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Rapid and molecular selective electrochemical sensing of phthalates in aqueous solution



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ABSTRACT

Reported research work presents real time non-invasive detection of phthalates in spiked aqueous samples by employing electrochemical impedance spectroscopy (EIS) technique incorporating a novel interdigital capacitive sensor with multiple sensing thin film gold micro-electrodes fabricated on native silicon dioxide layer grown on semiconducting single crystal silicon wafer. The sensing surface was functionalized by a self-assembled monolayer of 3-aminopropyltriethoxysilane (APTES) with embedded molecular imprinted polymer (MIP) to introduce selectivity for the di(2-ethylhexyl) phthalate (DEHP) molecule. Various concentrations (1–100 ppm) of DEHP in deionized MilliQ water were tested using the functionalized sensing surface to capture the analyte. Frequency response analyzer (FRA) algorithm was used to obtain impedance spectra so as to determine sample conductance and capacitance for evaluation of phthalate concentration in the sample solution. Spectrum analysis algorithm interpreted the experimentally obtained impedance spectra by applying complex nonlinear least square (CNLS) curve fitting in order to obtain electrochemical equivalent circuit and corresponding circuit parameters describing the kinetics of the electrochemical cell. Principal component analysis was applied to deduce the effects of surface immobilized molecular imprinted polymer layer on the evaluated circuit parameters and its electrical response. The results obtained by the testing system were validated using commercially available high performance liquid chromatography diode array detector system.

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1. Introduction

The endocrine system in living organisms is made up by the set of cells and glands that produce chemical signals called hormones. Hormones travel in the blood stream to reach their respective receptors in the target cells. The major function of the endocrine system is to regulate nutrient supply to all cells, growth and reproduction. Endocrine disruptors (EDs) are exogenous chemicals or mixture of chemicals that interfere the normal functioning of endocrine system and hormones. Among the known endocrine disruptors the most ubiquitous are esters of 1-2-benzenedicarboxylic acid commonly known as phthalates. These industrial chemicals have a large number of commercial uses, such as lubricants, additives, solvents, softeners for plastics including food and beverage packaging, cosmetics, insecticides, paints, medical

and pharmaceutical applications (Schettler, 2005). Since phthalate esters are not covalently attached to the polyvinyl chloride (PVC plastic) lattice structure they leach, migrate, and evaporate directly into foodstuffs and atmosphere exposing human beings through ingestion, inhalation and dermal routes (Montuori et al., 2008). Even directly infuse into body fluids via medication and disposable medical plastic products (Green et al., 2005). Phthalates have been declared as ubiquitous environmental pollutants and endocrine-disruptors (EDs) by a number of health monitoring agencies all over the world due to their carcinogenic and teratogenic effects observed as reproductive and developmental defects in rodents (Uscpsc, 2010). It had been concluded in research that phthalates pose highest toxicity and endocrine disruptive threat to human race, especially to young children, infants, pregnant and nursing mothers (Colacino et al., 2011). A number of recent researches have suggested declining trend in the reproductive hormonal levels, damage to sperm DNA and count in male adults (Meeker et al., 2009), whereas, elevated risk of altered breast development and breast cancer, premature puberty and prostate changes in females (Lopez-Carrillo et al., 2010; Colacino et al., 2011). Leaching

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of phthalates into food from packaging (Lee et al., 2011), from polyethylene terephthalate (PETE, PET) bottles into beverages and mineral water (Montuori et al., 2008) and from corks of glass bottles (Sendón et al., 2012) has been published. (Sendón et al., 2012) showed phthalates leaching into orange juice from tetra packaging grows 110 times higher than the safe intake limit of 6.0 $\mu\text{g/L}$ set by United States Environmental Protection Agency (US EPA) during its shelf life and until close to its expiry date. The guideline for safe drinking water given by World Health Organization (WHO) and European Union in their water policy is set to 8.0 $\mu\text{g/L}$ DEHP as safe limit in fresh and drinking waters, published in a list of priority compounds posing endocrine disrupting hazards to human (WHO, 2011).

