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Electrochemical impedance spectroscopy based MEMS sensors for phthalates detection in water and juices

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Abstract. Phthalate esters are ubiquitous environmental and food pollutants well known as endocrine disrupting compounds (EDCs). These developmental and reproductive toxicants pose a grave risk to the human health due to their unlimited use in consumer plastic industry. Detection of phthalates is strictly laboratory based time consuming and expensive process and requires expertise of highly qualified and skilled professionals. We present a real time, non-invasive, label free rapid detection technique to quantify phthalates' presence in deionized water and fruit juices. Electrochemical impedance spectroscopy (EIS) technique applied to a novel planar inter-digital (ID) capacitive sensor plays a vital role to explore the presence of phthalate esters in bulk fluid media. The ID sensor with multiple sensing gold electrodes was fabricated on silicon substrate using micro-electromechanical system (MEMS) device fabrication technology. A thin film of parylene C polymer was coated as a passivation layer to enhance the capacitive sensing capabilities of the sensor and to reduce the magnitude of Faradic current flowing through the sensor. Various concentrations, 0.002ppm through to 2ppm of di (2-ethylhexyl) phthalate (DEHP) in deionized water, were exposed to the sensing system by dip testing method. Impedance spectra obtained was analysed to determine sample conductance which led to consequent evaluation of its dielectric properties. Electro-chemical impedance spectrum analyser algorithm was employed to model the experimentally obtained impedance spectra. Curve fitting technique was applied to deduce constant phase element (CPE) equivalent circuit based on Randle's equivalent circuit model. The sensing system was tested to detect different concentrations of DEHP in orange juice as a real world application. The result analysis indicated that our rapid testing technique is able to detect the presence of DEHP in all test samples distinctively.¹

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1. Introduction

Esters of 1-2-Benzenedicarboxylic acid, commonly called phthalates are the most abundantly synthesized key industrial chemicals due to a number of their commercial uses. Owing to their low cost, these ubiquitous chemicals are most commonly used as plasticizers, solvents and additives in different products manufactured by industry [1]. For the reason of their use as plasticizer in almost every plastic product manufactured around the globe, phthalates with higher molecular weight i.e. DINP (diisononyl phthalates) and DEHP makeup nearly 80% of the total phthalates produced in the world. These include food and beverage packaging and most importantly, medical applications [2, 3]. Addition of plasticizer induces flexibility and mechanical strength to the Polyvinyl chloride (PVC) products but, unfortunately, do not bond to PVC molecules in the lattice structure. On the other hand, lower molecular weight phthalates, such as diethyl phthalate (DEP) and dimethyl phthalate (DMP) are used in consumer cosmetics, house hold insecticides, paints and pharmaceutical applications [3]. Being an odourless, colourless high density oily compound, phthalates do not get covalently bound to the molecular structure of the polyvinyl chloride (PVC) product, therefore, it has a large potential for non-occupational leaching and ingestion into packed food and beverages, gas out in the atmosphere or directly into human body fluids through medical products [1-3]. Phthalates' carcinogenicity and teratogenicity result in reproductive and developmental toxicities in rodents, and their potential for human exposure declares it an area of concern in environmental public health [2-6]. Figure 1 shows molecular structures of most common phthalates used in cosmetic, toys, PVC and food packaging industry.

The possible routes of human exposure to phthalates are ingestion (dietary), inhalation, dermal and parenteral exposure from plastic medical devices [6, 7]. Dietary exposures occur by accumulating phthalates either during the food processing and packaging from processing equipment or leaching into fatty foods, including dairy products and from packaging during storage. Dairy products consumption by children per kilogram body weight is higher as compared to the adults, posing greater risk of reproductive and developmental toxicities for young children [7]. Polymer toys softened with DINP were estimated exposures ranged from 5-44 $\mu\text{g/kg}$ body weight/day with 99th percentiles up to 183 $\mu\text{g/kg}$ body weight/day for infants via mouthing activities [8]. World Health Organization (WHO) and European Union (EU) has published a list of priority compounds posing endocrine disrupting hazards to humans and have incorporated DEHP in the field of water policy by setting the guideline value at 8.0 $\mu\text{g/L}$ in fresh and drinking waters [9,10]. Table 1 shows risk assessment of phthalates by agencies in EU, US and Canada.

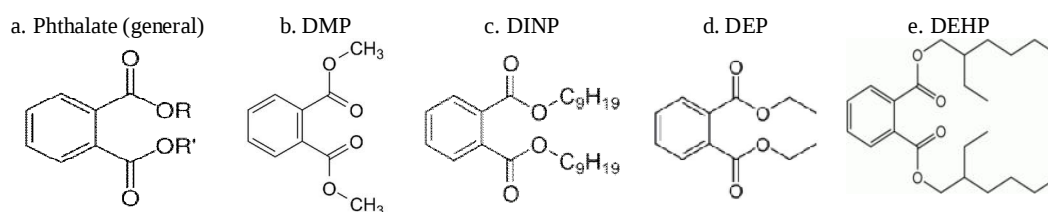


Figure 1. Molecular structures of commonly used phthalates; (a) Phthalate (general) (b) DMP (c) DINP, (d) DEP, (e) DEHP.

Several researchers have given an account for the evaluation of the migration of phthalates from food packaging materials, PVC gloves used in cooking and handling food, paper and cardboard [4,6,11], PET (PETE, polyethylene terephthalate) bottled beverages and mineral water [12,13], corks for glass bottles [6]. In light of the research studies carried out on phthalates, United States, Canada and

European Union have phased out use of phthalates in many consumer products, especially young children's products such as toys, lotions, sprays etc.

