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Dielectric properties could be potential tools for investigating materials (VOCs) toxicity

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ABSTRACT
A new approach applied to study the VOC's toxicity LC_{50} (Lethal concentration) using dielectric properties. In this paper a simple procedure with the combination of VNA and TDR was used for measuring the dielectric properties of selected volatile organic compounds. We have tried to draw a relationship between toxicity LC_{50} and the dielectric constant (Ɛ') of selected VOC's. The interesting findings are: for alkane (Isopentane, Octane), when the dielectric constant (Ɛ') goes high, the toxicity (LC_{50}) of the compounds rises accordingly. But the relationship for alcohol (butanol, ethanol & methanol) is just reverse. That is, when the Ɛ' increases , the toxicity (LC_{50}) of the compounds becomes low. The cause might be arising from the compounds structural orientation.

Keywords: Dielectric constant, Toxicity, LC_{50}, VNA, TDR.

1. Introduction

The study of harmful interactions between chemicals and biological system is named as toxicology. All the living animals (man, other animals, and plants) in the modern world are increasingly being exposed to chemicals of an enormous variety. The current challenges of toxicology are to apply basic biochemical, chemical, pathological and physiological knowledge to an understanding of why certain substances cause the disruption in a biological system which may lead to toxic effects. Statistically we found that around 65000 chemicals are currently produced in the USA and 500-1000 new chemicals are added each year. Because of the rapid introduction of the numbers of chemicals, our environment may become progressively toxic. It is thus very important to have some knowledge of the effects they may have and to attempt to substantiate and assess these effects [1].

Modern society currently faces extreme indoor air quality problem due to exposure of votalite organic compounds (VOC's). Cave dwellers are perhaps the first to be concerned with the indoor air quality problem, when they built fires inside their caves [2]. Most of the air quality problems arise from the indoor accessories like building materials, finishing agents, floor finishing, painting, new-furniture finishing materials and so on. Since people in developed countries spend approximately 90% of their time indoors, and VOC concentrations measured indoors typically exceed those outdoors [3], it is important to understand the potential health implications of indoor exposure to specific VOCs [4-5].

The scope of chemical compound selection in indoor air quality has now evolved to consider not only traditional material function (e.g., mechanical, optical and electrical properties) and manufacturing economics but also inherent potential toxicity to humans and ecosystems. A rising challenge to the chemical engineering community is the integration of a robust toxicity indicator tool for comparing various materials within components in products.

The measurement of dielectric properties of materials at radio frequency has gained increasing importance, especially in the research fields, such as material science, microwave circuit design, absorber development or noise suppressors [6-7], biological research, etc. Dielectric measurement is important because it can provide the electrical characteristics of the materials, which were proved useful in many research and development fields.

Many techniques have been developed to measure these dielectric properties such as techniques in time domain or frequency domain with one port or two ports, etc. Every technique is limited to specific frequencies, materials and applications by its own constraint. With the advance of new technologies, the techniques can be employed with a software program that measures the group delay (τ_g), complex reflection, transmission coefficients with a vector network analyzer and converts the data into the complex dielectric property parameter.

Electromagnetic properties of any materials are in general frequency dependent. Determination complex dielectric properties of dielectric materials were practiced for many years using conventional short-open circuit method using the slotted line. Dielectric properties of materials are usually derived from measurement of reflection or transmission coefficients, using both instances [6]. Reflection/transmission methods are being popular for obtaining broadband measurement in both time domain and frequency domain system.

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In this study, we apply a new approach to (i) study the selected VOC's dielectric properties to understand their harmfulness to compare with their known LC_{50} from MSDS (materials safety data sheet) in vitro toxicological test results, and (ii) explore the relationship between toxicological ranking with their dielectric properties. We measured the dielectric constant of some known dielectric volatile organic compounds using our prototype probe. Matlab and origin pro programs have been used for calculating the complex dielectric properties including group delay and correcting the phase shift to get the S-parameters from the surface plane of the sample. De-embedding technique which compensates both phase and magnitude is used to get rid of unwanted S-parameter from device under test (DUT). Their is a complete package model to study the dielectric properties of any liquids.

Online measurements and its non-invasive are necessary to investigate the physical and chemical properties of different environmental materials such as application of VOCs and their impact and minimize the environmental pollution. The development of technology in recent years has increased the number of methods and decreased the price of monitoring tools for application in environmental analysis. A few examples of the progress were observed to study the environmental pollutants physical and chemical properties of using into electrical signals and measurements in high frequency range.

