Rapid Detection of Organophosphates in Aqueous Solution Using a Hybrid Organic/Inorganic Coating on SH-SAW Devices

Arnold K. Mensah-Brown[1], Darlington Mlambo[2], Fabien Josse[1], Jeanne Hossenlopp[2]
[1]Department of Electrical and Computer Engineering and [2]Department of Chemistry
Marquette University
Milwaukee, WI, USA
Fabien.Josse@marquette.edu

***Abstract*—Rapid detection of organophosphates pesticides (OPs) in groundwater is necessary to allow for real-time monitoring and cleanup. Detection of OPs in the liquid phase has already been demonstrated using poly(epichlorohydrin) [PECH] and polyurethane as the sensing layer. However, the response times are relatively long, on the order of hours. In this work, a hybrid organic/inorganic chemically sensitive layer [bisphenol A-hexamethyltrisiloxane (BPA-HMTS)] is synthesized and investigated for the rapid detection and analysis of organophosphate pesticides. Direct chemical sensing in aqueous solutions is performed using the guided shear horizontal surface acoustic wave sensor platform on 36° rotated Y-cut $LiTaO_3$. It is shown that, for the same coating thickness, a 60% reduction in sensor response time is achieved without a significant reduction in sensitivity when compared with PECH. Considering the glass transition temperature, T_g, for the polymers, it is seen that the faster sensor response exhibited by the BPA-HMTS coating is due to the porous siloxane backbone, HMTS. Furthermore, sensor signal analysis in the form of the extended Kalman filter (EKF) is employed on-line during the detection process. This allows for the steady-state sensor response and absorption time constant to be extracted on-line well before equilibrium, thus further reducing the time required for analyte identification and quantification. 500 μg/L of parathion has been detected and a limit of detection of 20 μg/L (ppb) for parathion and 100 μg/L (ppb) of paraoxon is reported for the present non-optimized sensor.**

I. INTRODUCTION

There are various contaminants in the environment and early detection of these contaminants in surface water and groundwater sources is necessary. The toxins enter water through several means including runoff from agricultural regions, where pesticides are used extensively. From the six major class of pesticides, the agro-industry has increasingly relied upon organophosphate pesticides (OPs) to control pests because of their perceived rapid degradation in the environment [1, 2]. However, recent research shows that OPs persist in the environmental for relatively long periods [3].

Current methods for monitoring contaminants, such as OPs, include gas/liquid chromatography and mass spectroscopy [4]. Although these methods are very accurate, they often require samples to be taken to laboratories for analysis, are extremely time consuming, and expensive. Moreover, vital information can be lost during sample collection, transportation, and storage. Therefore, there is a need to develop *in-situ* monitoring systems for rapid analysis and characterization of samples. To make these possible, various bio(chemical) sensor technologies including acoustic wave devices are being investigated to implement real-time sensing [4]. Specifically, SH-SAW devices coated with poly(epichlorohydrin) (PECH) and polyurethane (PU) have been used for the in-situ reversible detection of OPs (phosmet and parathion) in aqueous environments with high sensitivity [5]. However, the sensor response times were relatively long, on the order of hours. One of the numerous approaches investigated to achieve near real-time detection involved using estimation-based modeling and sensor signal analysis. This allowed for the extended Kalman filter (EKF) to be used to reduce the time required for analyte identification and quantification by 60% [5]. While this is excellent, it is still necessary to develop functionalized coatings that will physically reduce the sensor response times for OP detection so that the full potential of the estimation technique can be realized.

In this paper, bisphenol A-hexamethyltrisiloxane (BPA-HMTS) is synthesized and investigated for rapid direct chemical sensing of OPs (parathion and paraoxon) in aqueous solution using the guided shear horizontal surface acoustic wave sensor platform on 36° rotated Y-cut $LiTaO_3$. The results are compared with those of other chemically sensitive layers [5] to facilitate the design of an optimum real-time chemical sensor for OP detection and quantification. Furthermore, the estimation technique is employed to further reduce the time required for analyte identification and quantification.