The ubiquitous presence of phthalates as an environmental pollutant and containment in laboratory apparatus seriously limits its minimal detection level below about 2 ppb even under the most stringent conditions and controlled setup (Cao, 2008). Solid phase micro-extraction (SPME) is a solvent free pre-concentration technique applied to extract phthalate metabolites from a mixture of compounds in order to measure its quantity using gas chromatography (GC) or high performance liquid chromatography (HPLC) (Lai et al., 2007; Li et al., 2008; Qi et al., 2011; Tamayo et al., 2007). Different types of detectors are used to measure the quantity of phthalates depending on the nature of the test sample. For example DEHP is measured by GC using electron capture detector (ECD) (Wagner and Oehlmann, 2009) and flame ionization detector (FID) (Lopez-Carrillo et al., 2010). Liquid chromatography (LC) coupled with mass spectrometry (MS) and UV detection are the most commonly applied well established techniques (Giam et al., 1975). Almost all contemporary analytical techniques described here are highly sensitive due to the requirement of measurement of trace levels of phthalates present in food and beverage samples. Unfortunately, on the other hand, these are time consuming, expensive, complicated, produce laboratory waste, need the expertise of highly trained professionals in addition to submission of samples to laboratories worth millions of dollars. Blood and urine are the most common matrices used for biomonitoring of EDCs but the results of these biomonitoring do not provide the complete picture of EDC intake, rather just provide the quantity of metabolites excreted, losing information about the amount of phthalate that has become the body burden. Therefore, it is necessary to have a rapid assay which may detect the quantity of phthalates present in food and beverages as initial intake via the oral route which is deemed to be the biggest source of human phthalate exposure due to the extensive use of plastics in our everyday life style. The requirement of instant screening of a batch of products manufactured at an industrial set up still requires attention of the researchers to device an assay which may be simple enough to be handled with minimal training needs and does not involve bulky and expensive support electronics. The objective of this research is to develop a low cost real time testing system which could readily be installed in an industrial setup.

Planar Interdigital (ID) capacitive sensors, own finger-like, parallel, in-plane electrode geometry designed in repeated patterns on a solid substrate. The repeated patterns of electrodes ensure measurable sensing signal strength and achieve better signal to noise ratio. Conventional ID sensors are based on repeated patterns of single sensing and single excitation (working) electrode pair on a solid substrate to achieve single side access and non-destructive testing. The penetration depth of the fringing electric field is a function of the spatial wavelength (distance between sensing and working electrode) of the thin film electrodes (Mamishv et al., 2004). Planar interdigital geometry, non destructive in situ testing capability, single side access, field penetration depth control, signal strength control, simplified modeling, and low cost renders planar ID capacitive sensors the

most suitable candidate for chemical and biological sensing applications. (Berggren et al., 2001; Limbut et al., 2007; Radke and Alocilja, 2005). These type of sensors have been used for quality monitoring of dairy, meat and leather products (Mukhopadhyay et al., 2008, 2005, 2006; Mukhopadhyay, 2007; Mukhopadhyay and Gooneratne, 2007).

2. Materials and methods

2.1. Materials and chemicals

Di(2-ethylhexyl) phthalate (DEHP), N,N-methylene-bis-acrylamide, methacrylamide, ammonium persulfate, Methanol, ethanol, acetonitrile, chloroform, dimethyl formamide (DMF), dichloromethane and 3-aminopropyltriethoxysilane (APTES) were procured from Sigma Aldrich, Germany. Deionized (DI) water MilliQ[®] was obtained from MILLIPORE water system (USA)—18 M Ω cm. Gravimetrically prepared di(2-ethylhexyl) phthalate (DEHP) solution at a concentration of 200 $\mu\text{g ml}^{-1}$ (200 ppm) in ethanol (99.5% purity) was ordered and received from ChemService[®] USA. Other working solutions of lower concentrations were achieved by serial dilution method in the deionized water MilliQ[®]. Pure deionized water with a 100 ppm concentration of ethanol was used as control solution for the experiments. pH meter from IQ Scientific Instrument Inc. USA was used to measure pH levels of the spiked and control solutions. The device was calibrated with buffer solutions provided by the manufacturer.

2.2. Novel design for planar ID sensors

In order to increase the penetration depth of the fringing electric field, a novel design of planar interdigital (ID) structures was modeled, simulated and fabricated with multiple sensing electrodes between two working electrodes. The new sensor design was simulated using finite element modeling software COMSOL[®] Multiphysics employing ACDC module in 3D workspace quasi-static mode. Simulation results showed that new sensor design proved to perform better compared to the conventional sensor design with respect to size, design, performance and sensitivity. Detailed account of the new design analysis and comparison results have been discussed elsewhere (Zia et al., 2013). New sensor was designed by keeping the substrate material and thickness, electrode material and thickness and effective sensing area constant. Design geometry was drawn in eleven sensing electrodes between two working electrodes with pitch length set at 50 μm , coded as (1-11-50). The pitch length was kept at a constant value of 50 μm . Sensing area was fixed to 2.5 mm \times 2.5 mm, electrode area 25 μm \times 2.425 mm and electrode thickness to 520 nm was taken as standard. COMSOL[®] Multiphysics software estimated an average electric field penetration depth of 437.6 μm for the new design.

2.3. Sensor fabrication

The sensor was fabricated on a single crystal silicon wafer, 525 μm thick, over native silicon dioxide (SiO_2) insulative layer by photolithography and etching steps commercially available to semiconductor device fabrication industry. 36 workable sensors were patterned on soda lime mask with mask laser writer. The sensors were fabricated using MEMS technology involving the steps of photoresist coating, UV exposed ID pattern transfer, plasma etching, gold deposition by DC magnetron sputtering using Argon gas plasma and lift off. Gold is the most preferred electrode material for sensing applications due to its excellent physicochemical stability, bio-affinity, low electrical resistivity and minimal

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