An important parameter for dielectric material (e.g., VOCs) monitoring is τ_g that directly influences the real part of the material permittivity known as dielectric constant (ε_r') of a material [8]. Indirect measurement of τ_g using its dielectric properties seems to be the right direction for the researchers. The objective of this study is to explore the relationship between materials (VOC's) toxicological ranking and dielectric properties (τ_g and ε_r'). Our research hypothesis to be convincing, our experiment is into four parts. Firstly, τ_g and ε' or ε_r' are studied for some selected VOC's, using Close-Ended Coax airline Probe with a vector network analyzer (VNA) and Time Domain Reflectometry (TDR) methods. Secondly, a comparison of τ_g obtained from the two methods for five VOCs is made. Thirdly, ε_r' is measured for some known dielectric VOCs materials and compared with the reference values at a specific frequency. Finally, the measured dielectric properties (τ_g, ε') data and their known LC_{50} values are interconnected to have a deeper understanding of their toxicological strength.

Theory

The most fundamental concept (Fig. 1) of high-frequency network analysis involves incident, reflected and transmitted waves travelling along transmission lines. It is helpful to think of travelling waves along a transmission line in terms of a light wave analogy. We can imagine incident light striking some optical component like a clear lens. Some of the light is reflected off the surface of the lens, but most of the light continues on through the lens. If the lens were made of some lossy material, then a portion of the light could be absorbed by the lens. If the lens had mirrored surfaces, then most of the light would be reflected and little or none would be transmitted through the lens. This concept is valid for RF signals as well, except that the electromagnetic energy is in the RF range instead of the optical range, and our components and circuits are electrical devices and networks instead of lenses and mirrors [9].

Network analysis is concerned with the accurate measurement of the ratios of the reflected signal to the incident signal and the transmitted signal

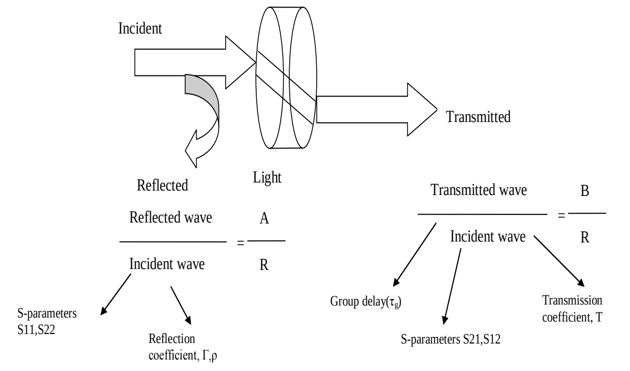


Fig. 1 Flow diagram of reflected and transmitted wave components. τ = group delay, scattering parameter S11, S21, S22 and S12. Reflected wave = A, Incident wave = R, and transmitted wave = B.

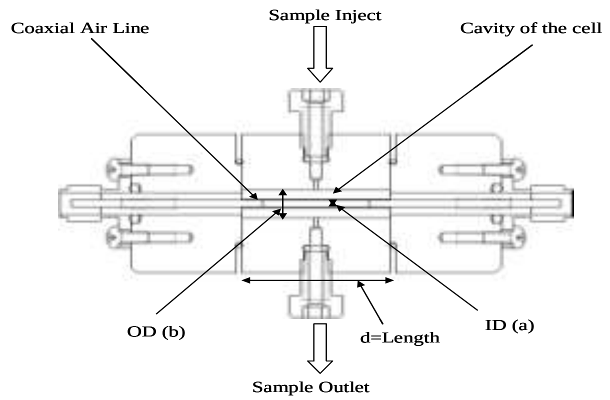


Fig. 2 Prototype probe diagram OD (b) = outer core diameter = 0.005 m and ID(a) = inner core diameter = 0.00196 m and length d = 0.02018 m.

to the incident signal. Based on fundamental concept form Fig. 1 we have measured reflected and transmission coefficients by using our proto type probe (Fig. 2). The dielectric properties of the VOCs materials can thus be studied with aid of this transmission and reflected wave data.

