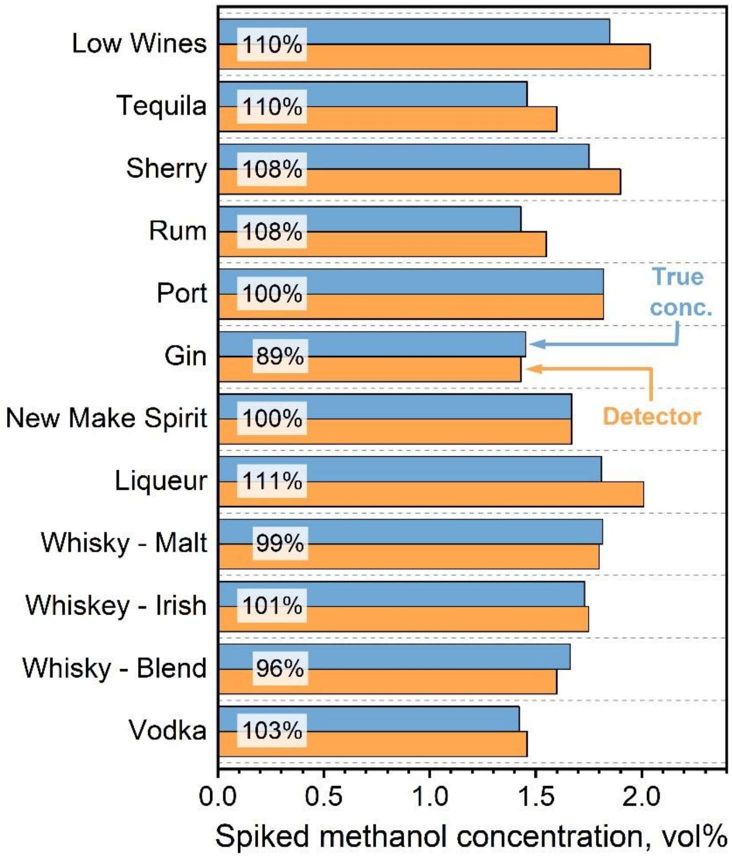

Fig. 8 Methanol concentration spiked to different spirits measured with the detector (orange) in comparison to the amount of methanol spiked to the samples (blue). Recovery percentages are given for all samples.