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Multi-Frequency Measurement of Volatile Organic Compounds With a Radio-Frequency Interferometer

Hao Li,

College of Physical Electronics, University of Electronic Science and Technology of China, Chengdu 61000, China (holly@uestc.edu.cn)

Zhe Chen,

Department of Electrical and Computer Engineering, Clemson University, Clemson, SC 29634 USA.

Nikolay Borodinov,

Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634 USA.

Yongzhi Shao,

Department of Electrical and Computer Engineering, Clemson University, Clemson, SC 29634 USA.

Igor Luzinov,

Department of Materials Science and Engineering, Clemson University, Clemson, SC 29634 USA.

Guofen Yu,

Department of Physics, University of Findlay, Findlay, OH 45840 USA.

Pingshan Wang

Department of Electrical and Computer Engineering, Clemson University, Clemson, SC 29634 USA.

Abstract

We present a radio-frequency (RF) sensor and its measurement results of three volatile organic compounds (VOCs) at multiple frequency points from ~ 2 to ~ 11 GHz, which is a convenient range in our examination. The sensor is based on a simple RF interferometer and uses two coplanar waveguides (CPWs), A and B of 5 and 25 mm length, respectively, as VOC sensing electrodes. Approximately 70-nm-thick poly copolymer films are coated on CPW surfaces for VOC adsorption and concentration. It is shown that ethanol, acetone, and isopropyl (IPA) induce frequency-dependent RF responses, which are also VOC-dependent. Thus, the frequency-dependent properties provide a possible new approach for better VOC sensing selectivity. With CPW A, the limit-of-detections (LODs) are ~ 600 ppm for ethanol, ~ 270 ppm for acetone, and ~ 330 ppm for IPA at 9.29 GHz. With CPW B, the LODs are roughly four times better. These LODs

are also better than most of other RF VOC sensor results. In the future work, it is promising to further improve RF sensitivity and selectivity significantly.

Keywords

RF interferometer; broadband; dispersion; VOC

I. INTRODUCTION

HIGH sensitivity detection and identification of volatile organic compounds (VOCs) are of great interest for various applications, including noninvasive disease diagnosis [1]–[5], real-time environment monitoring [6]–[8], and rapid security threat detection [9]. Gas chromatography (GC) [10] and ion mobility spectrometry (IMS) [11] are two of the established VOC analysis techniques. The use of mass spectrometry detectors with these techniques provides extremely high sensitivity and specificity. Nevertheless, the techniques are expensive, slow and require trained personnel to operate in a well-controlled environment. Thus, new VOC sensing and transduction techniques, some of which are in the context of electronic noses [12], are explored to address these issues.

Many of the efforts have reported part-per-billion (ppb_v) limit-of-detection (LOD). They include silicon nanowire [13] and carbon nanotube field effect transistors [14], nanoparticle based chemiresistor sensors [15], [16], surface acoustic wave (SAW) sensors [17], and surface plasmon resonance (SPR) spectroscopy [18]. Nonetheless, specificity has been a difficult problem since the sensors are often only partially selective despite the use of VOC recognition materials [19]. Thus, a large sensor array needs to be built and its multi-variate response analyzed to identify the components of complex VOC mixtures. As a result, developing individual sensors with improved selectivity is important for reducing array size and improving array performance [20]. Additionally, few of the new techniques have the potential to achieve an LOD for more challenging measurements [21], such as detecting the clinically significant 0.02 ppb indole in breath [22].

Microwave sensing is explored to help solve the sensitivity and specificity problems. Various designs, mostly resonator based and operated at a single frequency point [23]–[29], are demonstrated. Different materials, such as microporous beaded-activated-carbon (BAC) [24], TiO₂ nanotube arrays [30], polydimethylsiloxane (PDMS) [25], comb copolymer phthalocyanine (Pc) thin films [31], and cobalt phthalocyanine (CoPc) [23], are used to adsorb and concentrate VOC molecules in order to improve detector LOD to tens of ppm. At the same time, material-VOC dependent responses at the measurement frequency point yields some VOC selectivity [26], [32]. Nevertheless, measurement at a single frequency limits available VOC information. The limitation could be alleviated substantially by measuring material-VOC properties over a wide frequency range, as implied in the multi-parameter radio-frequency (RF) measurements of toxic vapors [33] which showed significantly enhanced sensor sensitivity and selectivity.