II. SENSOR PLATFORM: POLYMER-COATED SH-SAW

The three-layer geometry of the guided SH-SAW sensor is used in this investigation. It consists of a piezoelectric crystal ($LiTaO_3$) supporting a shear horizontal surface acoustic wave (SH-SAW), a polymer coating acting as both the waveguiding material and chemically sensitive layer, and a liquid layer for the transport of the analytes. The polymer layer acts as a guiding layer by trapping the acoustic energy near the surface. The amount of acoustic energy that is trapped by the sensing layer increases with film thickness up to an optimum value. Therefore, device sensitivity increases as the wave displacement amplitude increases at the surface i.e., as the film thickness is increased [5]. A metal layer is used between the input and output interdigital transducers (IDTs) to eliminate acoustoelectric interactions with the load [6]. Hence, only mechanical perturbations (both mass loading and viscoelastic changes) will account for the sensor response.

As the acoustic wave propagates along the surface, any surface perturbation will change its characteristics, i.e., phase velocity, v, and attenuation, α. The fractional change in the wave velocity, a measure of the sensitivity to surface mechanical perturbations, is related to the fractional change in the frequency of the device. In the present work, both the metallized path and the IDTs are coated with the polymer so that the sensing path length is equal to the propagation path length. Thus, the fractional change in the phase velocity ($\Delta v/vo$) of the propagating wave caused by any surface perturbation is equal to the fractional change in frequency ($\Delta f/fo$), provided the wave suffers negligible dispersion.

When the polymer-coated SH-SAW device is exposed to analyte solution, the analyte absorbs into the coating resulting in mechanical loading. This mechanical loading is a combination of added mass (Δm) and change in the complex shear modulus (ΔG) of the coating [7]. For relatively low ambient concentrations, Δm and ΔG are proportional to the ambient concentration [8]. In general, the observed frequency shift, Δf, for the SH-SAW sensor upon analyte absorption can be expressed as:

$$\Delta f = \Delta f_{mass} \pm \Delta f_{viscoelasticity} \qquad (1)$$

where the minus sign indicates that analyte/coating interaction is causing the coating to plasticize/soften and the plus sign indicates that the coating is becoming more glassy.

III. MATERIALS AND METHODS

A. Materials

Chloroform (99.8%), acetone (99%), anhydrous toluene (99.8%), 2-propanol, monobasic dihydrogen phosphate, 1,1,3,3,5 hexamethyltrisiloxane (HMTS), Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt-DVTMDS) complex solution in xylene (Pt ~2 %), 2,2'-diallylbisphenol A (BPA), dibasic monohydrogen phosphate, parathion, and paraoxon were purchased from Sigma-Aldrich (Milwaukee, WI) and used as supplied. The physical properties of the OPs studied in this work are shown in Table I. Note that the slight difference in physical properties is due to the sulfur and oxygen atoms (see Fig. 1). In the aqueous solutions, OPs degrade by means of chemical hydrolysis [3, 9, 10]. In general, this reaction is a first order process [3, 9]. They also exhibit a second-order breakdown process in which the hydrolysis reaction depends on the pH of the solution [3]. Thus, it is necessary for the pH of the aqueous solutions used in this work to be monitored. A phosphate buffer solution of pH 6.20 is used in this work because it offers a suitable compromise in the range from pH 5.5 to 8.5 typically found in surface, ground, and river waters [3, 9, 11].