In May 2011, Taiwan had to face the worst business set back when its ministry of health reported illegitimate addition of di(2-ethyl-hexyl) phthalate (DEHP), to certain medicines, foods and beverages manufactured in Taiwan. It had been legitimate to use DEHP as plasticizers in production of PVC food contact packaging material, but using as food additive, had never been allowed in food industry. In compliance to the limit set by WHO, TDI for DEHP in Taiwan and Hong Kong is 1.5 ppm. Long-time ingestion of DEHP at levels above the TDI can create hormonal imbalance in the human body, which may result in the decrease of male reproductive ability, and female precocious puberty, breast cancer and loss of gender uniqueness [14].

Table 1. Risk assessment by ASTDR, US-EPA, EU-CSTEE, Health Canada [1]

Phthalate type	Risk assessment of DEHP and DINP			
	Country, region	Committee/year	mg/kg bodyweight/day	MRL ¹ /TDI ² /RfD ³
DEHP	USA	US-EPA, 1993b	0.02	RfD
DEHP	USA	ATSDR, 2002	0.1	MRL
DEHP	Canada	Health Canada, 1994	0.044	TDI
DEHP	EU	CSTEE, 1998a,b	0.050	TDI
DINP	EU	CSTEE, 1998a,b	0.25	TDI
DEP	USA	ATSDR, 1995	7	MRL
DBP	USA	ATSDR, 2001	0.5	MRL
DBP	USA	US-EPA, 1990	0.1	RfD

¹ minimal risk level; ² tolerable daily intake; ³ reference dose levels

Detection and quantification of very low concentration levels of DEHP and DINP are purely laboratory based and are seriously limited by the ubiquitous presence of this compound as a contaminant in almost all laboratory equipment and reagents and hence cannot, generally, be accurately quantified below about 2-ppb even in the most controlled laboratory setup [5, 15]. Most commonly gas chromatography (GC) is used to measure the phthalate metabolites in biological matrix [16]. In addition to GC a more sophisticated technique called high performance liquid chromatography (HPLC) is also applied to measure phthalate concentrations in blood plasma and urine samples with a detection limit of 0.345µg/mL and 1.2ng/mL respectively [17]. The chromatography technique separates complex mixtures of organic compounds to detect, identify and measure the concentration of each individual compound by using a specific detector [18]. Detectors specific to identification and measurement of DEHP in samples are electron capture detector (ECD) [16] and flame ionization detector (FID) [19]. Methods based on HPLC coupled with mass spectrometry (MS) or ultra violet (UV) detection are also used for detection of phthalates [5, 20].

Contemporary analytical techniques used to measure phthalate concentrations in food products and beverages, such as gas chromatography/mass spectroscopy (GC/MS), require expensive and complicated instruments, trained professionals, and laboratory environment with stringent conditions over sampling procedures. It involves high testing cost and most importantly long testing time per sample which does not match the time constraint posed by industrial production. There is no low cost technique so far reported for on-site and real-time phthalate detection which may be deemed suitable for industrial use where batches of thousands of products are manufactured on daily basis. Requirement to develop a reliable and highly sensitive quantification system that may provide on-site

real-time detection and measurement of phthalates in beverages, food products and medicines dictates paramount importance and urgency at present.

2. Planar interdigital sensors

The term ‘planar interdigital’ (ID) refers to finger-like, parallel in-plane electrodes built in a periodic pattern on a rigid substrate. Conventional ID sensors are based on repeated patterns of one sensing (working) and one excitation (reference) electrode configuration on a solid substrate. This geometry exploits the capacitive effect produced as a result of applied alternating electric field that fringes through the material sample. The most important benefit of planar geometry for this type of sensor is its single side access to the material under test which is an advantage for in-situ measurements. It also allows non-destructive testing which is mandatory for a sensing system operating in an industrial setup. Since the penetration depth of the electric field depends on the spatial wavelength (distance between two electrode with same polarity) of the ID structures, this configuration is mostly used for bio sensing applications where the sample is pipetted on the sensor surface in a volume range of a few μL [21, 22]. Dielectric profiling and conduction properties of semi insulating sample materials are hence obtained using EIS tools. The dielectric properties measured using this type of sensor, can directly or indirectly be related to other physical characteristics like density, structural integrity, porosity and biological or chemical content in the material under test, hence providing effective means to evaluate parameters vital for scientific and industrial requirements [23].

2.1. New sensor design

To achieve the objective of phthalate detection in bulk sample, a new type of sensor was designed with enhanced penetration depth of the fringing electric field. The higher penetration depth was achieved by increasing the number of sensing (working) electrodes between the reference electrodes. Finite element modeling software COMSOL Multiphysics® was used to simulate the new design for the sensor and evaluate its performance on the basis of theoretical model. Two sensors with different geometries and number of working electrodes were modeled keeping the effective sensing area ($2.5\text{mm} \times 2.5\text{ mm}$), substrate material (Si, SiO_2), electrode thickness (520nm) and electrode area ($25\text{ }\mu\text{m} \times 2.425\text{ mm}$) constant. To obtain higher penetration depth and uniform electric field distribution throughout, the sensor’s geometry was designed with two configurations of five (1-5-50) and eleven (1-11-50) working electrodes with spatial wavelength of $50\text{ }\mu\text{m}$. The spatial wavelength for reference electrodes was kept to $425\text{ }\mu\text{m}$ and $875\text{ }\mu\text{m}$ for 1-5-50 and 1-11-50 respectively. Figure 2(a) shows the design parameters of the proposed sensor 5 working electrodes between 2 reference electrodes.

