Noncontact Rapid Vapor Sensor Using Capillary Condensation to Monitor Ethanol in Sanitizer

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***Abstract*— We propose a noncontact rapid vapor sensor to monitor an ethanol concentration in sanitizers using capillary condensation in a nanoparticle film. Owing to a capillary effect in nanopore, a layered nanoparticle film effectively condenses a vapor of liquids. The condensed liquid provides an electrical conduction due to ion current through the film. Vapor pressure of an ethanol-water mixture is defined by the composition ratio. When the sensor with a nanoparticle film is exposed to a headspace vapor from ethanol-water mixtures, we observe a transient impedance response of the sensor depending on the ethanol concentration. A higher ethanol concentration gives a faster decrement of impedance in the response. By using this nanoscale physical phenomenon, we evaluate ethanol concentration in commercial sanitizers within 30 s. The sensor finds the ethanol concentration without contacting the sanitizers. The proposed method is beneficial for on-site evaluation of ethanol concentration in sanitizers rapidly.**

***Index Terms*— Sanitizer, sensor, vapor, nanoparticle.**

I. Introduction

IDENTIFYING a liquid composition in mixture is a challenging issue in the field of electronic chemical sensors [1]–[3]. A mixture of ethanol and water is familiar in alcohol beverages (ethanol concentration: 5–50 vol%) and disinfecting sanitizers (60–80 vol%). Appropriate ethanol concentration is required in sanitizers to suppress viral activity [4], [5]. Precise chemical analysis to find ethanol concentration are chromatography and redox titration of ethanol [6]: however the preparation of the measurements is time-consuming. Electronic and portable devices are beneficial for on-site evaluation and Abbe refractometers are commercially used [7]. Owing to an anomalous refractive index of ethanol-water mixtures along the ethanol concentration, the measurement range of the refractometry is limited between 0 and 50 vol% of ethanol [8]. Toward a rapid evaluation, various methods are proposed to find ethanol concentration in beverage and fuel [9]–[17].

A layered nanoparticle film is beneficial for chemical sensing because of a high surface-to-volume ratio and a geometrical size effect [18]–[20]. As the size of nanoparticles is reduced to <100 nm, a capillary effect owing to Laplace pressure dominates the adsorption of vapor in the nanoparticle film. Because a contact point of touching nanoparticles has a nanoscale curvature down to a few nm, a nanoparticle film captures and condenses a vapor from air effectively [21], [22]. It was reported that the condensation and percolation of pure chemical vapors strongly affected a transient response of electrical transport in insulating nanoparticle films [23]. A vapor of pure alcohols (methanol, ethanol, 1-propanol, and 2-propanol) showed a typical impedance response, which was dependent on their vapor pressure and electrical conductivity [23]. A liquid with high vapor pressure and low impedance shows a clear sensor response.

Here, we develop a noncontact rapid vapor sensor to evaluate an ethanol concentration in sanitizers. By using this nanoscale capillary effect under vapor, the sensor can evaluate the concentration without contacting the target materials. Because a vapor pressure of an ethanol-water mixture changes by the composition ratio, the transient impedance response is dependent on the ethanol concentration. As a proof of concept, we evaluate the concentration of ethanol contained in commercial sanitizers by the proposed method within 30 s.

II. Theory

In an ideal liquid mixture consisting of chemicals 1 and 2, the total vapor pressure P_t at a liquid-gas interface is the sum of each partial vapor pressure P_1 and P_2: $P_t = P_1 + P_2$. P_i is defined as $P_i = n_i P_i^s/(n_1+n_2)$, where P_i^s is the saturated vapor pressure and n_i is the number of molecules in pure chemical liquid i ($i = 1, 2$). The value of $n_i/(n_1 + n_2)$ represents the molar ratio of the chemical i in the binary mixture. When the liquid only contains ethanol and water, this value directly relates to the volume concentration of ethanol in water. P_t of an ethanol-water mixture continuously changes by the ethanol concentration. A small amount of solid ingredients and aromas in sanitizers does not affect the signal since the partial pressure is nearly zero.

