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Spirit Distillation: Monitoring Methanol Formation with a Hand-Held Device

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ABSTRACT: Methanol occurs naturally in most alcoholic distillates. Yet, suitable detectors to check liquor adherence to legal limits and, most importantly, monitor *in situ* methanol content during distillation are not available. Usually, distillers rely on error-prone human olfaction while "gold standard" liquid or gas chromatography (GC) are rarely used being off-line, time-consuming, and expensive. Here, we explore monitoring the methanol concentration during industrial distillation of cherry, apple, plum, and herb liquor (196 samples) with a low-cost and hand-held detector combining a Pd-doped SnO_2 sensor with a packed bed separation column of Tenax TA. Therein, individual methanol concentrations (0.1−1.25 vol % or 153−3266 g methanol per hectoliter of pure ethanol) are quantified rapidly (within 2 min), bias-free and with high precision (i.e., 0.082 vol %) by headspace analysis, as confirmed by GC. Most importantly, methanol levels above E.U. and U.S. legal limits were recognized reliably without interference by much higher ethanol contents (5−90 vol %) and aromas. Also, the detector worked well even with viscous and inhomogeneous mash samples containing fruit pulp. As a result, this device can help consumers, legal authorities, and distillers to check product safety, guide distillation, and monitor even fermentation to possibly prevent occupational methanol exposure.

KEYWORDS: *food contamination, food safety, analytical method, alcohol*

1. INTRODUCTION

Methanol originates naturally from the degradation of pectins during fermentation (Figure 1).[1] Thereby, apples, pears,
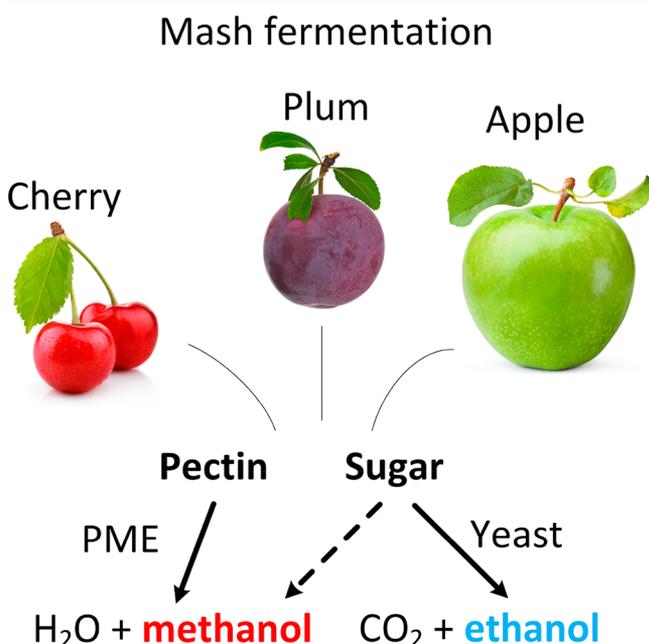

Figure 1. During fruit sugar fermentation to ethanol by yeast, methanol is formed primarily through degradation of pectin by pectin-methylesterase (PME).

plums, and oranges are particularly prone to high methanol concentrations, in contrast to spirits from wheats, roots or molasses such as whisky, vodka, or rum.[2] Also the strain and purity of the yeast[3] as well as the quality of the raw material (e.g., remainders of leaves, stems, or stones) may favor methanol formation.[4] The legal limits for methanol contamination in the E.U.[5] are 1350 g of methanol per hectoliter of ethanol for Williams pear spirit, 1200 g/hL for apple and plum spirit, and 1000 g/hL for cherry spirit. Significantly lower ones apply for brandy (i.e., 200 g/hL), vodka from agricultural alcohol (30 g/hL), and London gin (5 g/hL). Similar restrictions exist also in other countries (e.g., <0.35 vol % methanol in brandy in the U.S.A., corresponding to 1104.8 g/hL in the case of 40 vol % ethanol).[6] However, these limits are exceeded frequently, as shown for 183 commercial Williams pear spirits from Germany, France, Italy, Switzerland, and Luxembourg with methanol contents up to 1865 g/hL.[7]