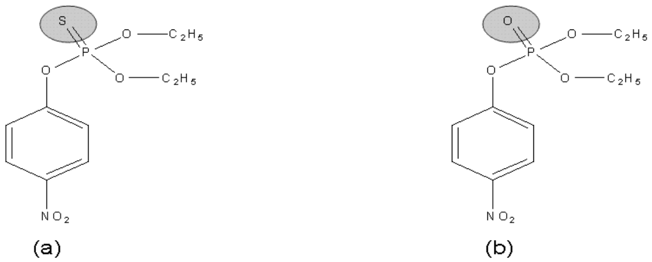

Figure 1. Chemical structures of organophosphates (a) parathion (b) paraoxon

B. Coating Synthesis

BPA-HMTS was synthesized by modifying a procedure reported by Grate et al. [12]. Briefly, (0.882 g, 0.00286 mol) of BPA (M_w = 308.41 g/mol) was dissolved in 10 mL of toluene in a vial. This mixture was stirred for about 5 min. until a homogeneous mixture was obtained. To this solution, (0.566g, 0.00271 mol) of HMTS (M_w = 208.48 g/mol) was added to give a mole ratio for reacting functional groups, r = [SiH]/[CH2=CH], of 0.95. 10 mL of toluene was added to this solution, stirred for about 1 min, and the presence of the Si-H (2125 cm^{-1}) group monitored by FTIR. Two drops (~ 0.02 g) of Pt-DVTMDS was added and the solution was heated and stirred at 110-115 °C in an oil bath. After 20 minutes, all of the Si-H had been consumed. This was confirmed by the disappearance of the Si-H group in the FTIR spectra (see Fig. 1). 0.17 g (for a total of 0.736 g, 0.00353 mol, r = 1.23) of HMTS was added to the reaction mixture so that excess Si-H was detected in the FTIR spectra. Five drops (~ 0.058 g) of the catalyst were added in order to terminate the polymer with vinyl groups. Polymerization took place in a three-neck round-bottom flask using a reflux set-up in an oil bath at 100-110 °C for 2 hours while stirring. At the end of the reaction, the catalyst was removed by adding activated carbon followed with filtering of the solution. Toluene was then removed by rotary evaporation. Subsequently, the sample was transferred to a watch glass and

TABLE I. PYSICAL PROPERTIES OF ANALYTES

Analytes	Molar Mass [g/mol]	Area [$Å^2$]	Volume [$Å^3$]
Parathion	291.26	298.26[a]	261.30[a]
Paraoxon	275.20	290.05[a]	251.72[a]

a. Calculation done using semi-empirical computational method at the PM3 level

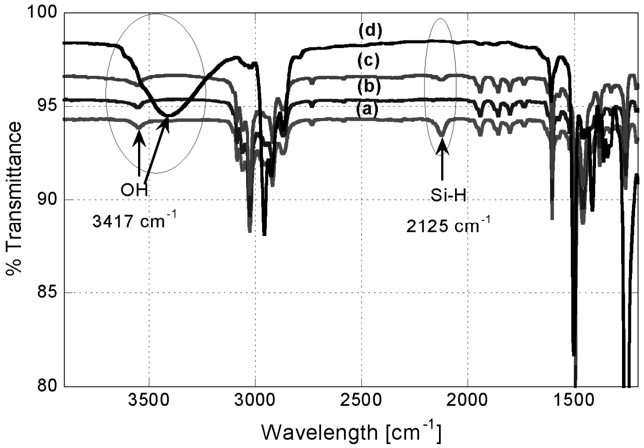

Figure 2. FTIR spectra characterization for the funtionalization of 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS) with 2,2'-diallybisphenol A (BPA) using the hydrosilylation reaction (a) before adding catalyst (b) after adding catalyst and stirring for 20 min (c) after adding excess HMTS and stirring for 20 min (d) final product after evaporation of the solvent

heated under vacuum at 60 °C for 36 hours to remove residual solvent.