Measurement Approach

Group delay and dielectric constant measurement approaches using VNA and TDR

The first approach used to estimate the dielectric constant was based on the relationship between Group delay (τ_g) and real part of permittivity (ε_r') or dielectric constant. Group delay is related to the dielectric constant of the materials. For example, S21 transmission coefficient is a complex number and is expressed in terms of magnitude and phase, S21 = |S21|ejφ. The phase φ is related to the dielectric constant (ε_r'(ω)) and the sample length (L) through the phase factor β as $\varphi = -\beta L = \{-2\pi\sqrt{\varepsilon'(\omega)}/\lambda_0\}L$ where λ_0 is the wavelength in vacuum. The real part of the dielectric constant (ε_r'(ω)) is then calculated from this formula.

Group delay is (i) a measure of device phase distortion, (ii) the transit time of a signal through a device, versus frequency, and (iii) the derivative of the device's phase characteristic with respect to frequency. Mathematically, the group delay can be expressed as bellows:

Group delay = $\tau_g = -\partial\varphi/\partial f = -1/360*\partial\theta/\partial f$ = time delay where θ = degree, f = ω/2π Hz

Time domain reflectometry (TDR) provides the estimation of changes in the group delay directly from measurements. The probe was then tested for the same materials using both TDR and VNA systems.

Transmission-line techniques are the simplest methods for electromagnetic characterization in wideband frequencies. They include short and open lines (one-port measurement) and transmission/reflection lines (two-port measurements). For the transmission/reflection method (TR), the measuring cell is made up of a section of coaxial airline filled with the sample to be characterized. The sample electromagnetic parameters are deduced from the scattering matrix defined between the sample planes and are usually measured with an automatic network analyzer. The Nicolson–Ross–Weir (NRW) procedure [10,11] is the most commonly used method for performing this calculation. This method has the advantage of being non-iterative and applicable to coaxial line cells.

We used TEM propagation mood for our coaxial airline probe system to measure the reflection and transmission scattering parameters S11 and S21. Then we transferred the data to our software program which is written by Matlab and Origin pro. It will correct the S11 and S21 phase shift value to get the accurate measurement scattering parameter value from the sample surface plane. Simple algorithm is used to correct the phase shift [12,13].

For S11(ω),

$\Delta\varphi_{11} = 2a * 2\pi f/c$, (1)

and for S21(ω),

$\Delta\varphi_{21} = (a+b) * 2\pi f/c$, (2)

where f = frequency, and c = light speed in vacuum.

The phase shift correction concept is drawn in Fig. 3.

We can the calculate permittivity and permeability using improved NWR methods [14-15] and scattering parameters of reflection and transmission S11, S21. Characteristic impedances are in unique for test materials under specified condition. As an electromagnetic sine wave within a specified frequency range is passed from ports 1 to 2 during traveling a specific length d of sample, the electromagnetic wave will produce reflection and transmission coefficient along the direction of propagation. As per Hao Zhou [14] improved and simplified technique, we can write,

From NWR method [10-11] C1 and C2 can be found

$C1 = \mu r/\varepsilon_r$ (3)

$C2 = \mu r * \varepsilon r$ (4)

The propagation coefficient

$T = \exp{-j\omega\sqrt{\mu\varepsilon} * d} = \exp[-j(\omega/c)\sqrt{\mu r * \varepsilon r} * d]$ (5)

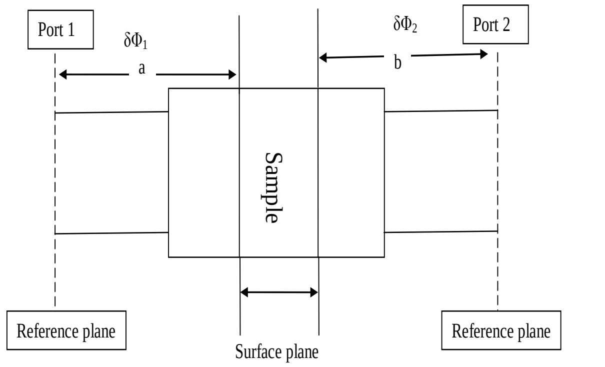


Fig. 3. Phase Rotation from reference plane to sample plane.