Traditionally, during distillation, unwanted compounds are recognized through human olfaction by the master distiller. Thereby, the first (so-called "head") and last fractions ("tail") are removed containing high (e.g., acetaldehyde, methyl acetate, or ethyl acetate) and low (e.g., 1-propanol, butanol, hexanol) volatility compounds compared to ethanol[8] as well as

aromatic molecules.[9] However, methanol has no distinct smell from ethanol.[10] The "gold standard" for methanol detection is gas (GC) or liquid chromatography. These, however, are rarely used as they are expensive (e.g., ~100 Euro per sample in Switzerland) and time-consuming with results being obtained typically after 1 week from external laboratories. Less time-consuming is the analysis by Fourier transform infrared spectroscopy,[11] but this still requires quite expensive equipment. Also, capillary electrophoresis with electrochemical derivatization coupled to conductivity measurement quantified methanol (0−4 vol %) in "moonshine" distillates, but required rather tedious sample preparation (e.g., 100-fold dilution with low concentrated HNO_3).[12] Finally, colorimetric indicator solutions (~20 US$ per test) are commercially available but these are single use and only semiquantitative (e.g., indicative if methanol >0.35 vol %).[13]

Methanol can be quantified also with compact and multiuse liquid or gas sensors.[14] These are promising for on-site analysis, particularly when incorporated into hand-held devices, and can enable even continuous monitoring during distillation if the sensor response and recovery times are sufficiently fast. To date, various sensor types have been explored including polymeric sensors that change their color,[15] conductance,[16] or fluorescence[17] in the presence of methanol. Also chemoresistive Ag-LaFeO$_3$,[18] Pt/WN particles,[19] or electrochemical cells[20] had been proposed. However, these feature rather high detection limits (e.g., 4 vol % for fluorescence sensors),[21] cannot distinguish methanol from ethanol (chemoresistive sensors),[18,19] or require bulky instrumentation (e.g., photoluminescence spectrometer).[15,17] Furthermore, none has been validated on the different fractions of distillation, where particularly high volatility compounds in the "head" might interfere with the sensors.

Here, we demonstrate the accurate monitoring of methanol with a hand-held and low-cost device in an industrial distillery in Switzerland. The portable device combines a separation column with a chemoresistive gas sensor.[22] It has quantified methanol selectively in artificially spiked exhaled human breath[23] for medical diagnostics,[24] as well as in the headspace of liquors[25] and hand sanitizers.[26] Here, *naturally* occurring methanol at challenging contents (0.1−1.25 vol %) from all stages of distillation of cherry, plum, apple, and herb spirits are traced and compared to GC measurements. A key focus of this study is the detector robustness to distillation-related confounders (e.g., acetates, acetaldehydes, 2-methyl propanol, and 3-methyl butanol). Finally, adherence to U.S. and E.U. limits is assessed by simultaneous detection of ethanol.

2. MATERIALS AND METHODS

Distillation and Sampling. Mash of plum (*Prunus domestica* L.), apple (*Malus domestica* Borkh.), cherry (*Prunus avium* L.), as well as a mixture of agricultural alcohol and herbs (for herb spirit) were processed in a distillery (Figure 2a) located in Oberarth, Switzerland (S. Fassbind AG). In brief, ~350 L of fruit mash were filled into a copper still (350 L modular design from Arnold Holstein) and heated indirectly with steam while being stirred. The resulting vapors were passed through a Cu catalyst (for the adsorption of unwanted acids and cyanides) and transferred to a 3-stage column amplifier with dephlegmator before reaching the water-cooled condenser. The distillations lasted between 134 and 187 min. In parallel, samples were drawn every 1−10 min (as compatible with the still operation) at the outlet of the condenser for sensor and GC analysis. Samples were collected in small vials (SCR 20 ML, VWR) that were sealed
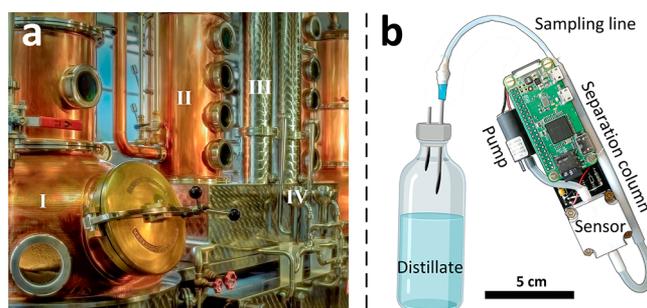

Figure 2. (a) Sample collection during distillation in an industrial distillery. The (I) pot still, (II) column amplifier, (III) condenser, and (IV) outlet where the sample is drawn are indicated. (b) Schematic of the portable methanol detector during analysis.

immediately with septum containing caps (Teflon-faced silicon septa, Supelco) to preserve their chemical composition.