Previously, we demonstrated the operation of RF interferometers tunable from ~ 10 MHz to ~ 40 GHz [34] with $\sim 10^6$ effective quality factors and 10 fg DNA measurement sensitivity

[35]. Therefore, it is of great interest to investigate if such high-performance interferometer techniques can help address the VOC sensitivity and selectivity challenges discussed above. Additionally, we showed that polymer conductivity changes significantly when VOC molecules are absorbed [36]. Nanoscale polymer layer on sensor surface swells in the presence of VOCs. The swelling further increases the local concentration of VOCs in the vicinity of the sensing surface, thus, it could give a significant boost to the performance of RF interferometers. It is also expected that different VOCs induce different polymer-VOC property changes, which may depend on measurement frequencies even though such information is not currently available. In this work, we show effective detection of a few VOCs over a broad frequency range with a simple interferometer, which uses polymer coated coplanar waveguides (CPWs) as the detection electrodes. We also show that different VOCs induce different frequency responses, which may be further explored to enhance selective VOC sensing. The results indicate that RF interferometer based broadband measurements are promising to provide a new approach for VOC detection and identification.

II. RF INTERFEROMETER BASED VOC MEASUREMENT SYSTEM

Fig. 1(a) shows the experimental set up for RF VOC measurements at multiple frequencies. VOC gases, i.e. ethanol, acetone, and isopropyl (IPA) in this work, are evaporated from VOC liquids. The liquids are stored in a bottle, which is placed in a thermal bath. Dry nitrogen (with 99.9997% N₂ and 0.41 ppm moisture) is used as the carrier gas to dilute VOC gas concentration, i.e. $C_i = F_1 \times V_{p_i} / (F_1 + F_2)$, where C_i is the concentration of the i^{th} VOC component, F_1 and F_2 the flow rates in the two channels, and $V_{p_i} = v_{p_i} \times x_i$ with v_{p_i} the partial vapor pressure of the i^{th} VOC and x_i its molar fraction. The use of two mass flow controllers (MFCs) is to help monitor and maintain a constant flow rate, $F = F_1 + F_2$, in measurements.

Fig. 1(a) also shows a schematic of the RF interferometer. The design and operation of such an interferometer has been described in our previous publication [37]. In this work, the simplified interferometer architecture uses the minimum number of components for RF transmission measurements. Harmonic frequency operations are exploited to cover multiple frequencies over a wide frequency range [38], as listed in Table I. For a nondispersive measurement system, identical frequency shifts, i.e. f in Fig. 1(a), should be observed at each harmonic frequency if polymer-VOC properties are frequency independent.

Fig. 1(b) shows the layout of two CPWs, i.e. CPW A and B in Table I, which are used in VOC measurements. The CPWs are built with conventional micro-fabrication processes. A metal cap is used to cover the CPWs, Fig. 1(b), to guide VOCs to pass over the CPW sensing areas. The meandered signal line of CPW B is ~ 5 times longer than the straight signal line CPW A. Different lengths are used to investigate their effects on sensor performance, such as sensitivity. Both lines are designed for 50 Ohms characteristic impedance. Their cross section dimensions are shown in Fig. 1(c), which also illustrates ~ 70 nm thick coating of Poly (glycidyl methacrylate-ran-oligoethylene glycol methacrylate) (PGMA/POEGMA) copolymer over the sensing areas. The thickness is chosen due to our

previous research experience which indicates that sub-micron PGMA/ POEGMA [39] polymer layers can be utilized as efficient sensing coatings for optical resonators.

PGMA/POEGMA copolymer is used due to its ability of polyethylene glycol units to interact with a wide range of chemical compounds [40], [41]. It is prepared by free-radical polymerization using glycidyl methacrylate and oligoethylene glycol methacrylate (average Mn 950) monomers. Azobisisobutyronitrile is utilized as an initiator. Nuclear magnetic resonance (NMR) data show that PGMA/POEGMA copolymer has 66.4 mol % OEGMA and 33.6 mol % GMA units. Its glass transition temperature is at -59.6°C and melting temperature at 30.5°C . According to dynamic light scattering (DLS) measurement results, the diameter of PGMA/POEGMA coil in methyl ethyl ketone coil was 25.2 nm. The number average degree of polymerization, calculated on the basis of the calibration premised on a set of polystyrene standards, yields $x_n = 2950$. The number average molecular weight derived from NMR and DLS data is 2,100,000 Da. Then, the CPWs are thoroughly washed in DI water, treated by plasma for 10 min in order to activate the surface. Polymers are deposited on the surface of the corresponding device from chloroform 1.5% solutions by dip-coating followed by annealing at 130°C for 6 hours, similar to previously published work [36], [42]. The ungrafted polymer is washed away with chloroform. In this work, the polymer is stable during our ~ 8 months testing period, consistent with our previous results [43]. Currently, we have experimented at least hundreds of cycles, the polymer is still effective.