We can write the transmission coefficient as per Ruler formula

$T = \cos\theta - j\sin\theta$, (6)

where the period is $t = d/c\sqrt{C2}$ and θ = ω*t, ω = phase velocity, and the reflection coefficient,

$\Gamma = \sqrt{C1}-1/\sqrt{C1}+1$, (7)

so that

$S11(\omega) = (1+T2)*\Gamma/ 1-\Gamma 2 * T2$, and (8)

$S21(\omega) = (1-\Gamma 2) * T/ 1-\Gamma 2 * T2$. (9)

Furthermore, relative permittivity and permeability can be calculated as follows.

$\varepsilon r = m * Z$, and (10)

$\mu r = m/Z$, (11)

where Z is the characteristic impedance [16].

$m = \varphi/(k0 * d)$, (12)

where $k0 = \omega/c = 2\pi f/c$, f is the frequency and c is the velocity of light and then

$\varphi = -j.\log(p) + 2\pi n$. (13)

We can use this algorithm to calculate materials dielectric constant.

TDR principle

The time domain reflectometer is set up as shown in Fig. 4.

The step generator produces a positive going incident wave which is fed into the transmission system under test. The oscilloscopes high impedance input bridges the transmission system at its junction with the step generator. The step travels down the transmission line at the velocity of propagation of the line. If the load impedance is equal to the characteristic impedance of the line, no wave is reflected, and what will be seen on the oscilloscope is the incident voltage step recorded as the wave passes the point on the line monitored by oscilloscope.

If a mismatch exists at the load, part of the incident wave will be reflected. The reflected voltage wave will appear on the oscilloscope display algebraically added to the incident wave. The reflected wave is readily identified since it is separated in time from the incident wave. The quality of the transmission system is indicated by the ratio of this reflected wave to the incident wave origination at the source [17]. This

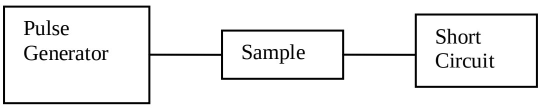


Fig. 4 TDR measurement system.

ratio is called voltage reflection coefficient (ρ) and is related to the transmission line impedance by the followingequation:

$\rho = Er/Ei = Z_L - Z_0 / Z_L + Z_0$, (14)

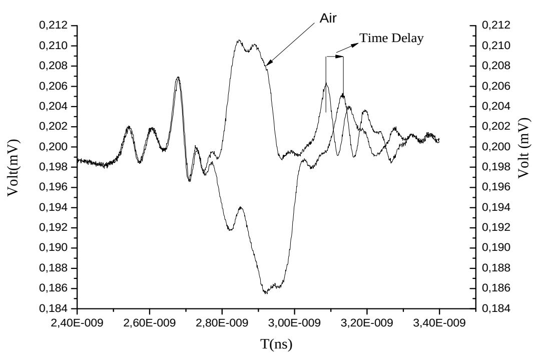
where Er = reflected wave and Ei = incident wave, Z_L= load impedance Z_0 = characteristics impedance.

The time is also valuable in determining the length of the transmission system from the monitoring point to the mismatch. If D = length,

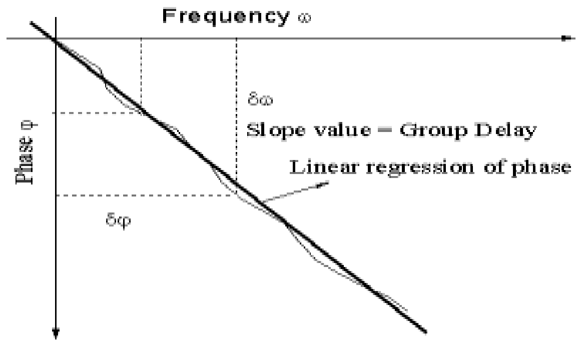
$D = vp*T/2$, (15)

where, vp = velocity of propagation, T = total transit time of the round trip from the monitoring point to mismatch.

Calculating the group delay (Fig 5) directly from TDR system and VNA, slope of unwrap S21 phase of the materials ($\tau_g = -\partial\Phi/\partial f$). Then we can get an accurate dielectric material delay of materials from TDR subtracting the time of known materials like air value.



TDR



VNA

Fig 5 Time Delay measuring using TDR and VNA

Instrumentation

Matlab and origin pro softwares are combined to perform the following objectives. These are, to save the scattering reflection S11 and transmission coefficient S21 from the VNA to computer, then interlink those parameters with our Matlab and origin pro program for setting up various parameters to format the data, calculate the group delay and dielectric constant by using the derived formula and, to display and save the various graphs and results.