Figure 1(a) shows the schematic sensing mechanism. Based on Fick's first law and the ideal gas law under a constant temperature, a molecular diffusion flux (J) of ethanol/water vapor into a void is $J = -D\nabla P/RT$. Here, D is the diffusion constant, ∇P is the vapor pressure difference, R is the gas constant, and T is the temperature. If P_t is larger, ∇P at the top interface of the nanoparticle film becomes larger: thus, vapor diffuses faster into void space. A vapor condensation occurs at the nanoscale void between nanoparticles by the Kelvin effect [24]. Because ethanol and water are polar molecules, the condensed vapor shows an ac ionic conduction. Thus, a time response of the impedance of the condensed liquid reflects P_t.

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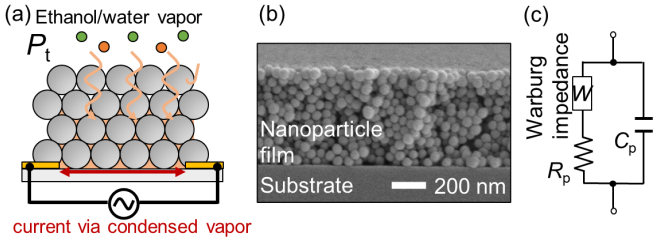

Fig. 1. (a) Sensing mechanism. (b) Cross-section of sensor. (c) Equivalent circuit. R_p and C_p are parasitic resistance and capacitance.

III. Experiment

Gold interdigitated electrodes were prepared on a thermally oxidized silicon wafer. The thickness of the oxidized layer was 1 μm for insulation. An 80-nm thick gold with a titanium adhesive layer was deposited on the wafer by sputtering (j-sputter, ULVAC). The electrodes and contact pads were fabricated by photolithography and Ar-ion milling. The widths of line and spacing in the electrodes were 10–20 μm, respectively. The active area was $\approx$30 mm^2 with 6 mm of the finger length. No heater layer was employed in the structure. The electrode surface was cleaned by oxygen plasma treatments and a colloid of nonporous silica nanoparticles (Aldrich) was spin-coated on the electrodes in ambient air. The size of the nanoparticle was 50 nm in diameter and the concentration was 1% w/v in ethanol. The nanoparticle film was dried at 50 °C. Fig. 1(b) is a scanning electron microscope (S-4800, Hitachi High-Tech) image of a cross-section of the sensing film (thickness: 600 nm). We confirmed that the nanoparticle surface was not terminated with organic ligand molecules by infrared spectroscopy (IRSpirit, Shimadzu) [22]. Therefore, a void space between the nanoparticles is maintained for condensing the vapor.

Electrical impedance of the sensing film was measured by an LCR meter (ZM2376, NF instruments). Ethanol (Wako) and pure water were used for preparing ethanol-water mixtures. The volume of the liquids was 2 ml in total. The liquids were introduced into a vessel and left for a few minutes to obtain an equilibrium of a headspace vapor. For measuring transient response of the sensor impedance, a frequency and an amplitude of the AC voltage were 1 Hz and 1 V, respectively. In this frequency, the sensor impedance was dominant on Warburg impedance (W in the circuit of Fig. 1(c)) which depended on a condensed vapor due to ion current [23].

IV. Ethanol Concentration in Water

Fig. 2(a) shows transient impedance response when the sensor is exposed to a vapor of ethanol-water mixtures from the liquids. The volume concentration of the ethanol is prepared by 10 vol% steps. Two consecutive results are shown. From 100 to 40 vol% of ethanol concentration, the impedance response becomes slower as the concentration decreases. Fig. 2(b) summarizes the response (t_{res}) and recovery (t_{rec}) time of the curves. t_{res} changes from 3 (100 vol%) to 18 s (40 vol%). On the contrary, t_{res} does not largely change in 40 to 0 vol% since the response is not saturated. The average and standard deviation of t_{res} in this range are 16 and 3 s, respectively. Instead, the minimum of the impedance response increases as the concentration decreases from 40 to 0 vol%. t_{rec} does not depend on the concentration. Without heating the sensor, the

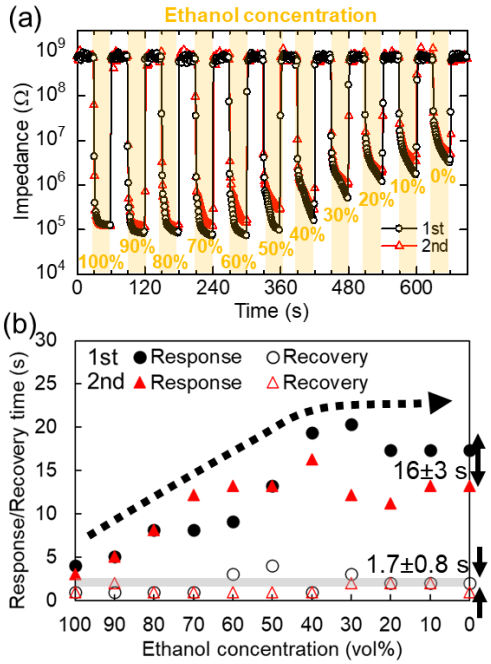

Fig. 2. (a) Transient impedance exposed to a headspace vapor of ethanol-water mixture. (b) Response and recovery time.