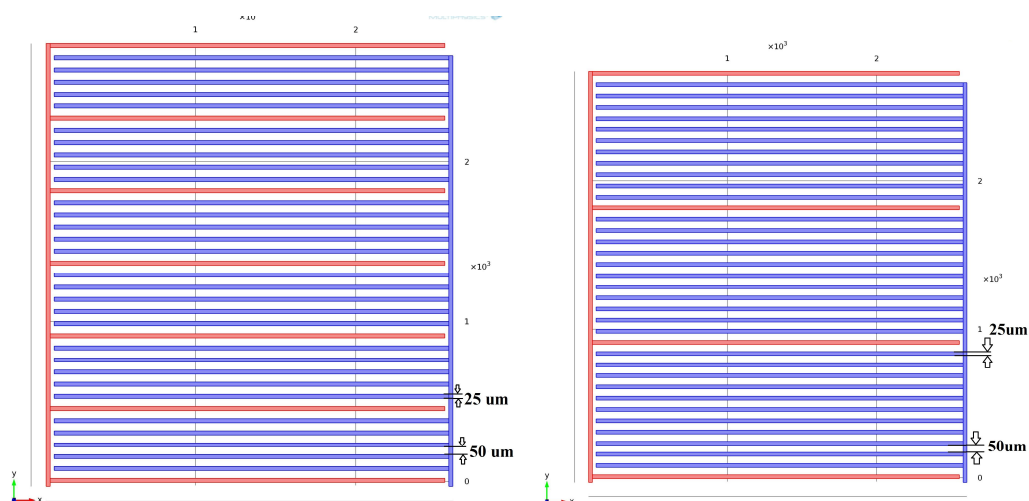


Figure 2. (a) Design parameters of (1-5-50) 5 working electrodes between two reference electrodes (b) Design parameter of (1-11-50) 11 working between two reference electrodes.

Figure 2(b) shows 11 working electrodes between two reference electrodes. Single crystal silicon substrate with thickness $525\mu\text{m}$ and relative permittivity $\epsilon_r = 4.2$ was used in the models so that the optimized model design may be fabricated practically on commercially available 4 inch silicon wafer. In order to calculate capacitance, stored electrical energy, penetration depth of electric field lines and field intensity the models were sequentially exposed to a dielectric medium on the sensing area with a dielectric constant of 80.1 and 5.1 simulated at 20°C . These are the dielectric constant values corresponding to pure MilliQ water and DEHP, respectively, which were selected to observe the model response of each sensor towards the material under test. The calculated values of capacitance and total electrical energy stored for the two simulated sensors for MilliQ and DEHP is given in table 2 below.

Table 2: Evaluated capacitance and total electrical energy stored using COMSOL Multiphysics®.

Sensor type	Milli Q. $\epsilon_r = 80.1$		DEHP $\epsilon_r = 5.1$	
	Capacitance. (pF)	Energy density (J)	Capacitance. (pF)	Energy density (J)
1-11-50	13.94	6.9e-12	1.52	7.6e-13
1-5-50	8.46	4.2e-12	0.92	4.6e-13

Figure 3 is the plot for the calculated values of capacitance for modeled sensors simulated for different media.

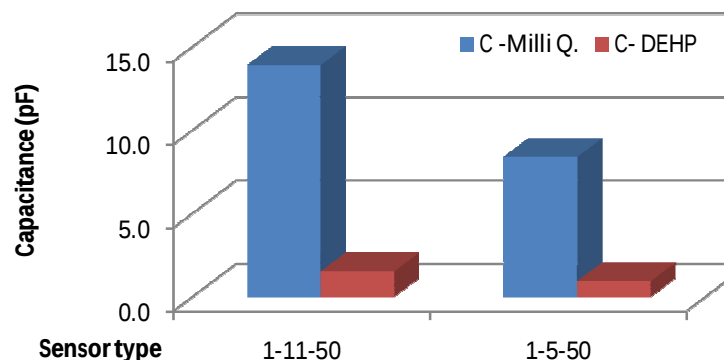


Figure 3. COMSOL simulated sensors' capacitance with MilliQ and DEHP.

2.2. Sensor fabrication

The analysis results using COMSOL simulation displayed better capacitive response for the sensor design with 11 working electrodes as compared to the design with 5 working electrodes; therefore 1-11-50 was selected for fabrication. Single crystal Si wafer (4 inch diameter, $525\mu\text{m}$ thickness) with native SiO_2 layer was used to fabricate the new types of planar interdigital (ID) structures. 36 workable sensors with total area of 100 mm^2 per sensor and a sensing area of 6.25 mm^2 per sensor were patterned on 4 inch single crystal Silicon wafer for the fabrication. The patterns were written for periodic interdigital structure with 11 sensing between 2 excitation electrodes for spatial wavelength of $50\mu\text{m}$

with the width of electrodes and the sensing area set to values of $25\ \mu\text{m}$ and $2.5\ \text{mm} \times 2.5\ \text{mm}$ respectively. The sensors were fabricated using MEMS technology used in semiconductor fabrication industry. It involves the steps of photoresist coating, UV exposed ID pattern transfer, plasma etching, and metal deposition by DC magnetron sputtering and lift off. Owing the properties of inertness, resistive to corrosion and flexible in the methods available for deposition as thin film, Gold was selected for electrodes' material. DC magnetron was used to sputter $500\ \text{nm}$ of Gold (Au) on top of $20\ \text{nm}$ thin film of Chromium (Cr) which provides strong adhesion of the Gold ID structures on the