Portable Methanol Detector. The methanol detector is shown in Figure 2b and elaborated in detail elsewhere.[25] In brief, it consists of a needle (Sterican, B. Braun AG) mounted on a 4 mm (inner diameter) Teflon tube, a packed bed separation column[27] with 150 mg of Tenax TA particles (60−80 mesh, 35 m^2/g, Sigma-Aldrich), a flame-made chemoresistive gas sensor of 1 mol % Pd-doped SnO$_2$ nanoparticles (particle size 16 nm)[28] on μ-hot plate substrates and a rotary vane pump (135 FZ 3 V, Schwarz Precision). All tubing and the sensor chamber are made of inert Teflon to minimize analyte adsorption. The pump and sensor are controlled by a microcontroller (Raspberry Pi Zero W) mounted on a tailor-made printed circuit board with wireless communication to a laptop or smartphone.

Prior to each measurement, the vial containing the sample is shaken for 30 s to guarantee equilibrium between the liquid and headspace concentrations.[29] Next, the sampling needle is inserted through the septum and the headspace is extracted at 25 mL/min for 10 s. Note that a second needle enabled pressure compensation. Thereafter, the sampling needle is removed from the vial and ambient air is drawn for 6 min to convey the sample through the separation column and to analyze it by the sensor. Finally, the column and sensor are recovered by flushing with ambient air at increased flow rate (i.e., 65 mL/min) until the baseline is regenerated.

The chemoresistive gas sensor converts analyte concentration into a measurable resistance change (i.e., sensor response S) defined[30] as

$$S = \frac{R_{air}}{R_{sample}} - 1 \tag{1}$$

where R_{air} is the resistance in ambient air directly before the measurement and R_{sample} is the one during sample exposure evaluated at the corresponding retention times of the analytes.[31] The sensor is calibrated in ternary mixtures of 0.1, 0.3, 0.5, 0.70, 1, and 1.25 vol % methanol (>99.9%, Sigma-Aldrich) in 10, 30, 50, 70, and 90 vol % ethanol (>99.8%, Fisher Scientific) and water (Milli-Q Synthesis A10, Merck) to convert sensor responses to analyte concentration. Calibration is done once per day. Methanol is quantified from the sensor response (Figure S1a) while the retention time is used for ethanol (Figure S1b).[25]

Gas Chromatography. To identify and quantify compounds contained in the distillates, a gas chromatograph (GC, Varian 3800, Agilent U.S.A.) is used featuring a column (Zebron ZB-624, Brechbühler AG) and a flame ionization detector operated at 45 and 200 °C, respectively. Samples of 5 μL are injected at 4 psi and 210 °C with a split ratio of 20. Methanol and ethanol concentrations are quantified by comparing areas under the peak curves to ternary mixtures of 0.05, 0.1, 0.25, 0.5, 0.75, 1, and 2 vol % methanol and 5, 10, 25, 50, 75, and 90 vol % ethanol in water with the software Varian Star Chromatography Workstation (Agilent). Additionally, distilled water mixtures of 1 vol % acetaldehyde (>99.5%, Sigma-Aldrich), methyl acetate (>99.8%, Sigma-Aldrich), ethyl acetate (>99.7%, Sigma-Aldrich), 2-methyl propanol (>99.9%, Sigma-Aldrich), and 3-

methyl butanol (>98%, Sigma-Aldrich) are used to identify the presence of these analytes in distillates.

The portable methanol detector performance is compared to GC by Bland-Altman analysis.[32] This method is standard, for instance, in medicine to compare newly developed measurement techniques or apparatus to established ones. The bias (i.e., mean) and precision (i.e., 95% confidence intervals) are evaluated under intermediate precision conditions.[33] Statistical significance of the bias is assessed by a two-tailed z-test. The level of significance was set at $p \leq 0.05$.