C. *Coating Characterization*

Spectroscopic characterization was obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer and Varian 400 NMR spectrometer. Differential Scanning Calorimetry (DSC) was perfomed under nitrogen on a DSC 822e Mettler Toledo Inc (Columbus Ohio) instrument. Glass transition temperature, T_g, is reported as the inflection point in the DSC trace. Decomposition temperature, T_d, is reported as the temperature at 10 % mass loss in Thermogravimetric data. The results obtained for the characterization are shown in Fig. 2 and described as:

FTIR (cm^{-1}): 3411 (O-H stretch), 2953, 2917, 2861 (C-H stretch), 1603 (C=C ring stretch), 1500 (Benzene ring vibration), 1411 (C-OH stretching mode), 1344 (O-H in-plane bending), 1255 (14B, Wilson's notation), 1040 (Si-O-Si stretch), 789 (CH3 rocking). ^{1}HNMR (σ 400 MHz, CDCl3) 7.25 (d), 7.08-7, 15 (m), 6.69 (m), 5.31 (br), 5.03 (br), 4.6 (s), 3.7 (d), 2.5-2.6 (m), 1.32-1.6 (m), 0.5-0.59 (m), -0.02 – 0.1 (m). 13CNMR (CDCl3) σ 153.8, 133.0, 122.1, 127.9, 128.9, 128.1, 125.6, 124.5. T_g (DSC) 4.95 °C, T_d (TGA) 255 °C, ρ_f 1.15 g/cm^3.

D. *Measurement Procedures*

The 36° YX-LiTaO$_3$ guided SH-SAW device, with a center frequency of approximately 103 MHz for an uncoated device, is used in this work as the sensing platform. The measurement set-up consists of the coated guided SH-SAW device, a flow cell for exposing the coated device to the solution of interest, a peristaltic pump, a vector network analyzer (VNA), and a PC-Based HP VEE program for collecting data (loss, phase, frequency, and temperature). In this study, temperature control of the sensor was achieved by placing the device holder in contact with a Peltier thermo-electric cooler (TEC) module. The TEC was mounted on a heat sink and placed in a temperature controlled chamber. A MAX1978 PC board, a DC power supply, and a 10 kΩ NTC thermistor (YSI 44006) was used to implement a temperature control system for the Peltier TEC module.

Before depositing the film, the devices are first cleaned for 3 min in ultrasonic baths of chloroform, acetone, and 2-propanol, respectively. The devices are then rinsed with Milli-Q de-ionized (DI) water (resistivity 18.2 MΩ-cm) and dried with nitrogen. Afterwards, BPA-HMTS solutions of either 2.8 %wt or 4.6 %wt prepared in chloroform was spin coated at 3000rpm for 33s (3s ramp time and 30s holding time) using a P6708D spin coater (Specialty Coating Systems) to obtain 0.3 μm and 0.5 μm – thick layers, respectively. The coated device was allowed to dry at room temperature 21.7 – 22.5 °C in a desiccator for at least 15 hours. The film thickness was calibrated using identical coating conditions to deposit films on glass slides having the same dimensions as the devices. Due to the rubbery nature of the BPA-HMTS, a layer of chromium was deposited over the entire surface so that a profilometer could be used for step-height measurement.

A reference solution was created by mixing 960 mL of phosphate buffer solution (PBS) [pH = 6.20 ±0.05] with 1.11 mL of methanol and stirring for 1 hour at 1000 rpm. Afterwards, a concentrated solution of parathion and paraoxon were prepared by mixing 25.8 μL and 25.7 μL in 3 mL of methanol, respectively. The solution was stirred at 1000 rpm for 15 minutes. From each stock solution, 140 μL aliquots were added to 120 mL of phosphate buffer solution PBS and stirred at 600 rpm for 2 hours to create a solution of approximately 12.62 mg/L (ppm) parathion and 12.61 mg/L (ppm) paraoxon, respectively. Each solution is then diluted with the reference solution to obtain desired concentrations. It is noted that the pH of the solutions is that the buffer.

A typical experimental run is started by exposing the coated device to the reference solution at a flow rate of 0.70 mL/min until the frequency response is stable. The coated device is then exposed to various analyte concentrations. Between analyte exposures, the sensor response was returned to its initial value by flushing the flow-cell with the reference solution. The differential measurement thus reflects the sensor response due to perturbations caused by only analyte absorption.