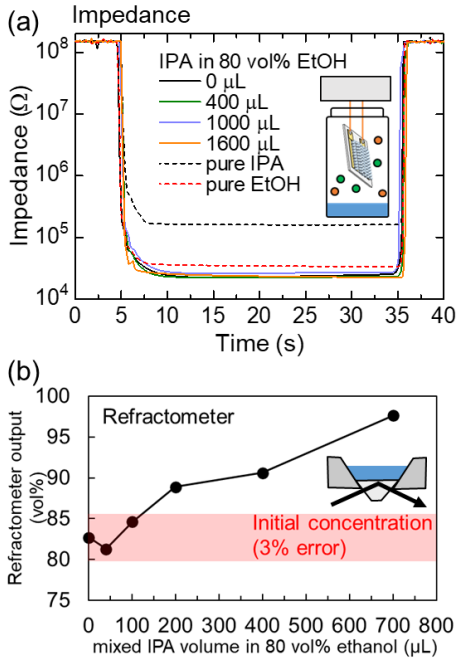

Fig. 3. (a) Effect of IPA mixed in 80 vol% of ethanol (2 mL). Response to pure IPA and ethanol are shown as a reference. (b) Refractometer output affected by mixed IPA in 80 vol% ethanol (2 mL).

average and standard deviation of t_{rec} are 1.7 and 0.8 s, respectively. This result indicates that the ethanol concentration in liquids can be estimated by observing the onset curve of the response. Time series of the sensor output reflect the ethanol concentration.

Mixing 2-propanol (IPA) in 80 vol% of ethanol does not affect the response as shown in Fig. 3(a). Because the vapor impedance of ethanol is one-fifth of that of IPA, the effect of IPA (up to 1600 μL, 44 vol% of the total volume) is not obvious in the response. In a commercial refractometer,

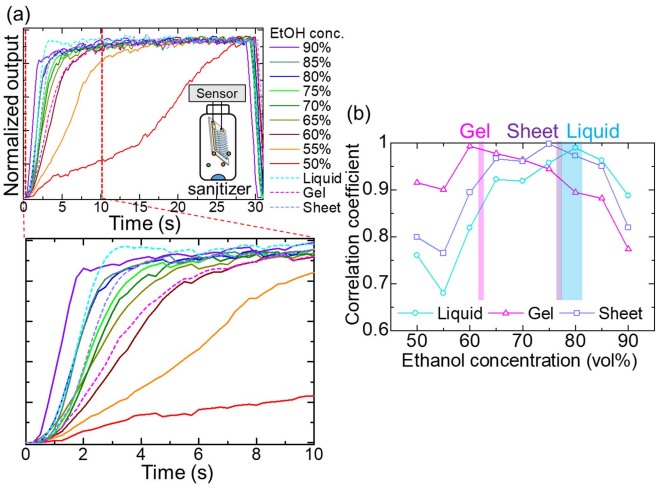

Fig. 4. (a) Sensor outputs exposed to a headspace vapor in 30 s. Onsets of the outputs are enlarged. (b) Correlation coefficients between the outputs of disinfecting sanitizers and reference mixtures.

mixing IPA into the liquid affects the evaluation of ethanol concentration due to the similar refractive index (1.377 and 1.366 in IPA and ethanol, respectively). Figure 3(b) shows the output of a refractometer is changed by the addition of IPA in 80 vol% ethanol. More than 200 μL of IPA (corresponding to 9 vol% of the total volume) obviously increases the output over the expected concentration (82.7±3 vol%, noted as a colored region).