3. RESULTS AND DISCUSSION

Detector Design, Bias, and Precision. The present device (Figure 2b) analyzes distillates by drawing head space air through a separation column of nonpolar[34] Tenax TA particles and quantifies their constituent analytes sequentially by a highly and broadly sensitive (e.g., formaldehyde down to 3 ppb at 90% RH)[35] but nonselective[36] chemoresistive Pd-doped SnO_2 gas sensor.[28] This is demonstrated exemplarily with ternary mixtures of 0.5 vol % methanol with 50 vol % ethanol in water in the Supporting Information, Figure S1c. In fact, methanol emerges after 1.4 min retention time and is hardly affected by nonretained compounds (e.g., H_2O, H_2, CO, or CH_4, all <0.5 min) and ethanol that comes after 2.6−2.8 min, in agreement with literature.[22] Thus, these two alcohols are detected selectively with small intrasample variabilities (standard deviation of four consecutive measurements) of 8.1% and 5.4% for methanol and ethanol, respectively.

The methanol sensitivity is 4.5 vol %$^{-1}$ with high response linearity (Pearson's correlation coefficient $r > 0.99$) between 0.05−1.25 vol %, as shown in Figure S1a. The lowest measured concentration is 0.05 vol % (Figure S1d) that was detected with a signal-to-noise ratio (SNR) of 19. As a result, the extrapolated LOD (SNR = 3) is even lower with 0.008 vol % in agreement with Abegg et al.[25] After the measurement, the column is regenerated with surrounding air and can be reused after 8 min. Also, the sensor is multiuse (recovers within 10 s) and shows good operational stability, as had been demonstrated during 107 days of repeated measurements.[25] Please note that the effect of varying temperature and humidity for the same detector was studied previously[22] and can be compensated, for instance, with colocated temperature/humidity sensors, as had been done for the latter with sensor arrays.[30]

First, the hand-held detector's accuracy was compared to benchtop GC (Figure 3a) with 196 samples of herb (stars), cherry (squares), apple (circles), and plum (triangles) distillates. Most importantly, methanol is detected over the entire relevant range of 0.1 to 1.25 vol %, in close agreement (ideal line, broken; coefficient of determination, $R^2 = 0.92$) to GC. Note that fruit-specific R^2 can be found in Table S1. Bland Altman analysis (Figure 3b) quantified the mean difference (solid line) and 95% confidence intervals (CI, dotted lines) showing that there is no bias (mean = 0.003 vol %) since the null hypothesis was positive ($p = 0.86$). The precision is ±0.082 vol % that is comparable to the lowest measured methanol concentrations (0.1 vol %) and almost four times below the regulatory limit for brandy in the U.S.A. (i.e., 0.35 vol %),[6] thus sufficiently low for reliable distillate analysis.

As a result, the detector is hardly interfered by other compounds highlighting its outstanding methanol selectivity. More specifically, these distillates contain acetaldehyde, methyl/ethyl acetate, 2-methyl propanol, and 3-methyl butanol among others, as suggested by GC (with a Zebron ZB-624 column) of plum (Figure S2), apple (Figure S3), cherry
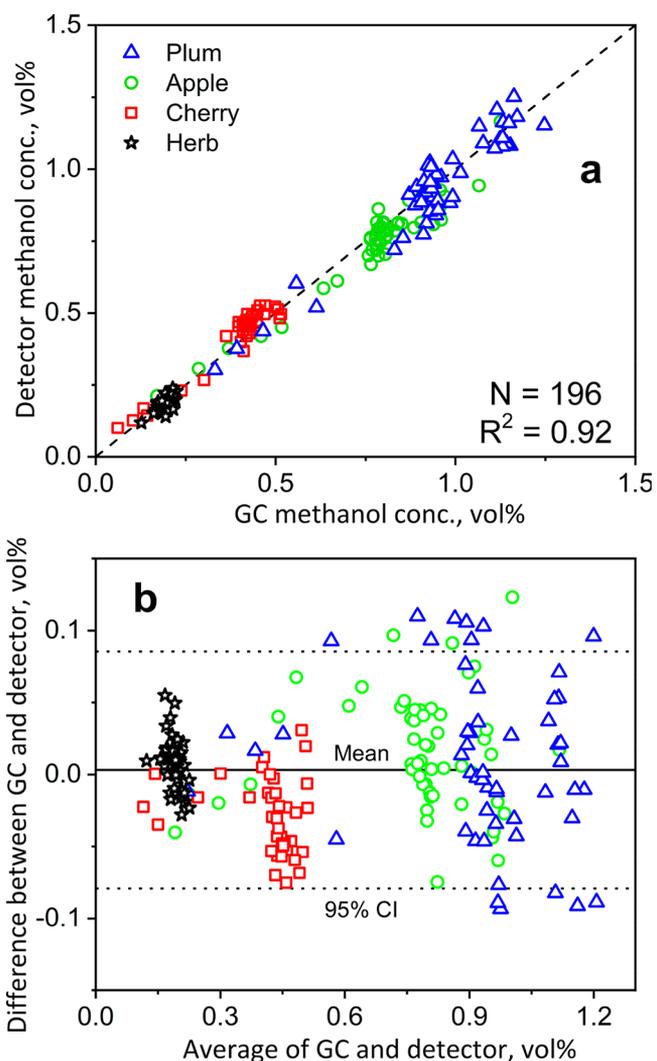