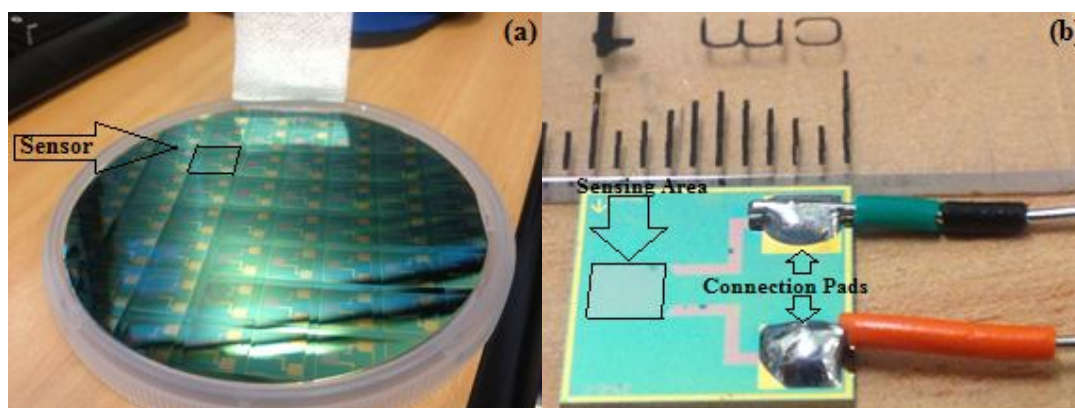


Figure 4. (a) Sensors in wafer form (b) individual sensor.

substrate surface. After lift-off, the wafer was coated with a $1\ \mu\text{m}$ layer of Parylene C by a conformal coater. The Parylene C is an industrial polymer used to coat fabricated circuits to avoid environmental effects on circuit operation. Parylene C coating is uniform and pinhole free. It does not edge, bridge or gap and can withstand continuous exposure to air at high temperatures for long periods of time. It helps avoid corrosion of electrodes by chemical reaction in addition to its inherent dielectric properties which makes it a better choice for capacitive sensing systems. Photolithographic steps were repeated and plasma etching was used to open the area with bonding pads to facilitate the connections to the reference and working electrodes on the sensor. Detail of sensors' fabrication has been explained elsewhere [24]. Figure 4 below shows sensors in wafer form and individually against scale.

3. Methods and materials

3.1. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a popular technique used in conjunction with ID sensors that describes the response of an electrochemical cell to a low amplitude sinusoidal perturbation as a function of frequency. This technique has the inherent potential of non-destructive testing, single side access and label-free detection for biological and chemical analysis and has been reported for estimation of fat contents in meat [25], to detect bio toxins in shell fish [26], evaluate electrical impedance of food products [27] and many other applications. The impedance Z of a system is determined by applying a small signal perturbation as a function of frequency and analysis of the resultant current that flows through the system in terms of amplitude and phase shift in comparison to voltage-time function. The complex value of impedance is interpreted in terms of its real and imaginary values at different frequencies. In absence of a redox probe the Z_{real} refers to the ionic molecular concentration present in the material under test, whereas, the Z_{imag} translates capacitive nature of the bulk medium. The results of an impedance measurement can be graphically demonstrated using bode and Nyquist (Cole-Cole) plot for all applied frequencies with real part of impedance Z plotted along X-axis and Imaginary part plotted along Y-axis in the later. The impedance spectrum

obtained, allows the characterization of surface, layers and concentrations in addition to the interpretation of exchange and diffusion processes used to describe the system kinetics. This analysis is achieved by translating the impedance spectrum into an equivalent series/parallel circuit, commonly consisting of resistances and capacitances representing the different electrochemical and physiochemical properties of the system under analysis [28].

The most frequently cited equivalent circuit used to interpret EIS experimental spectrum in electrical model form is Randle's equivalent circuit as shown in figure 5(a). It shows uncompensated solution resistance R_s in series to a parallel combination of double layer capacitance C_{dl} to the charge transfer resistance R_{ct} in series with Warburg impedance Z_w [29]. The Nyquist plot (Cole-Cole plot)

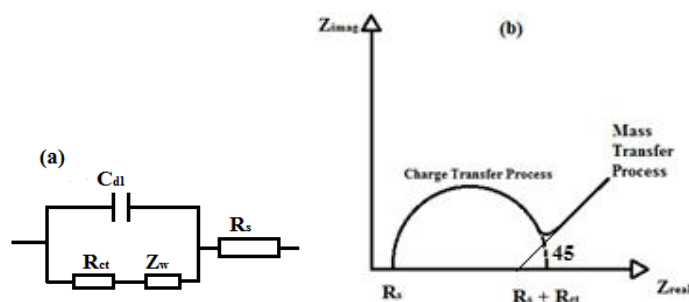


Figure 5. (a) Randle's Equivalent Circuit. (b) Nyquist plot.

for the equivalent circuit shows a semicircular region followed by a 45° straight line as shown in figure 5(b). The straight line interprets a faster mass-transfer limited process due to electron flow from electrode surface in the bulk solution at lower frequencies, whereas, the semicircular portion describes a relatively slower charge-transfer limited process at higher frequencies. C_{dl} can be calculated from the frequency at the maximum of semicircular region in the Nyquist plot using $\omega = 2\pi f = 1/R_{ct}C_{dl}$, whereas, R_{ct} is calculated by extrapolating the semicircle to Z_{real} axis as shown in figure 5(b). The double layer capacitance C_{dl} and charge-transfer resistance R_{ct} are the key electrical parameters to determine the impedance change for analysis of the system kinetics required to observe the change in dielectric properties of the medium due to the presence of phthalates. Macdonald discusses the in-depth analysis of electrochemical impedance spectroscopy technique in [23].