With the measurement setup in Fig. 1(a), N_2 gas is turned on at the targeted flow rate for ~ 30 minutes or more to purge the system and minimize possible interference effects from moisture or other gases. Then, the RF interferometer is manually adjusted to achieve -95 dB or better $|S_{21}|_{\min}$ while the system is stabilized for an extended period of time. After that, a computer is used to automatically record measurement results, including $|S_{21}|$, every 3 or 6 seconds. Valves 1 and 2 in Fig. 1(a) are manually opened simultaneously to inject VOC(s) from the bottle. Each set of measurements takes 6–30 minutes depending on VOC gases and the targeted concentration level. Fig. 2 shows typical measured $4|S_{21}|$, before and after VOC injection. The solid line in Fig. 2(a) is the $|S_{21}|$ trace at the beginning of measurement. Corresponding f vs time establishes the baseline in Fig. 2(b). The dashed line in Fig. 2(a) is when 5770 ppm IPA is injected, which corresponds to the mid-point in Fig. 2(b) in time. As discussed above, the adsorption of VOCs by the coated copolymer film changes polymer-VOC dielectric property, $\epsilon(f) = \epsilon'(f) - j\epsilon''(f)$. As a result, the electromagnetic properties of the CPW structure, including its characteristic impedance Z_0 and signal propagation constant $\gamma(f) = \alpha(f) + j\beta(f)$, are changed by the VOC presence. The changes are indicated by f_0 , $|S_{21}|_{\min}$ and $|S_{21}|_0$ illustrated in Fig. 1(a). Thus, a comparison of the measured scattering parameters with and without VOCs provides VOC information.

III. EXPERIMENTAL RESULTS

Each measurement is repeated multiple times to make sure the results, e.g. Fig. 2(b), are repeatable and reliable. In the measurements, the VNA (Agilent N5230A) sweeps over a frequency window (e.g. Fig. 2(a)) that is set at $\sim 2 \times f_{\max}$ for 401 frequency points with 100 Hz IF and 10 dBm power. The value of $f_{\max}$ is the largest frequency shift anticipated for the particular measurement. RF cables (PE300–48 from Pasternack, and SCA54086–12

from Fairview Microwaves) are used for signal transmission between port 1 and 2 in Fig. 1. Nevertheless, noise is a serious issue in our high sensitivity measurements, as indicated in Fig. 3(a). The measured f in Fig. 3(a) is with CPW A and with only N_2 gas flowing at a flow rate of 200 mL/minute. Instead of being 0, f changes with time. The change includes a seemingly linear drift and a high frequency fluctuation component. Similar drift exists when VOC is introduced or turned off. For device B, comparable drift exists, and the drift is reversed when VOC is turned off, as shown in Fig. 3 (b). The exact sources of such drifts need further investigation, and it is possibly related to the mechanical and thermal relaxation of the RF cables and the sensing CPWs. In data processing, the drift can be modeled and removed. The high frequency fluctuation components in Figs. 3(a) and (b) are noise, as shown in Figs. 3(c) and (d). Nevertheless, the fluctuation is usually within ± 10 kHz, which sets the minimum detectable frequency shift of the system in Fig. 1(a).

Fig. 4 shows measured f and $|S_{21}|_{f0}$ over time for different VOCs at different concentration levels after frequency drift is removed. During T_1 , N_2 is on at 200 mL/minute flow rate while VOC is off. The results set a reference baseline for VOC detection. The choice of T_1 is arbitrary, and it also depends on VOC flow rate. T_2 is the response rise time of the system in Fig. 1(a) after VOC is manually turned on at a flow rate of ~ 1 mL/minute, i.e. switched from direct path to the path through VOC. When the gas mixtures reach the sensing zone, it is adsorbed by the coated polymer layer and induces permittivity changes. As a result, the operating frequency and transmission signal magnitude change quickly. After the sensor outputs reach stable and saturated state, VOC is manually turned off, roughly in the middle of T_3 . Then, the polymer layer goes through a degassing process with a fall edge of T_4 . Eventually, the RF sensor returns to the reference baseline state, T_5 . For ethanol and IPA measurements, both f and $|S_{21}|_{f0}$ stay unchanged during T_3 . For acetone, however, a step drop occurs right after acetone gas is turned off, followed by a flat response before the sensor returns to its baseline state.

The results in Fig. 4 show that both f and $|S_{21}|_{f0}$ are largely symmetric and regular in T_2 - T_4 regions for all the three VOCs. In T_1 and T_5 regions, f is reasonably well behaved while $|S_{21}|_{f0}$ shows relatively large fluctuations in dB. However, the absolute $|S_{21}|_{f0}$ variations are in fact quite small. Thus, $|S_{21}|_{f0}$ looks better behaved in linear scale. Another observation is that the rise time T_2 and fall time T_4 of each measured signal are similar, which implies that polymer-VOC adsorption and desorption processes are similar and reciprocal. The delay between turning off VOC (roughly in the middle of T_3) and the start of fall edge is likely due to the connection tubes between VOC switch and CPW sensing zone in Fig. 1(a) (i.e. VOC gas tube, length L). the VOC gases in the tubes need time to be depleted.