Figure 3. (a) Scatter plot of the detector- and GC-measured methanol concentrations of (N) 196 samples of plum (triangles), apple (circles), cherry (squares), and herb (stars) distillates. Ideal line (broken) and overall coefficient of determination (R^2) are indicated. (b) Corresponding Bland−Altman analysis indicating the difference in methanol concentrations between sensor and GC over their averages. Solid and dotted lines represent the mean and 95% confidence intervals (CI, mean ±1.96 σ), respectively.

(Figure S4), and herb (Figure S5) spirits and in agreement with literature.[8] These compounds are adsorbed at increased strength on the Tenax TA surface due to their longer C−H chain lengths and thus higher van der Waals forces. Consequently, they are retained longer than methanol and ethanol[31] and do not interfere with the sensor measurement. In fact, acetaldehyde was retained 2.5 times longer than methanol, as had been shown by van den Broek et al.[37] This is confirmed also by the sensor's outstanding precision (Figure 3b), as evident from the respective detector response profiles for such distillates (Figure S6) that feature distinct, major peaks only for methanol and ethanol to deduce concentration differences accurately. Some minor peaks are visible before methanol's (i.e., $t < 0.5$ min) that should be related to traces of nonretained volatiles (e.g., H_2O, H_2, CO, CH_4).[25] It should be noted that a similar high coefficient of determination ($R^2 = 0.93$) is obtained also for ethanol quantification (4−91 vol %,

Figure S7a) but at lower precision (±9.33 vol %, Figure S7b) due to the larger concentration range of ethanol.

Monitoring Distillation. Next, the methanol content in the initial mashes and in selected distillate samples during an entire distillation cycle of plum (triangles), apple (circles), cherry (squares), and herb (stars) spirits are shown for the detector (Figure 4a) and GC (b). Already low methanol
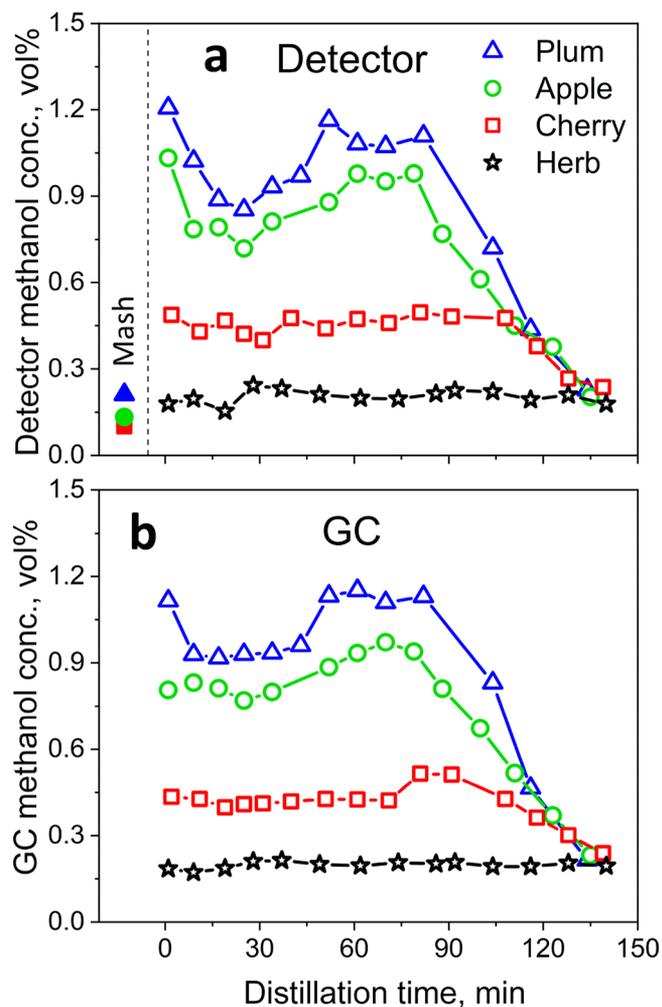