3.2. Sample preparation

Gravimetrically prepared 99.5 % pure di(2-ethylhexyl) phthalate (DEHP) solution with a concentration of 100 μ g/mL (100 ppm) in ethanol was procured from ChemService® USA. Two set of working solutions were prepared by serial dilution method in deionized water MilliQ® (MILLIPORE USA) at 0.002 through 2 ppm concentration levels of DEHP. Pure deionized water with 2 ppm 99.7% pure ethanol was used as the control solution to create reference standard for impedance change observation. pH of the control and working solutions were tested using IQ Scientific Instrument Inc. USA after calibration with buffer solutions. Commercially available bottled orange juice was spiked at a concentration of 5, 10 and 20 ppm with DEHP for testing the sensor in acidic medium (pH 3.35 at 20°C). These concentrations of DEHP in juice were selected below and above TDI calculated over an average person of 60 Kg mass as given in table 1. Pure juice was used as reference standard for test results' comparison with the spiked samples.

3.3. Experimental setup

EIS experiments were carried out using Hioki 3522-50 LCR Hi precision Tester (Japan) at laboratory temperature (23°C). All experiments were performed using slow mode of testing equipment to achieve an error rate of less than 0.05%. A constant voltage 1V_{rms} sinusoidal signal was applied to the sensor with a frequency sweep of 1 Hz to 10 kHz with 20 data points per decade on log scale. LabView® data

acquisition program was used to write the measured values in Microsoft excel® file for post processing and analysis on the attached desktop computer. Automatic data acquisition system was linked using RS232C hardware interface with the Hi precision tester. After setting up the test apparatus and circuitry, the tester was calibrated using the built-in function of self-calibration in open and short circuit mode. This calibration ensures to offset any stray capacitance appearing in the testing data due to the length of testing lead in addition to suppressing any noise in the observed signal, hence improving signal to noise ratio. The sensor was cleaned with acetone, rinsed with deionized water and dried with nitrogen before testing the next concentration. An average of three set of experiments were used to ensure reproducibility and reliability of the results. Figure 6 shows the test bench setup and LabView based front panel of automatic data acquisition system developed for the experiments.

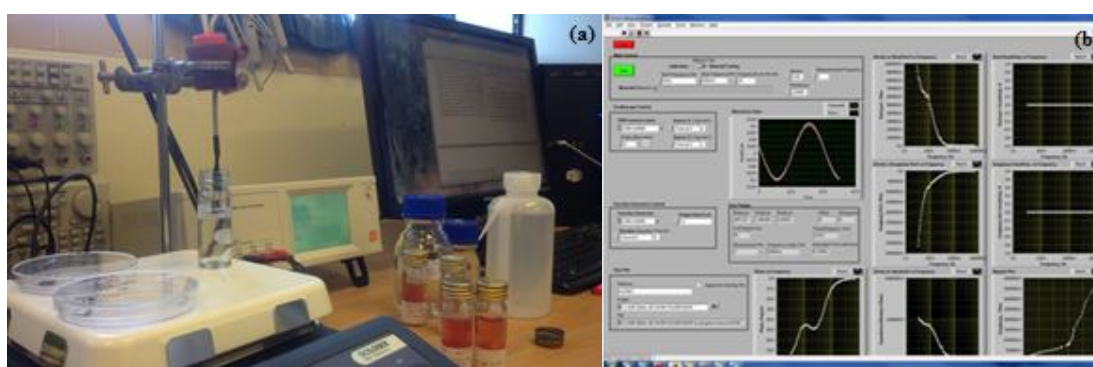


Figure 6. (a) Test bench setup (b) LabView based data acquisition system front panel.

4. Results and discussions

4.1. DEHP detection in MilliQ

MilliQ water (18MΩ cm) with 2ppm ethanol was used as control in the EIS experiments. pH of the control solution at 23°C was measured as 7.3. Gravimetrically prepared 100 ppm DEHP in ethanol was added to MilliQ to obtain a stock solution of 2ppm DEHP in water. Ethanol was used as a polar solvent to dissolve DEHP in deionized water. The pH of the stock solution was measured as 6.98 at 23°C which showed that the addition of phthalate had very less impact on the pH of the system. 0.2ppm, 0.02ppm and 0.002ppm concentrations of DEHP were obtained from the stock solution by using serial dilution method. Sample testing by proposed sensing system was carried out immediately after sample preparation. All the experiments were performed in laboratory environment at 23°C with 47% humidity level. Figure 7 below shows the plot for imaginary and real part of impedance vs. frequency for all four DEHP concentrations. The capacitive reactance (Z_{imag}) shows a good variation with changing concentrations of DEHP especially at lower frequency range (10 Hz-400Hz), whereas, the corresponding change in Z_{real} is not dominant which could be explained on the basis of ionic concentration in the test samples. The pH value observed for all concentrations of DEHP does not vary and is approximately the same for each concentration, therefore, Z_{real} which depends on the Faradic current flowing through the bulk medium is same for all concentrations as shown in the plot in figure 7. A drastic change in $Z_{imaginary}$ (reactance) with variation of DEHP concentrations in samples is however observed in the said plot which is attributed to the dielectric properties of the DEHP molecules. The Nyquist plot shown in figure 8 demonstrates: (1) the fast mass transfer process in form of a straight line which corresponds to the Warburg resistance in the equivalent circuit suggested in the next section and (2) the slow charge transfer process is translated by semi-circular region of different diameters corresponding to the DEHP concentrations in the test solutions. This slow charge transfer process occurs due to the accumulation of DEHP molecules on the electrode solution interface. This happens due to the adsorption of the DEHP molecules on the electrode surface as a result of electron transfer from the electrodes into the solution [23].