V. Ethanol Concentration in Sanitizers

Disinfecting sanitizers are requisite under the current society with viruses. To confirm the disinfecting ability of sanitizers on site, it is useful to evaluate an ethanol concentration rapidly. Thus, we demonstrate a portable device to evaluate an ethanol concentration in commercial formulation of sanitizers. The setup of the measurements is as follows. The sensor measures a headspace vapor in the vessel containing each disinfectant: liquid (Willstella, Saraya, ethanol concentration: 77–81 vol%), gel (MS solutions, 62 vol%), and tissue sheet (Algauze, Saraya, 77 vol%). The sanitizers do not have aromatic ingredients. A few ml of liquid/gel and one tissue sheet are placed in the vessels. The sensor impedance response is converted to a voltage output and measured by a MetaMotionC (MbientLab) via Bluetooth. The sampling rate is 4 Hz and the data are digitally smoothed for noise reduction. Fig. 4(a) compares the sensor signals for disinfecting sanitizers with those for reference ethanol/water mixtures. The volume concentration of the reference is prepared by 5 vol% steps. As a rough comparison, we evaluate the concentration by finding the maximum correlation coefficient as shown in Fig. 4(b). The maximum values are observed at 60 vol% in gel, 75 vol% in tissue sheet, and 80 vol% in liquid, which agrees to the specifications.

Table I compares common methods to measure the ethanol concentration in alcohol beverage and disinfecting sanitizer. The advantage of this vapor sensing is a rapid and noncontact method. In refractometry, it is necessary to dilute sample liquids to less than 50 vol%. While hydrometry is a classical and quick method, more than 100 mL of liquids are required for floating a gauge to read the density. In this work, 1–2 ml of the liquids is sufficient to evaluate the concentration in a full range ideally. Table II shows a comparison with reported ethanol sensors. Previous studies focused on measuring ethanol concentration in fuels and liquors. Wijaya *et al.* proposed a silver nanoplate colloid to quantify ethanol concentration in liquid sanitizers [13]. In their method, a nanoplate colloid needs to be dispersed in the liquid. Our method is applicable for solid and gel materials as well as liquids. Because a vapor phase of ethanol is used for detection, a fast recovery of the signal is exhibited [9], [16]. These features are beneficial for on-site evaluation of ethanol concentration everywhere. Our approach can be applied to a mixture with aromatic compounds. The concentrations of saturated ethanol and water vapor are estimated to be 7 and 3 %. Since the aromatic vapor concentration is usually an order of ppm, the effect of the aromatic compounds is negligible.

This study has a limitation to evaluate the reproducibility and detection limit. A pattern recognition system trained by many data sets is a candidate to evaluate a chemical sensor output in time series quantitatively [25]–[27]. A pioneering study to apply machine learning to chemical sensors has been given by Vergara *et al.*: 13,910 time series sequences are used for the calibration of sensor output [25]. We need to build a new time series analysis for this sensor in the future.

TABLE I
Common Methods to Measure Ethanol Concentration

Method	Range (vol%)	Rapid (< 30 s)	Noncontact to liquid	Reference
Hydrometry	0–100	✓		[28]
Distillation	0–90			[29]
Colorimetry	0–100			[13]
Refractometry	0–50	✓ (w/o dilution)		[8]
Impedance with vapor	0–100	✓	✓	This work

TABLE II
Comparison With Reported Ethanol Sensors

Sensing mechanism	Detection phase	Real sample	Ethanol conc. (vol%)	Fast recovery (<3 s)	Reference
Conductance	Vapor	Fuel	5 to 100 (wt%)	✓	[16]
Capacitance	Liquid	Fuel	1 to 10		[17]
Mass	Vapor	Liquor	0 to 45	✓	[9]
Viscosity	Liquid	Liquor	0 to 40		[12]
Optical absorption	Liquid	Liquor, Sanitizer	0 to 100		[13]
Resistance	Vapor	Liquor	0 to 95		[14]
Impedance	Vapor	Sanitizer	0 to 100	✓	This work

VI. Conclusion

We proposed the noncontact rapid sensor to evaluate ethanol concentration by using capillary condensation in a nanoparticle film. The transient impedance response depended on the ethanol concentration owing to the vapor pressure. We demonstrated that this method was useful for the noncontact evaluation of ethanol concentration in commercial sanitizers. The ethanol concentration in sanitizers was evaluated in 30 s.

REFERENCES

[1] E. S. Snow, F. K. Perkins, and J. A. Robinson, "Chemical vapor detection using single-walled carbon nanotubes," *Chem. Soc. Rev.*, vol. 35, no. 9, pp. 790–798, 2006, doi: 10.1039/b515473c.