Fig. 5 shows repeated measurements of acetone with CPW B for different time length. It shows consistent step drop: the step size and the flat T_3 region after acetone is turned off are approximately constant. The exact mechanism for the step drop is the subject of further investigation. But they may provide an approach for VOC adsorption and desorption studies. The measurements also show that sufficient time is needed for the sensing process to reach saturation state. Additionally, the step drop may provide a method for acetone differentiation from mixtures with IPA or ethanol in our RF system, as shown in Fig. 5(b).

Fig. 5(b) is the measured frequency shift of an acetone (2364 ppm) and IPA (720 ppm) mixture. When the VOC is turned off, there is a 55.8 kHz step drop, which is due to acetone only since IPA does not have such a characteristic (Fig. 4(e)). From the measured 2319 ppm and 1126 ppm acetone responses (the two blue lines in Fig. 5(b)), it is shown that there is 2701 ppm acetone for the observed 55.8 kHz drop. The obtained concentration is within 20% of the actual IPA concentration value (i.e. 720 ppm).

Fig. 6 presents the measured frequency shifts induced by VOCs over a wide concentration range and at different frequencies for CPW A. Each data point in Fig. 6 is the averaged results from 5 different measurements. It shows that (i) at 3.11 GHz, the sensitivity of the three VOCs is ~ 10 kHz/500 ppm (ethanol), ~ 10 kHz/223 ppm (acetone), and ~ 10 kHz/281 ppm (IPA), which are different from each other, (ii) for all three VOCs, the obtained sensor sensitivities at 3.11 GHz, 5.16 GHz, 7.33 GHz and 9.29 GHz have strong and nonlinear frequency dependence, which is quite different from the expected linear frequency-sensitivity relationship for a nondispersive electrode-VOC system. Above ~ 3000 ppm, IPA measurements show strong nonlinear dependence on IPA concentration at 5.16 GHz, and (iii) all three VOCs have significantly higher sensitivities at 9.29 GHz, Fig. 6(d). They are ~ 10 kHz/200 ppm for ethanol, ~ 10 kHz/110 ppm for IPA, and ~ 10 kHz/96 ppm for acetone. Currently, these observed frequency and concentration dependences are not well understood.

Fig. 7 summarizes acetone and IPA measurement results with CPW B, which has ~ 5 times longer sensing electrodes than CPW A. It shows that the CPW B has sensitivities up to ~ 10 kHz/30 ppm for acetone and ~ 10 kHz/38 ppm for IPA, which are ~ 4 times higher sensitivity (Fig. 7). This is expected because the CPW detection is with traveling waves, not standing waves as in resonators. A 5-time longer sensing zone enables 5-time larger phase shifts, thus, 5-time larger frequency shifts. Secondly, acetone and IPA have different sensitivities; the sensitivities depend on frequencies (dispersive); and the dependence is clearly different for the two VOCs. The dispersions are also different from that of CPW A. Factors that could induce the relatively strong dispersion include (i) enhanced sensor sensitivities, which also amplify sensitivity differences, (ii) possible frequency dependent properties of the coated polymers as well as the adsorbed VOCs, and (iii) intrinsic dispersions of CPW B. The later two factors are likely to be coupled together and further magnified by the first one to yield the observed results.

Following the definition of $\text{LOD} = 3\sigma/S$ used for SAW gas detectors [17], where σ is noise (i.e. 10 kHz in this work) and S is sensitivity in ppm/Hz, the obtained LOD of CPW A is ~ 600 ppm for ethanol, ~ 270 ppm for acetone and ~ 330 ppm for IPA. For CPW B, the LODs are ~ 100 ppm. These values compare favorably with some of the published microwave sensor results, such as the 256 ppt (part-per-thousand) in [25]. The microwave sensors in [26]–[29] did not report their LODs but often tested their VOCs at higher concentration levels. Nevertheless, our LODs are much worse than the 20 ppb RF measurement of NH_3 in [33], ~ 15 ppm SAW measurement of ethanol [17], ~ 12 ppm quartz crystal microbalance (QCM) measurement of ethanol [44], and ~ 1 ppm metal oxide semiconductor (MOS) nanowire array measurement of hexane [45] even though some of these values were reported as sensitivity. Therefore, improving sensitivity is necessary for applications that demand

sensitivities, such as 0.02 ppb indole in breath [22]. For the system in Fig. 1, digital filtering of high frequency noise is expected to significantly reduce the 10 kHz noise σ . Thus, the LOD can be significantly improved for measurements that do not have high-frequency variations. Another possible approach is to use longer RF sensing structures since CPW A and B showed that longer sensing lines have proportionally higher frequency sensitivities. This approach is unique to the proposed traveling wave measurement method, and it does not apply to resonator based measurements. Meanwhile, we demonstrated that resonators and filters can be embedded in the interferometer arrangement in Fig. 1(a) to significantly improve system sensitivity [38], [46]. Additionally, more effective VOC sorption materials (e.g. thicker PGMA/POEGMA or other polymers) and better test systems (e.g. shorter tube length L in Fig. 1(a)) are expected to further improve system sensitivity significantly.