Figure 4. Methanol concentration of plum (triangles), apple (circles), cherry (squares), and herb (stars) mash (filled symbols) and spirit (open) as a function of the distillation time measured by (a) the device and (b) GC.

concentrations of 0.1 (cherry), 0.13 (apple), and 0.21 vol % (plum) contained in the mashes (filled symbols) are detected by the device following the expected pectin contents in these fruits (e.g., apple > cherry)[38] that governs methanol formation during fermentation.[1] Noteworthy, mash samples could not be analyzed by GC without preprocessing due to their inhomogeneous composition (Figure S8a) containing still pieces of fruit pulp in contrast to their distillates (Figure S8b). This highlights an advantage of the present hand-held device that samples headspace air directly from vials (Figure 2b) being unaffected by sample viscosity (as with antiseptic gels[26]) and color that could be challenging for colorimetric indicator solutions.[13]

The highest methanol levels occur in plum distillates (triangles, open symbols in Figure 4a) that vary between 1.2

and 0.85 vol %, are significantly higher than the detectors intrasample variability (±0.081 vol % at 1 vol %, Figure S1c) and only drop significantly after 80 min reaching 0.2 vol % at the end of distillation in agreement with GC (Figure 4b). Note that methanol is present throughout the distillation cycle, which is typical for the distillation of low alcohol mixtures (e.g., fruit mash)[39] and had been observed already for melon,[40] plum,[8] and pear[7] distillates. So, despite different boiling points (i.e., 65 vs 78 °C), it is rather difficult to separate methanol from ethanol due to their azeotrope mixture with water,[39] as shown here by fairly similar methanol and ethanol dynamics (Figures S9 and S10).

Similar methanol dynamics were observed for apple (circles) though at slightly lower concentrations ranging from 1 to 0.7 vol % for t < 80 min. Distinctly lower methanol levels (0.5−0.4 vol %) were measured for cherry (squares), in line with its lower pectin content.[38] Lastly, there is herb spirit (stars) where methanol concentrations stayed constantly below 0.22 vol % during the entire distillation cycle (in agreement with GC), as this spirit does not undergo any fermentation prior to distillation. Note that different methanol dynamics of the spirits are also associated with individual adjustment of distillation parameters done by the master distiller. However, the hand-held detector is able to follow the specific methanol dynamics of fruit and herb distillation. It is promising also for the monitoring of hybrid spirit distillation (e.g., cherry bounce moonshine), where methanol dynamics might be different.[12]

Adherence to Legal Limits. In the E.U.,[5] legal limits for methanol depend on ethanol liquor concentration. The methanol per ethanol content of the 196 distillate samples is shown in Figure 5. The highest methanol per pure ethanol contents were detected for plum (triangles) and apple (circles) distillates with levels ranging between 865−1319 and 821−1157 g/hL, respectively, during the first 60 min. Some contents in plum exceeded the E.U. legal limit (i.e., 1200 g/hL,[5] solid line in Figure 5a), as detected with the present device. Lower specific methanol contents were observed for cherry (422−808 g/hL, squares in Figure 5b) and herb (152−218 g/hL, stars in Figure 5b) distillates that were below legal limits (i.e., 1000 g/hL for cherry,[5] dotted line in Figure 5b), as traced with the detector in agreement with GC (Figure S11).