[2] S. H. Lim, L. Feng, J. W. Kemling, C. J. Musto, and K. S. Suslick, "An optoelectronic nose for the detection of toxic gases," *Nature Chem.*, vol. 1, no. 7, pp. 562–567, Oct. 2009, doi: 10.1038/nchem.360.

[3] M. Momtaz and J. Chen, "High-performance colorimetric humidity sensors based on konjac glucomannan," *ACS Appl. Mater. Interfaces*, vol. 12, no. 48, pp. 54104–54116, Dec. 2020, doi: 10.1021/acsami.0c16495.

[4] A. T. Güntner, L. Magro, J. van den Broek, and S. E. Pratsinis, "Detecting methanol in hand sanitizers," *iScience*, vol. 24, no. 2, Feb. 2021, Art. no. 102050, doi: 10.1016/j.isci.2021.102050.

[5] T. Møretrø, L. K. Vestby, L. L. Nesse, S. E. Storheim, K. Kotlarz, and S. Langsrud, "Evaluation of efficacy of disinfectants against Salmonella from the feed industry," *J. Appl. Microbiol.*, vol. 106, no. 3, pp. 1005–1012, 2009, doi: 10.1111/j.1365-2672.2008.04067.x.

[6] H.-B. Seo, H.-J. Kim, O.-K. Lee, J.-H. Ha, H.-Y. Lee, and K.-H. Jung, "Measurement of ethanol concentration using solvent extraction and dichromate oxidation and its application to bioethanol production process," *J. Ind. Microbiol. Biotechnol.*, vol. 36, no. 2, pp. 285–292, Feb. 2009, doi: 10.1007/s10295-008-0497-4.

[7] H. Sobral and M. Peña-Gomar, "Determination of the refractive index of glucose-ethanol-water mixtures using spectroscopic refractometry near the critical angle," *Appl. Opt.*, vol. 54, no. 28, p. 8453, Oct. 2015, doi: 10.1364/AO.54.008453.

[8] R. J. J. Riobóo, M. Philipp, M. A. Ramos, and J. K. Krüger, "Concentration and temperature dependence of the refractive index of ethanol-water mixtures: Influence of intermolecular interactions," *Eur. Phys. J. E*, vol. 30, no. 1, pp. 19–26, Sep. 2009, doi: 10.1140/epje/i2009-10496-4.

[9] K. Shiba, R. Tamura, G. Imamura, and G. Yoshikawa, "Data-driven nanomechanical sensing: Specific information extraction from a complex system," *Sci. Rep.*, vol. 7, no. 1, pp. 1–12, Dec. 2017, doi: 10.1038/s41598-017-03875-7.

[10] T. P. Vello, R. F. de Oliveira, G. O. Silva, D. H. S. de Camargo, and C. C. B. Bufon, "A simple capacitive method to evaluate ethanol fuel samples," *Sci. Rep.*, vol. 7, no. 1, p. 43432, Apr. 2017, doi: 10.1038/srep43432.

[11] H. Hosokawa, Y. Funasako, and T. Mochida, "Colorimetric solvent indicators based on Nafion membranes incorporating nickel(II)-chelate complexes," *Chem.-Eur. J.*, vol. 20, no. 46, pp. 15014–15020, Nov. 2014, doi: 10.1002/chem.201403996.

[12] R. Paxman, J. Stinson, A. Dejardin, R. A. McKendry, and B. W. Hoogenboom, "Using micromechanical resonators to measure rheological properties and alcohol content of model solutions and commercial beverages," *Sensors*, vol. 12, no. 5, pp. 6497–6507, 2012, doi: 10.3390/s120506497.

[13] Y. N. Wijaya, J. Kim, S. H. Hur, S. H. Park, and M. H. Kim, "Metal nanocrystal-based sensing platform for the quantification of water in water-ethanol mixtures," *Sens. Actuators B, Chem.*, vol. 263, pp. 59–68, Jun. 2018, doi: 10.1016/j.snb.2018.02.111.

[14] J. van den Broek, S. Abegg, S. E. Pratsinis, and A. T. Güntner, "Highly selective detection of methanol over ethanol by a handheld gas sensor," *Nature Commun.*, vol. 10, no. 1, pp. 1–8, Dec. 2019, doi: 10.1038/s41467-019-12223-4.