For selectivity, the differentiation of acetone and IPA mixture in Fig. 5(b) as well as the RF responses in Figs. 6–7, which depend on measurement frequency, VOC species, concentration levels, and CPW devices, offer a possible approach for compound identification from a complex VOC mixture. In liquids, a multivariate analysis of broadband dielectric spectra is demonstrated for the detection and identification of glucose in a multicomponent aqueous solution [47]. It is expected that our multi-frequency measurements will similarly enable VOC selectivity and help solve the difficult selectivity challenge in VOC sensing. Nevertheless, more work is needed to further characterize polymer-VOC RF properties, including moistures which are significant interferents in real applications, and develop models and algorithms to identify VOC RF fingerprints.

IV. CONCLUSIONS

In summary, we demonstrated a simple RF interferometer for multi-frequency VOC measurements from ~ 2 GHz and 11 GHz. Two CPWs are built with conventional micro-machining techniques and used as RF sensing electrodes. Approximately 70 nm thick PGMA/POEGMA copolymer is coated on the electrodes to adsorb and concentrate VOCs for their enhanced sensing. Harmonic frequency operations were exploited to characterize ethanol, acetone and IPA vapors at concentration levels down to ~ 200 ppm. For the shorter CPW A, the achieved LOD is ~ 600 ppm for ethanol, ~ 270 ppm for acetone and ~ 330 ppm for IPA at 9.29 GHz. The 5 times longer CPW B has ~ 4 times lower LODs at ~ 11 GHz due to the use of traveling waves for sensing. The measurement results depend on RF frequency, VOC species, concentration levels, and CPW devices, which may be exploited for better sensor selectivity operation. More work is needed to understand RF sensing of copolymer-VOC processes and improve system sensitivity and selectivity.

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Biography

Hao Li was born in Jiangxi, China, in 1977. He received the master's and Ph.D. degrees in physical electronics from the University of Electronic Science and Technology of China, Chengdu, China, in 2003 and 2009, respectively.

In 2003, he joined the School of Physical Electronics, University of Electronic Science and Technology of China. Since 2008, his research includes high-power microwave transmission and antennas, quasi-optical devices, and numerical simulations in electromagnetic engineering.

Zhe Chen was born in Anhui, China, in 1991. He received the B.E. degree in electronic information engineering from the University of Science and Technology of China, Hefei, China, in 2013. He is currently pursuing the Ph.D. degree with Clemson University, Clemson, SC, USA. His research includes the development of electron paramagnetic resonance (EPR) spectroscopy and RF/microwave sensors.

Nikolay Borodinov received the B.S. degree in chemistry, physics, and mechanics of the materials and the M.S. degree in chemistry from Moscow State University, Moscow, Russia, in 2011 and 2013, respectively. He is currently pursuing the Ph.D. degree in materials science and engineering with Clemson University, Clemson, SC, USA. His research interest includes the development of surface modification agents and procedures for novel sensor setups and control over the adhesion and wettability in complex systems, including composite materials and biomedical devices.

Yongzhi Shao received the B.Eng. degree in automation from the Huazhong University of Science and Technology in 2010 and the M.S. degree in electrical engineering from Clemson University in 2015. He is now working in the field of RF communication devices and technology.

Igor Luzinov received the Ph.D. degree in polymer chemistry from Lviv Polytechnic National University, Ukraine, in 1990. He is currently a Professor of Polymer Science with the Department of Materials Science and Engineering, Clemson University, SC, USA. Prior to joining the faculty of Clemson University, he was a Senior Research Scientist at the Physical Chemistry Institute, National Academy of Science of Ukraine, a NATO Research Fellow at the University of Liege, Belgium, and a Post-Doctoral Research Associate at Iowa State and Western Michigan Universities. The research program of Dr. Luzinov's Group is focused on fundamental and applied research problems in nanofabrication of thin-polymer films.

Guofen Yu received the B.S. degree in applied physics from the University of National Defense Technology, Changsha, China, in 1987, and the M.S. degree in electronic physics and device and the Ph.D. degree in physical electronics from the University of Electronic Science and Technology of China (UESTC), Chengdu, China in 1990 and 1999, respectively.

She started as a Lecturer and Researcher with UESTC in 1990 and moved to a Full Professor in 2002. She visited Old Dominion University from 1999 to 2001 and North Carolina Central University from 2003 to 2006. She joined the University of Findlay in 2007 as a Professor of Physics. Her research interest includes microwave theory and technology and bioeffects of electromagnetic waves.

Pingshan Wang received the Ph.D. degree in electrical and computer engineering from Cornell University, Ithaca, NY, USA, in 2004. He is currently a Professor with the Department of Electrical and Computer Engineering, Clemson University, Clemson, SC, USA. His current research is on developing high-frequency lab-on-a-chip techniques, for which he and his group develop electronic devices, circuits, and systems at microwave and terahertz frequencies. They also develop high-frequency microfluidic and nanofluidic devices and study the high-frequency properties of biological and chemical substances.