We used Agilent E8358A VNA, Agilent. Infiniium86100C DCA-J TDR and Matlab with origin pro 8.0 programming language were used to measure the parameters and design the software.

Measurement Results

Simulation of Close-ended coaxial airline with the dominant TEM mode is performed using the high frequency structure simulator. Measurement is performed using Agilent E8358A VNA, Agilent and infiniium86100C DCA-J TDR with appropriate calibration.

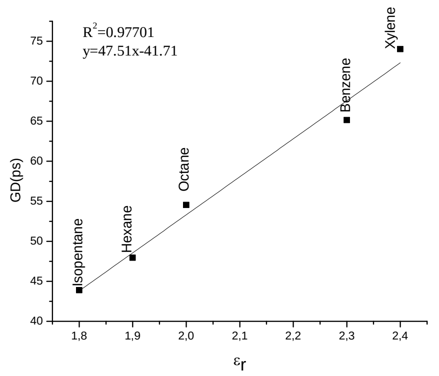
TDR measurement results

For TDR system, we directly connected our close-ended coaxial airline probe with 0.0035 m SMA connector.

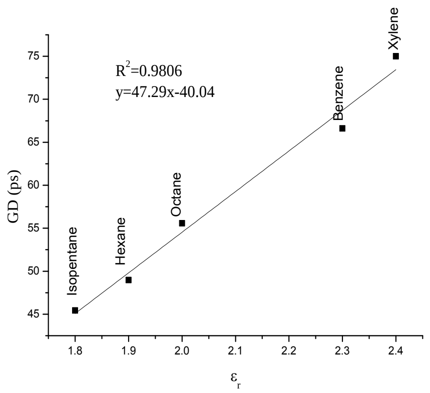
During the TDR portion of testing, the sample assemblies were connected directly to the TDR sampling head while the opposite end was terminated with a 0.0035 m precision short circuit standard. This was done to ensure a well-defined and controlled termination. For the TDR time delay measurement, a sample assembly, fitted with precision short circuit termination, was connected to the TDR and the round-trip time delay value was recorded using our own origin-pro program time delay measurement algorithm. The time delay was recorded at a 205 mV level. The round trip time delay was taken as the total time required to travel the sine-wave through the coaxial airline probe from one end to the other end which is short circuited. And the time delay of materials was calculated by subtracting the air time delay from the materials time delay as shown in Fig. 5. The actual sample assembly time delay is one half the measured round-trip time delay, as shown in Fig. 6.

VNA Measurement Results:

Simulation of coaxial line is performed with proper selection of boundaries and ports. The sample cavity is placed in the middle of the coaxial line. Coaxial line with dimensions inner radius of the outer conductor 0.005 m, outer radius of inner conductor 0.00196 m and length 0.002018 m with samples, which fit in the coaxial line with thickness of 0.00130 m, is used in both simulation and measurement to obtain values of S-paameters. De-embedding techniques are used to obtain the S-parameters of the sample which are at the center of the coaxial line, canceling the effect of unwanted regions. For the de-embedding, S-parameters were obtained from the port



TDR Time Delay



VNA Group Delay

Fig 6 Comparison of Group delay with TDR and VNA system.

extension technique in VNA. Since simulation of unknown sample is not possible, measurement was performed by using some known samples like air, water, methanol, ethanol, and butanol (Fig.7).

For our analysis, fluid samples are injected to the cavity 0.0013L (coaxial airline probe) to the dimensions of coaxial line and the results are verified at a 3×10^9 Hz frequency data with references Von hipple. The de-embedded S-parameters from simulation and measurement are analyzed, following the techniques used in Refs. [12-13,18]. The values of real part of permittivity of samples at 3×10^9 Hz frequency [19] are presented in Fig.8.

There exists an uncertainty when the length of the sample is comparable to half wavelength of the electromagnetic wave propagating through it [20]. That's why the thickness of sample was chosen relatively small, presently 0.002018 m to avoid uncertainties due to length. Also the measurement values are not consistent throughout the frequency range due to some mechanical imperfections and environmental factors such as temperature, pressure, humidity during experimentation.