[15] M. S. Rocha and J. Simões-Moreira, "A simple impedance method for determining ethanol and regular gasoline mixtures mass contents," *Fuel*, vol. 84, no. 4, pp. 447–452, Mar. 2005, doi: 10.1016/j.fuel.2004.09.011.

[16] A. R. V. Benvenho, R. W. C. Li, and J. Gruber, "Polymeric electronic gas sensor for determining alcohol content in automotive fuels," *Sens. Actuators B, Chem.*, vol. 136, no. 1, pp. 173–176, Feb. 2009, doi: 10.1016/j.snb.2008.11.012.

[17] M. Irshad, A. Mujahid, A. Afzal, S. Z. Bajwa, T. Hussain, U. Latif, and M. M. Athar, "A miniaturized electronic sensor for instant monitoring of ethanol in gasohol fuel blends," *RSC Adv.*, vol. 8, no. 41, pp. 22952–22962, 2018, doi: 10.1039/C8RA02170H.

[18] X. Zhao, J. Guo, T. Xiao, Y. Zhang, Y. Yan, and B. A. Grzybowski, "Charged metal nanoparticles for chemoelectronic circuits," *Adv. Mater.*, vol. 31, no. 45, pp. 1–8, 2019, doi: 10.1002/adma.201804864.

[19] G. Konvalina and H. Haick, "Effect of humidity on nanoparticle-based chemiresistors: A comparison between synthetic and real-world samples," *ACS Appl. Mater. Interfaces*, vol. 4, no. 1, pp. 317–325, Jan. 2012, doi: 10.1021/am2013695.

[20] A. Zabet-Khosousi and A.-A. Dhirani, "Charge transport in nanoparticle assemblies," *Chem. Rev.*, vol. 108, no. 10, pp. 4072–4124, Oct. 2008, doi: 10.1021/cr0680134.

[21] W. H. Wade, "The surface area of water preadsorbed on powdered substrates," *J. Phys. Chem.*, vol. 68, no. 5, pp. 1029–1034, May 1964, doi: 10.1021/j100787a009.

[22] S. Kano and H. Mekaru, "Capillary-condensed water in nonporous nanoparticle films evaluated by impedance analysis for nanoparticle devices," *Nanotechnology*, vol. 31, no. 45, Nov. 2020, Art. no. 455701, doi: 10.1088/1361-6528/aba7e0.

[23] S. Kano and H. Mekaru, "Liquid-dependent impedance induced by vapor condensation and percolation in nanoparticle film," *Nanotechnology*, vol. 33, no. 10, Mar. 2022, Art. no. 105702, doi: 10.1088/1361-6528/ac3d63.

[24] L. R. Fisher, R. A. Gamble, and J. Middlehurst, "The Kelvin equation and the capillary condensation of water," *Nature*, vol. 290, no. 5807, pp. 575–576, Apr. 1981, doi: 10.1038/290575a0.

[25] A. Vergara, S. Vembu, T. Ayhan, M. A. Ryan, M. L. Homer, and R. Huerta, "Chemical gas sensor drift compensation using classifier ensembles," *Sens. Actuators B, Chem.*, vols. 166–167, pp. 320–329, May 2012, doi: 10.1016/j.snb.2012.01.074.

[26] G. Imamura, K. Shiba, G. Yoshikawa, and T. Washio, "Free-hand gas identification based on transfer function ratios without gas flow control," *Sci. Rep.*, vol. 9, no. 1, pp. 1–14, Dec. 2019, doi: 10.1038/s41598-019-46164-1.

[27] L. Dang, F. Tian, L. Zhang, C. Kadri, X. Yin, X. Peng, and S. Liu, "A novel classifier ensemble for recognition of multiple indoor air contaminants by an electronic nose," *Sens. Actuators A, Phys.*, vol. 207, pp. 67–74, Mar. 2014, doi: 10.1016/j.sna.2013.12.029.

[28] B. Danahy, D. Minnick, and M. Shiflett, "Computing the composition of ethanol-water mixtures based on experimental density and temperature measurements," *Fermentation*, vol. 4, no. 3, p. 72, Aug. 2018, doi: 10.3390/fermentation4030072.

[29] W. A. Noyes and R. R. Warfel, "The boiling-point curve for mixtures of ethyl alcohol and water," *J. Amer. Chem. Soc.*, vol. 23, no. 7, pp. 463–468, 1901, doi: 10.1021/ja02033a004.