REFERENCES

- [1]. Miekisch W, Schubert JK, and Noeldge-Schomburg GF, "Diagnostic potential of breath analysis—Focus on volatile organic compounds," *Clin. Chim. Acta*, vol. 347, pp. 25–39, 9 2004. [PubMed: 15313139]
- [2]. Shirasu M and Touhara K, "The scent of disease: Volatile organic compounds of the human body related to disease and disorder," *J. Biochem*, vol. 150, pp. 257–266, 3 2011. [PubMed: 21771869]
- [3]. Adiguzel Y and Kulah H, "Breath sensors for lung cancer diagnosis," *Biosens. Bioelectron*, vol. 65, pp. 121–138, 3 2015. [PubMed: 25461148]
- [4]. Ibrahim B, et al., "Non-invasive phenotyping using exhaled volatile organic compounds in asthma," *Thorax*, vol. 66, no. 9, pp. 804–809, 2011. [PubMed: 21749985]
- [5]. Phillips M et al., "Volatile organic compounds in breath as markers of lung cancer: A cross-sectional study," *Lancet*, vol. 353, pp. 1930–1933, 6 1999. [PubMed: 10371572]

- [6]. Pejic B, Eadington P, and Ross A, "Environmental monitoring of hydrocarbons: A chemical sensor perspective," *Environ. Sci. Technol.*, vol. 41, no. 18, pp. 6333–6342, 2007. [PubMed: 17948776]
- [7]. Barletta B et al., "Volatile organic compounds in 43 Chinese cities," *Atmos. Environ.*, vol. 39, no. 32, pp. 5979–5990, 2005.
- [8]. Sarigiannis DA, Karakitsios SP, Gotti A, Liakos IL, and Katsoyiannis A, "Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk," *Environ. Int.*, vol. 37, no. 4, pp. 743–765, 2011. [PubMed: 21354626]
- [9]. Fitch JP, Raber E, and Imbro DR, "Technology challenges in responding to biological or chemical attacks in the civilian sector," *Science*, vol. 302, pp. 1350–1354, 11 2003. [PubMed: 14631029]
- [10]. Lerner BM et al., "An improved, automated whole-air sampler and gas chromatography mass spectrometry analysis system for volatile organic compounds in the atmosphere," *Atmos. Meas. Techn.*, vol. 10, no. 1, pp. 291–313, 2016.
- [11]. Westhoff M, Litterst P, Freitag L, Urfer W, Bader S, and Baumbach JI, "Ion mobility spectrometry for the detection of volatile organic compounds in exhaled breath of patients with lung cancer: Results of a pilot study," *Thorax*, vol. 64, pp. 744–748, 3 2009. [PubMed: 19158121]
- [12]. Wilson AD, "Advances in electronic-nose technologies for the detection of volatile biomarker metabolites in the human breath," *Metabolites*, vol. 5, pp. 140–163, 6 2015. [PubMed: 25738426]
- [13]. Paska Y, Stelzner T, Christiansen S, and Haick H, "Enhanced sensing of nonpolar volatile organic compounds by silicon nanowire field effect transistors," *ACS nano*, vol. 5, pp. 5620–5626, 6 2011. [PubMed: 21648442]
- [14]. Kuzmych O, Allen BL, and Star A, "Carbon nanotube sensors for exhaled breath components," *Nanotechnology*, vol. 18, no. 37, p. 375502, 8 2007.
- [15]. Ibañez FJ and Zamborini FP, "Chemiresistive sensing of volatile organic compounds with films of surfactant-stabilized gold and gold-silver alloy nanoparticles," *ACS Nano*, vol. 2, pp. 1543–1552, 7 2008. [PubMed: 19206357]
- [16]. Peng G et al., "Diagnosing lung cancer in exhaled breath using gold nanoparticles," *Nature Nanotechnol.*, vol. 4, pp. 669–673, 10 2009. [PubMed: 19809459]
- [17]. Viespe C and Grigoriu C, "Surface acoustic wave sensors with carbon nanotubes and SiO₂/Si nanoparticles based nanocomposites for VOC detection," *Sens. Actuators B, Chem.*, vol. 147, no. 1, pp. 43–47, 2010.
- [18]. Chen Y-Q and Lu C-J, "Surface modification on silver nanoparticles for enhancing vapor selectivity of localized surface plasmon resonance sensors," *Sens. Actuators B, Chem.*, vol. 135, pp. 492–498, 1 2009.
- [19]. Jurs P, Bakken G, and McClelland H, "Computational methods for the analysis of chemical sensor array data from volatile analytes," *Chem. Rev.*, vol. 100, pp. 2649–2678, 6 2000. [PubMed: 11749299]
- [20]. Potyrailo RA and Morris WG, "Multianalyte chemical identification and quantitation using a single radio frequency identification sensor," *Anal. Chem.*, vol. 79, no. 1, pp. 45–51, 2007. [PubMed: 17194120]
- [21]. Di Natale C, Paolesse R, Martinelli E, and Capuano R, "Solid-state gas sensors for breath analysis: A review," *Anal. Chim. Acta*, vol. 824, pp. 1–17, 11 2014. [PubMed: 24759744]
- [22]. Konvalina G and Haick H, "Sensors for breath testing: From nanomaterials to comprehensive disease detection," *Accounts Chem. Res.*, vol. 47, no. 1, pp. 66–76, 2013.
- [23]. Rossignol J et al., "Microwave-based gas sensor with phthalocyanine film at room temperature," *Sens. Actuators B, Chem.*, vol. 189, pp. 213–216, 12 2013.
- [24]. Zarifi MH, Fayaz M, Goldthorp J, Abdolrazzaghi M, Hashisho Z, and Daneshmand M, "Microbead-assisted high resolution microwave planar ring resonator for organic-vapor sensing," *Appl. Phys. Lett.*, vol. 106, p. 062903, 6 2015.
- [25]. Zarifi MH, Sohrabi A, Shaibani PM, Daneshmand M, and Thundat T, "Detection of volatile organic compounds using microwave sensors," *IEEE Sensors J.*, vol. 15, no. 1, pp. 248–254, 1 2015.