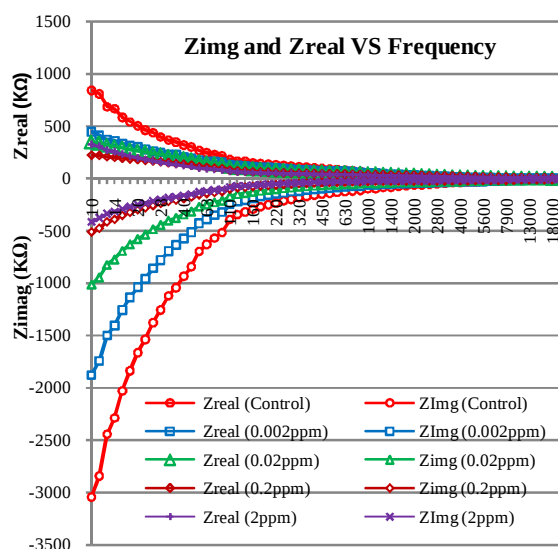


Figure 7. Imaginary and real part of Impedance vs. Frequency.

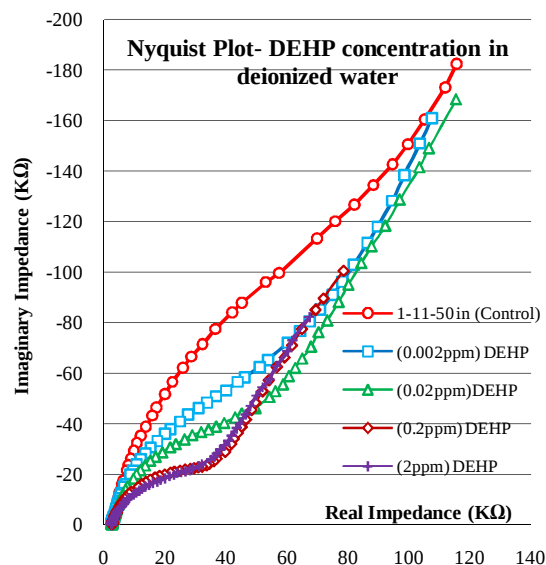


Figure 8. Nyquist Plot for different test concentrations of DEHP.

4.1.1. Data analysis using non-linear least square curve fitting.

The diameter of the semi-circular region in the Nyquist plot dictates the value of charge transfer resistance R_{ct} which in turn changes the double layer capacitance C_{dl} at the sensor-solution interface. The variation in the diameter of the semi-circular trace with changing concentrations of DEHP molecules in the bulk medium shows the capability of the sensor to monitor the variation of DEHP as low as 0.002ppm in deionized water.

Using Randle's cell model, the real and imaginary impedance at the electrode solution interface could be derived as shown by the equation (1)

$$Z(\omega) = R_s + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} - \frac{j\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} \quad (1)$$

The equivalent circuit was estimated using theoretical calculations by electrochemical spectrum analyser algorithm which suggests an equivalent circuit by fitting the experimental values over theoretical response of the most probable circuit by performing iterations over the experimental data. The circuit parameters were estimated by non-linear least square fitting technique which fits the measured impedance data on theoretically estimated values. The algorithm performs statistical analysis to calculate the residual mean square for experimentally observed values in the measured spectra against the calculated values based on the theoretical response of suggested equivalent circuit. The optimization of the calculated data is achieved by the number of iterations it takes to solve the mathematical model for the proposed equivalent circuit. Figure 9 shows the electrical circuit equivalent to the kinetic processes taking place in the electrochemical cell for a single concentration of DEHP in bulk solution. This equivalent circuit was proposed at the most optimal curve fitting with an error rate of less than 5% in 300 iterations. The fitted Nyquist plot is shown in figure 10 and the least square curve fitting plot for absolute values of impedance is traced in figure 11. The bold line curve displays the modelled behaviour of the equivalent circuit whereas; the markers represent the experimentally observed response from the electrochemical cell in both plots.

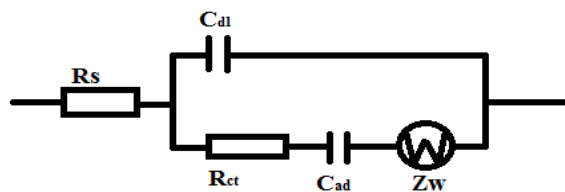


Figure 9. Equivalent circuit proposed by the least square curve fitting algorithm.

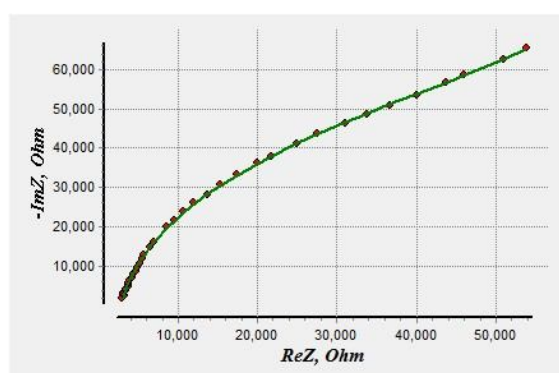


Figure 10. Least square curve fitting for Nyquist plot. Solid line shows calculated curve, markers show experimental data points.