IV. RESULTS AND DISCUSSION

Several experiments were conducted for two analyte/coating pairs for the same coating thickness. It is noted that the analytes (parathion and paraoxon) have nearly identical masses and volumes (see Section III). Fig. 3 shows sensor responses (frequency shift) for a guided SH-SAW sensor coated with 0.5 μm-thick BPA-HMTS exposed to various concentrations of parathion (0.5–2.5 mg/L) and paraoxon (1-3 mg/L) in aqueous solutions. The reversible nature of the sensor response indicates that analyte/coating interaction is physical rather than chemical and the analyte/coating interaction is reversible. Therefore, the present sensor could be reused. Within the measured range, the frequency shift (*Δf*) is linear with analyte concentration

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[1] Assignment of benzene ring vibrations.

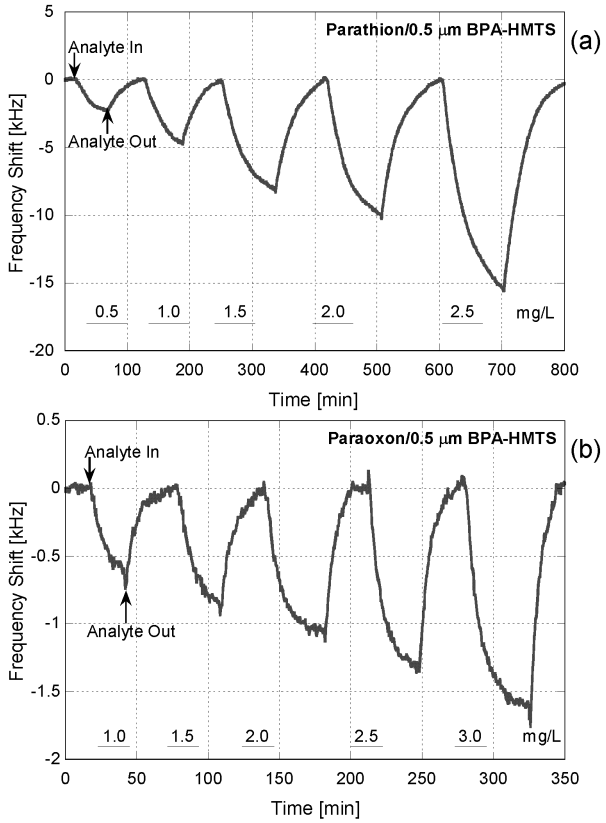

Figure 3. Measured frequency shifts in the detection of (a) 500 μg/L (ppb) to 2.5 mg/L (ppm) of parathion and (b) 1 mg/L (ppm) to 3 mg/L (ppm) of paraoxon using 0.5 μm-thick BPA-HMTS on LiTaO3 SH-SAW device.

and the downward shift indicates that analyte/coating interaction produces a plasticization effect in addition to mass loading. Preliminary measurement for concentrations of parathion greater than 3 mg/L suggests that as viscoelastic changes increases, the slope for the sensitivity curve changes. The sensitivity of the BPA-HMTS towards the analytes was evaluated using the relation *Δf/ΔC*, where *ΔC* is the change in concentration. It is noted that *Δf* is determined when the response has reached steady-state upon exposure to a given concentration of analyte. Equation (2) gives the sensitivities in the present experiments.

$$\begin{cases} \Delta f_{BPA-HMTS} = -6.0128(kHz/ppm)\cdot C_{parathion} \\ \Delta f_{BPA-HMTS} = -0.547(kHz/ppm)\cdot C_{paraoxon} \end{cases} \tag{2}$$