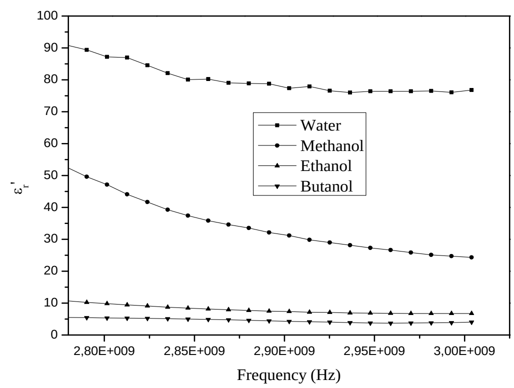


Fig. 7 The permittivity of VOCs as a function of frequency.

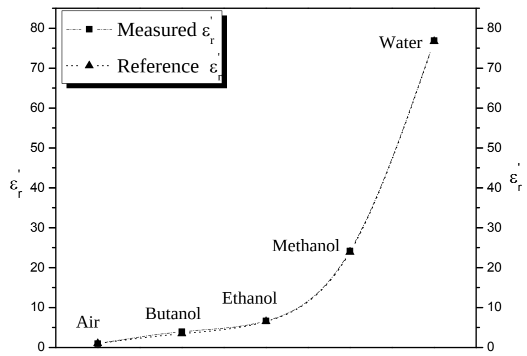


Fig. 8 Compare the measured dielectric constant value with reference value at 3*109Hz.

Relationship between toxicity LC_{50} and dielectric properties

The data show a good accordance relationship between the dielectric constant and the group delay. When the group delay number goes high, so does the permittivity of the compounds, the correlation being positive. When we come to the relationship between the toxicity and ~~the~~ dielectric constant, some exciting phenomena are observed. For alkane (Isopentane,Octane), when the dielectric constant rises, the toxicity of the compounds follows the same. But this relationship in alcohol (butanol, ethanol & methanol) is just opposite. As the permittivity grows, the toxicity of the compounds declines (Fig. 9). Even though, they have a possible relation in common, that is the structure of their carbon chain. The more carbon in the chain the compound contains, the more toxic it is. We don't know the exact relationship between the structure and their toxicity, but we do believe they are connected each other, and this is what we will do in the next step.

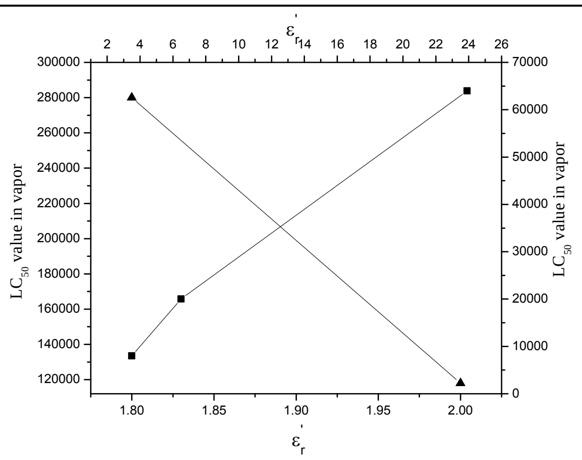


Fig. 9 Exploring the relationship between εr' and LC_{50} in vapor.

Conclusion:

The fundamental goal of this paper was to explore a relationship between dielectric properties (group delay and real part of permittivity) and toxicity strength (LC_{50}) of the materials. We found higher the group delay higher the real part of dielectric permittivity/dielectric constant (εr'). Good correlation for both time and frequency domain system measured the group delay where R^2 >0.95. So it is revealed that our probe is sensitive enough to measure dielectric constants of fluids. And it is a simple method for easily and effectively measuring the group delay and the complex permeability and permittivity of any fluids material.

When it comes to the relationship between toxicity and the dielectric constant, we also find some exciting phenomenta: for alkane (Isopentane, Octane), when the dielectric constant (ε_r') increases, the toxicity (LC_{50}) of the compounds correspondingly follows the same trend. But this relationship in the alcohol (Butanol,Ethanol & Methanol) is just opposite, an increase in the permittivity (ε_r') accompanies a decrease in the toxicity (LC_{50}) of the compounds.

The results prove that the proposed method is an effective alternative way to study the dielectric properties of fluid materials and it could be a potential tool to extract inherent information on the toxicity of the materials. Our next plan is to study the compound morphology which could possibly lead us to understand the insight into materials' toxicity.

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