- [26]. Chen W, Stewart K, Mansour R, and Penlidis A, "Novel undercoupled radio-frequency (RF) resonant sensor for gaseous ethanol and interferents detection," *Sens. Actuators A, Phys.*, vol. 230, pp. 63–73, 6 2015.
- [27]. Chen W, Stewart K, Carroll J, Mansour R, Abdel-Rahman E, and Penlidis A, "Novel gaseous phase ethanol sensor implemented with underloaded RF resonator for sensor-embedded passive chip-less RFIDS," in *Proc. 17th Int. Conf. Solid-State Sens., Actuators Microsyst. Trans. Eur., (TRANSDUCERS EUROSENSORS)*, 6 2013, pp. 2059–2062.
- [28]. Zarifi MH, Shariaty P, Hashisho Z, and Daneshmand M, "A non-contact microwave sensor for monitoring the interaction of zeolite 13X with CO₂ and CH₄ in gaseous streams," *Sens. Actuators B, Chem.*, vol. 238, pp. 1240–1247, 1 2017.
- [29]. Sohrabi A, Shaibani PM, Zarifi MH, Daneshmand M, and Thundat T, "A novel technique for rapid vapor detection using swelling polymer covered microstrip ring resonator," in *Proc. IEEE MTT-S Int. Microw. Symp. Dig.*, 10 2014, pp. 1–4.
- [30]. Zarifi M, Farsinezhad S, Abdolrazzagh M, Daneshmand M, and Shankar K, "Selective microwave sensors exploiting the interaction of analytes with trap states in TiO₂ nanotube arrays," *Nanoscience*, vol. 8, no. 14, pp. 7466–7473, 2016.
- [31]. Rydosz A, Maciak E, Wincza K, and Gruszczynski S, "Microwave-based sensors with phthalocyanine films for acetone, ethanol and methanol detection," *Sens. Actuators B, Chem.*, vol. 237, pp. 876–886, 12 2016.
- [32]. Polaert I, Estel L, Huyghe R, and Thomas M, "Adsorbents regeneration under microwave irradiation for dehydration and volatile organic compounds gas treatment," *Chem. Eng. J.*, vol. 162, pp. 941–948, 6 2010.
- [33]. Potyrailo RA, Surman C, Go S, Lee Y, Sivavec T, and Morris WG, "Development of radio-frequency identification sensors based on organic electronic sensing materials for selective detection of toxic vapors," *J. Appl. Phys.*, vol. 106, p. 124902, 10 2009.
- [34]. Cui Y, Sun J, He Y, Wang Z, and Wang P, "A simple, tunable, and highly sensitive radio-frequency sensor," *Appl. Phys. Lett.*, vol. 103, no. 6, p. 062906, 2013.
- [35]. Cui Y, Li J, Cao W, and Wang P, "Highly sensitive RF detection and analysis of DNA solutions," in *IEEE MTT-S Int. Microw. Symp. Dig.*, 6 2014, pp. 1–4.
- [36]. Giammarco J et al., "Towards universal enrichment nanocoating for IR-ATR waveguides," *Chem. Commun.*, vol. 47, pp. 9104–9106, 3 2011.
- [37]. Cui Y and Wang P, "The design and operation of ultra-sensitive and tunable radio-frequency interferometers," *IEEE Trans. Microw. Theory Techn.*, vol. 62, no. 12, pp. 3172–3182, 12 2014.
- [38]. Shao Y, Chen Z, and Wang P, "Exploiting filter stopband for radio frequency interferometer operation," *IEEE Sensors J.*, vol. 15, no. 10, pp. 5813–5820, 10 2015.
- [39]. Borodinov N et al., "Gradient polymer nanofoams for encrypted recording of chemical events," *ACS Nano*, vol. 10, no. 12, pp. 10716–10725, 2016. [PubMed: 27754643]
- [40]. Kianpour E and Azizian S, "Polyethylene glycol as a green solvent for effective extractive desulfurization of liquid fuel at ambient conditions," *Fuel*, vol. 137, pp. 36–40, 12 2014.
- [41]. Li Z, Ma RY, Bai SS, Wang C, and Wang Z, "A solid phase microextraction fiber coated with graphene-poly (ethylene glycol) composite for the extraction of volatile aromatic compounds from water samples," *Talanta*, vol. 119, pp. 498–504, 2 2014. [PubMed: 24401447]
- [42]. Borodinov NL et al., "Stability of grafted polymer nanoscale films toward gamma irradiation," *ACS Appl. Mater. Int.*, vol. 7, pp. 19455–19465, 9 2015.
- [43]. Borodinov N et al., "Stability of grafted polymer nanoscale films toward gamma irradiation," *ACS Appl. Mater. Int.*, vol. 7, pp. 19455–19465, 10 2015.
- [44]. Boutamine M, Belle A, Sahli S, Segui Y, and Raynaud P, "Hexam-ethyldisiloxane thin films as sensitive coating for quartz crystal microbalance based volatile organic compounds sensors," *Thin Solid Films*, vol. 552, pp. 196–203, 11 2014.
- [45]. Cho S-Y et al., "High-resolution p-type metal oxide semiconductor nanowire array as an ultrasensitive sensor for volatile organic compounds," *Nano Lett.*, vol. 16, pp. 4508–4515, 12 2016. [PubMed: 27304752]
- [46]. Shen C, Chen Z, Shao Y, and Wang P, "Engineering spectrum and dispersion with filters for high-sensitivity RF detections," *Appl. Phys. Lett.*, vol. 105, p. 032902, 7 2014.