Finally, all fruit distillates featured increasing specific methanol contents toward the end of distillation consistently exceeding (up to 2.7 times) the corresponding legal limits. This, however, is associated rather to the rapid drop in ethanol content after roughly 70 min of distillation (Figure S9), since methanol content declined slower, as shown exemplarily for plum in the Supporting Information, Figure S10. This had been recognized[7] and attributed to the change in the azeotrope mixture at low ethanol contents.[39] In fact, late distillates have a higher water content that also leads to higher methanol concentrations due to its higher solubility in water than ethanol.[39] Such high ethanol-specific methanol contents in the last part (i.e., "tail") of distillation are problematic if this fraction is kept in the final product or redistilled.

In conclusion, we showed the accurate tracking of absolute and ethanol-specific methanol concentrations during distillation of fruit- and herb-derived liquor with a hand-held and inexpensive device. It detected methanol within 2 min without interference by other compounds, as confirmed by the "gold standard" GC. As a result, this device is capable to identify critical methanol levels exceeding E.U. and U.S. limits and could support partitioning by the master distiller given the
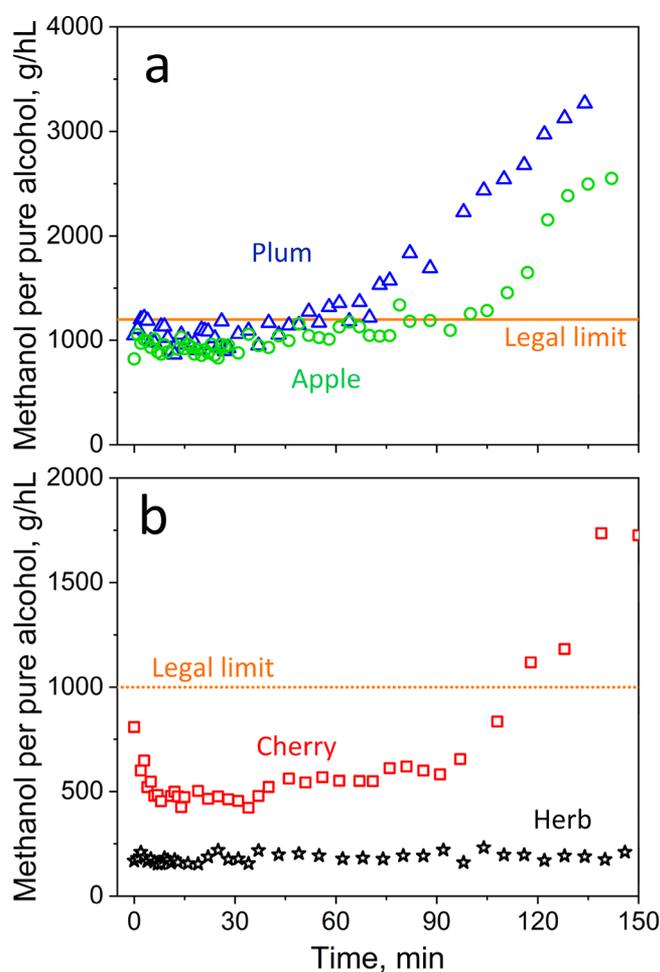
Figure 5. Methanol to ethanol ratio during distillation of (a) plum (triangles) and apple (circles) as well as (b) cherry (squares) and herb (stars) spirits measured by the portable device. Legal limits for plum and apple (solid line in (a)) and cherry (dotted line in (b)) spirits in the E.U.[5] are indicated.

indistinct smell of methanol over ethanol. Since the detector is fully integrated, pocket-sized, battery-operated, indicates the results on a laptop or smartphone and consists mostly of low-cost components, it is ideal for on-site application and even for small/home distilleries. Furthermore, it could be integrated into automated process and product quality control in larger distilleries, as had been suggested already[11] for more expensive near-infrared and Fourier transform infrared spectroscopy. Finally, it might be also applied for the monitoring and maybe even the control (e.g., with PME inhibitors)[41] of methanol formation during fermentation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsfoodscitech.1c00025.

> Calibration curves and intrasample variability, GC spectra, detector response to spirits after 60 min of distillation, ethanol quantification by sensor and GC, pictures of plum, apple, and cherry mashes and spirits, ethanol concentration profiles during distillation, ethanol vs. methanol concentration profiles of plum, GC-

measured methanol per pure alcohol contents, individual coefficient of determination (PDF)

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https://pubs.acs.org/10.1021/acsfoodscitech.1c00025

Notes

The authors declare the following competing financial interest(s): A patent application for this methanol detector has been submitted by ETH Zürich.

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