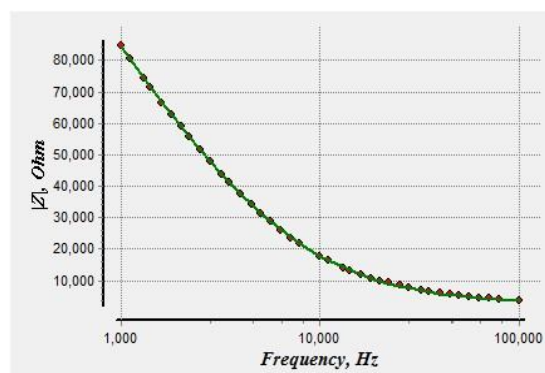


Figure 11. Least square curve fitting for absolute value of Impedance. Solid line shows calculated curve, markers show experimental data points.

The electrical parameters for the components estimated in the constant phase equivalent circuit shown in figure 9 are calculated by electrochemical spectrum analysis algorithm for all concentrations of DEHP in aqueous medium. Table 3 provides the values of double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), Warburg resistance (Z_w) and solution resistance (R_s). It is observed that an additional parameter adsorption capacitance (C_{ad}) appears in the equivalent circuit shown in figure 9 consequent to electrochemical spectrum analysis for the sensing system. This parameter interprets the process of ion diffusion from the electrode surface into the bulk solution. These ions are produced as a result of the electron transfer from the solution into the electrode surface especially at low frequencies [30]. This parameter tends to increase with an increase in the concentration of phthalates in the samples indicating more number of phthalate molecules adsorbing to the electrodes' surface.

Table 3: Evaluated electrical parameters obtained by using electrochemical spectrum analyzer for 300 iterations.

Eq. Circuit Parameters (units)	Electrochemical spectral analysis for DEHP concentrations in MilliQ							
	2 ppm		0.2 ppm		0.02 ppm		0.002 ppm	
	Value	Error (%)	Value	Error (%)	Value	Error (%)	Value	Error (%)
R_s (Ω)	2021.1	3.10	2681.6	1.985	2845.7	4.47	2890	2.82
Z_w (K Ω)	291.5	4.47	513.1	2.6064	1702.4	3.411	2187.2	1.6126
R_{ct} (K Ω)	48.8	0.68	42.3	0.416	64.5	1.29	91.1	0.57
C_{ad} (F)	1.14E-8	4.03	1.28E-8	2.452	1.32E-8	4.05	5.889E-9	2.72
C_{dl} (F)	1.003E-8	0.52	2.313E-9	0.4254	1.7E-9	0.931	1.584E-9	0.322

4.2. DEHP detection in orange juice

Due to strict health policy observed by MoH New Zealand, the beverages available in the local markets are assumed to be DEHP free. The sensor's response was tested for locally available orange juice available in a glass bottle. Glass-bottled juice was selected to avoid the potential chances of DEHP leaching into the content from the PET packaging of the juice [6]. The juice was spiked with 5, 10 and 20 ppm concentrations of DEHP, prepared at 23°C temperature and was tested immediately after sample preparation. These tested concentrations were selected to observe sensing system's

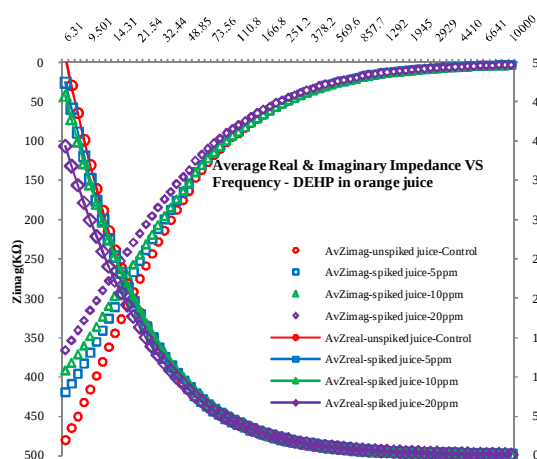


Figure 12. Real and imaginary part of the impedance spectra for different concentrations of DEHP in orange drink plotted against frequency

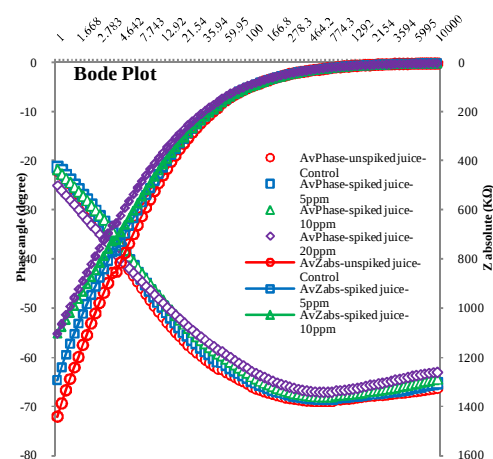


Figure 13. Bode plot for the measured impedance spectra for different concentrations of DEHP in energy drinks.