It is noted that even though parathion is only 5.8% heavier than paraoxon (because the sulfur atom is heavier than the oxygen atom), BPA-HMTS exhibited about 10 times higher sensitivity. This result suggests that mass loading may not be the dominant contribution to the measured frequency shift and that the analyte-coating interaction is more significant for parathion i.e., the partition coefficient for parathion/BPA-HMTS is larger than for paraoxon/BPA-HMTS. It is noted that measurement of the analyte/coating partition coefficient using similar methods described in [13, 14] will provide further insight into the nature of the analyte/coating interaction. It is seen in Fig. 3 that the absorption times for parathion and paraoxon are different. The absorption time depends on the coating properties (i.e., thickness and porosity) and the absorption kinetics (i.e., surface penetration and diffusion). From previous work [5], it was observed that the absorption process for parathion was penetration limited. Therefore, for the same coating thickness and surface porosity, the difference in absorption time for parathion and paraoxon may be attributed to their molecular sizes. Note that paraoxon is only 3.8% smaller than parathion (see Table I). Furthermore, since the coating is partially selective, the difference in absorption time can be used to improve selectivity, especially for the case where the analytes have similar steady-state responses (see Fig. 4).

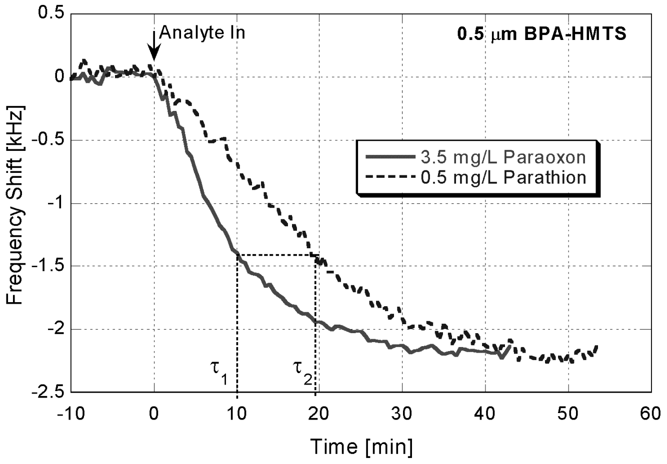

Figure 4. Sensor responses with similar steady-state values, but different absorption times. Increased selectivity is achieved using this difference in the absorption time (paraoxon (τ_1 = 10 min) and parathion (τ_2 = 20 min)).

The limit of detection (LOD) of a chemical sensor is defined as the minimum measurable concentration that corresponds to a frequency shift no smaller than three times the root-mean-square noise level [8, 16]. It is a function of both the sensitivity and measurement noise. Using this definition and eq. (2), a limit of detection of 20 μg/L (ppb) and 100 μg/L (ppb) is estimated for parathion and paraoxon respectively, for the present non-optimized sensor.

Fig. 5 compares the performance of BPA-HMTS to PECH. Here, the same thicknesses of the polymers were deposited on the SH-SAW device on $LiTaO_3$ and exposed to 4 mg/L of parathion. Note that the sensor responses are allowed to run longer than necessary for the purpose of comparison and the sensor response time, t_{90}, is given by 2.3*absorption time. Comparing the glass transition temperature (T_g) for PECH (-25.5 °C) to the T_g for BPA-HMTS (4.95 °C), it is expected that PECH will be more rubbery at room temperature [15] and thus exhibit a faster absorption process. However, from the measurements, it is observed that the sensor response time is decreased by at least 60% without loss of sensitivity for BPA-HMTS. The faster response time of BPA-HMTS is due to the inorganic part of the polymer i.e., HMTS. The porosity of HMTS increases the surface-to-volume ratio. As a result, parathion is able to penetrate the surface of the coating rapidly and hence a faster