- [47]. Nakamura M, Tajima T, Ajito K, and Koizumi H, "Selectivity-enhanced glucose measurement in multicomponent aqueous solution by broadband dielectric spectroscopy," in *IEEE MTT-S Int. Microw. Symp. Dig.*, 5 2016, pp. 1–3.

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Fig. 1.

(a) A schematic of the RF VOC measurement system with an RF interferometer. (b) A layout of two CPWs used for VOC measurements. (c) A cross-section view of the CPW with polymer coated, where $G = 10.16 \mu\text{m}$, $W = 81.28 \mu\text{m}$, $T = 1\text{mm}$, $t = 2 \mu\text{m}$ and $p = 70 \text{ nm}$. The substrate is fused silica with a permittivity of 3.826 and loss tangent of 0.000015 at 1 MHz. A $\sim 40 \text{ nm}$ TiW was used as the adhesion layer for $2 \mu\text{m}$ gold deposition.

Fig. 2.

(a) Typical $|S_{21}|$ (dB) measured with the VNA. Left (blue solid) is when no VOC is present at $f_0=9.29$ GHz. Right (dash red) is with VOC IPA at 5770 ppm by use of CPW A. (b) Measured Δf vs time.

Fig. 3.

(a) Measured f vs time with no VOC flow (CPW A). (b) Measured f vs time with VOC flow (CPW B). VOC gas flow is turned off at 5000 s. (c) Fluctuation of interferometer frequency (f_{noise}) vs time after the drift in (a) is subtracted in data processing. (d) f_{noise} vs time for a section of f in (b).

Fig. 4. Measured Δf and $\Delta|S_{21}|_{f_0}$ of ethanol (a) and (b), acetone (c) and (d), and IPA (e) and (f) at three different frequencies with CPW A.

Fig. 5.

(a) Measured CPW B responses to acetone gases for different time length. (b) Measured acetone and IPA mixture with CPW A at 9.29 GHz. Solid (top most): IPA and acetone; circle (second top): acetone (2319 ppm); dash-dot: acetone (1126 ppm), dot: IPA (1126 ppm), dash: IPA (577 ppm) (bottom).

Fig. 6. Measured CPW A responses at different frequencies and VOC concentration levels for (a) ethanol, (b) acetone, and (c) IPA. (d) IPA acetone and ethanol measurements at 9.29 GHz.

Fig. 7. Measured CPW B responses at different frequencies and VOC concentration levels for (a) acetone and (b) IPA. The curves are obtained from binomial data fitting.

Table I

MEASUREMENT FREQUENCIES AND CORRESPONDING INTERFEROMETER HARMONIC NUMBERS

CPW	B	A	A	B	A	A	B
Frequency (GHz)	2.15	3.11	5.16	6.77	7.33	9.29	11.47
Harmonic number	1	2	3	2	4	5	3