response above and below the minimum risk level (MRL) intake limit for DEHP calculated for an average individual of 60 kg body weight given in table 1. Un-spiked original drink was used as control solution to create standard reference curve. Figure 12 shows the plot for real and imaginary part of the impedance spectra for the spiked juice compared to the standard reference for the original juice. The sensor provides change of impedance in the capacitive reactance (Z_{imag}) dominating the corresponding real impedance values in a frequency range of 10 Hz to 1.3 kHz. The change in Z_{imag} is higher in magnitude at lower frequencies especially below 100 Hz range and the plot shows a sequential change in the capacitive reactance with increasing concentration of phthalate molecules. Figure 13 displays the bode plot for the same frequency range. As observed, the change in absolute impedance (Z_{abs}) is visible only at lower frequencies whereas the phase shift is distinctive for pure and spiked samples especially for a DEHP concentration as high as 20ppm. It is observed that the real impedance of the juice samples has drastically reduced in comparison to the DEHP testing in pure deionized water as shown in figure 7. It is due to the ionic presence in the acidic medium (juice) of pH 3.04 at 23 °C, causing an appreciable change in the solution resistance variable R_s .

5. Conclusions

Non-invasive, real time detection technique for phthalates in water and juice has been reported. Sensitivity optimization for designed MEMS based interdigital sensors was achieved on the basis of mathematical modelling simulation software, COMSOL and was discussed to analyse the sensitivity concerns. Optimized design was fabricated using MEMS based semiconductor device fabrication techniques. Sensor was able to detect phthalate ester, DEHP, in deionized water and orange juice as a practical application of the sensing system. Analyses of the results have been carried using non-linear

least square curve fitting statistical technique to discuss the kinetic processes taking place inside the electrochemical cell on basis of Randle's cell equivalent circuit model. Sensors performance was evaluated for commercially available orange juice and the experimental results proved its detection ability in such products. Selectivity of the sensing system is the major challenge being worked upon in the on-going research in order to render the testing system usable for industrial applications.

References

- [1] J Heudorf U, Mersch-Sundermann V, Angerer J 2007 *Int. J. Hyg. Environ. Health* **210** 623-634
- [2] T E D Schettler 2006 *International Journal of Andrology* **29** 134
- [3] Hauser R, Duty S, Godfrey-Bailey L, Calafat AM 2004 *Environ. health perspect.* **112** 751
- [4] USCPSC 2010 *Toxicity Review of Di(2-ethylhexyl) Phthalate (DEHP)*. (Bethesda: MD)
- [5] K Fiselier, E Rutschmann, G McCombie *et al* 2010 *European Food Res. and Tech.* **230** 619
- [6] R Sendón, A Sanches-Silva, J Bustos *et al* 2012., *Journal of Separation Science* **35** 1319
- [7] R Kavlock, K Boekelheide, R Chapin *et al* 2002 *Reproductive toxicology* **16** 655
- [8] ATSDR 2002 *Toxicological Profile for Di(2-ethylhexyl) Phthalate*. (Atlanta: GA)
- [9] WHO (World Health Organization) 2003 *Guidelines for drinking-water quality* **180** Chap8 3 ed.
- [10] European Union Council 2001 *J. Eur. Commun. L* Decision No. 2455/2001/EC. Directive 2000/60/EC Off. p331
- [11] M Biedermann, K Fiselier, G Marmiroli *et al* 2008 *European Food Res. and Tech.* 226 1399
- [12] X L Cao 2008 *Journal of Chromatography A* **1178** 231
- [13] M Wagner and J Oehlmann 2009 *Environmental Science and Pollution Research* **16** 278
- [14] L López-Carrillo, R U Hernández-Ramírez, A M Calafat *et al* 2010 *Environ. health perspect.* **118** 539
- [15] C Giam, H Chan, and G Neff 1975 *Analytical chemistry* **47** 2319
- [16] M R Lee, F Y Lai, J Dou *et al* 2011 *Analytical Letters* **44** 676
- [17] K Kambia, T Dine, R Azar *et al* 2001 *International journal of pharmaceutics* **229** 139
- [18] K Shintani, M Taki, H Ootera *et al.* 2000 *Plasma processing apparatus using a partition panel* Google Patents
- [19] V Triantafyllou, K Akrida-Demertzi, and P Demertzis 2007 *Food Chemistry* **101** 1759
- [20] A K Malik, C Blasco, and Y Picó 2010 *Journal of Chromatography A* **1217** 4018
- [21] Berggren C, Bjarnason B, Johansson G, 2001 *Electroanalysis* **13** 173
- [22] Sadik OA, Aluoch AO, Zhou A. 2009 *Biosensors and Bioelectronics* **24** 2749
- [23] E. Barsoukov and J. R. Macdonald, 2005 *Impedance spectroscopy: theory, experiment, and applications*: John (Wiley and Sons)
- [24] A I Zia, A Mohd Syaifudin, S C Mukhopadhyay *et al.*, 2012 *IEEE Transactions on Instrumentation and Measurements* 1220
- [25] S C Mukhopadhyay, and C P Gooneratne 2007 *IEEE Sensors Journal* **9** 1340
- [26] A R M Syaifudin, K P Jayasundera, and S C Mukhopadhyay 2009 *Sensors and Actuators B-Chemical* **137** 67
- [27] X Li, K Toyoda, and I Ihara 2011 *Journal of Food Engineering* **105** 563
- [28] F Lisdat, and D Schäfer 2008 *Analytical and bioanalytical chemistry* **391** 1555
- [29] M I Prodromidis 2010 *Electrochimica Acta* **55** 4227
- [30] Kerner, Z Pajkossy 2002 *Electrochimica Acta* **47** 2055