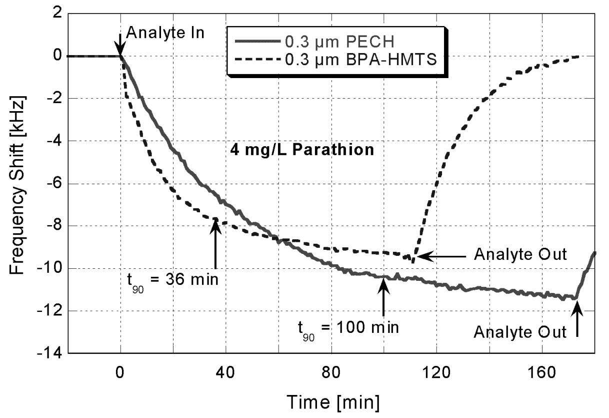

Figure 5. Measured frequency shift in the detection of 4 mg/L (ppm) parathion using 0.3 μm-thick PECH and BPA-HMTS on SH-SAW device.

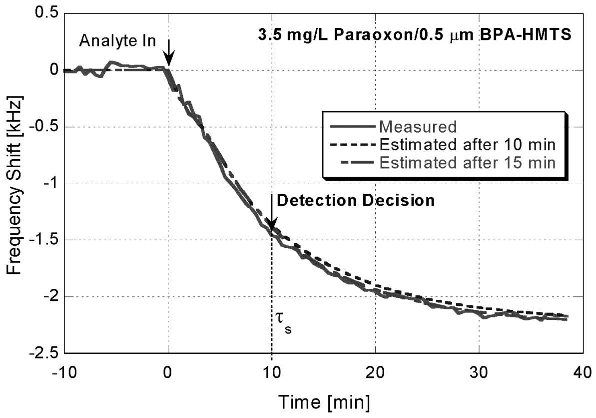

Figure 6. Estimated output obtained using an extended Kalman filter for the detection of 3.5 mg/L (ppm) paraoxon using 0.5 μm-thick BPA-HMTS on $LiTaO_3$ SH-SAW device. On-line predictions were done using the first 10 and 15 minutes of measured data. Absorption time (τ_s) and point of detection decision are shown.

absorption process. The sensitivity exhibited by BPA-HMTS is due to the organic part i.e., BPA. BPA has hydroxyl groups which provide targeted sites for hydrogen-bond interaction.

After achieving a 60% reduction in the sensor response time, it is still possible to speed up the time required for analyte identification and quantification. This can be done by using nonlinear estimation to model sensor and sensor responses [5, 16]. This allows for the extended Kalman filter (EKF) to be used as an on-line technique to extract the absorption time and estimate the entire sensor response before equilibrium is reached. Consequently, an additional 50% reduction in the time required for analyte identification and quantification is possible by processing the measured data on-line. In Fig. 6, it is seen that there is very good agreement between the measured response and the estimated response using just 10 minutes of measured data. Therefore, analyte identification and quantification can be done after 10 minutes instead of waiting until steady-state.

V. CONCLUSIONS

A partially selective, water-stable, hybrid coating (BPA-HMTS) has been synthesized and characterized for rapid absorption of OPs. With this coating, under the same experimental conditions i.e., thickness, a 60% reduction in the sensor response time has been achieved over PECH without loss in sensitivity. Concentrations as low as 500 μg/L (ppb) parathion have been measured. This is significantly much lower than the typical concentrations found on agricultural produce (≥ 10 ppm). For an absorption process that is penetration limited, the porosity of the coating dictates the absorption time of OPs rather than the glass transition temperature. Even though paraoxon is only 3.8% smaller than parathion, its absorption time is 50% faster than parathion. This transient information can be used to improve analyte recognition. Furthermore, using on-line sensor signal processing, allows for a further reduction (at least 50%) in the time required for analyte identification and quantification. The different sensitivity levels exhibited by the coating towards the analytes suggests that the coating has different partition coefficients for the analytes, even though the analytes have only one atom difference in their chemical structures. With the present non-optimized chemical sensor, a limit of detection of 20 μg/L (ppb) for parathion and 100 μg/L (ppb) for paraoxon can be achieved.

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