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# Online Drift Compensation for Chemical Sensors Using Estimation Theory

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# Online Drift Compensation for Chemical Sensors Using Estimation Theory

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*Abstract*—Sensor drift from slowly changing environmental conditions and other instabilities can greatly degrade a chemical sensor's performance, resulting in poor identification and analyte quantification. In the present work, estimation theory (i.e., various forms of the Kalman filter) is used for online compensation of baseline drift in the response of chemical sensors. Two different cases, which depend on the knowledge of the characteristics of the sensor system, are studied. First, an unknown input is considered, which represents the practical case of analyte detection and quantification. Then, the more general case, in which the sensor parameters and the input are both unknown, is studied. The techniques are applied to simulated sensor data, for which the true baseline and response are known, and to actual liquid-phase SH-SAW sensor data measured during the detection of organophosphates. It is shown that the technique is capable of estimating the baseline signal and recovering the true sensor signal due only to the presence of the analyte. This is true even when the baseline drift changes rate or direction during the detection process or when the analyte is not completely flushed from the system.

*Index Terms*—Baseline drift compensation, chemical sensors, sensor drift, sensor signal processing.

## I. INTRODUCTION

SENSOR signal drift is a common problem that occurs in most chemical sensors; this is especially true in the field, where the sensor's environment is not controlled and temperature and humidity can fluctuate drastically depending on the time of the day or weather conditions. Two types of drift have been identified: baseline fluctuations and sensitivity changes [1]. Device and coating degradation and aging can cause sensitivity changes in a chemical sensor as well as changes in the speed of response and other transient parameters. This "device drift" due to aging often occurs over long periods of time such as days or weeks. When a sensor suffers from device drift, it may need to be recalibrated periodically. In a sensor array, device drift manifests itself as a slow movement, in the feature space, of the clusters corresponding to a specific analyte. In this case, the sensor array may need to be periodically retrained in order to correct for device sensitivity drift.

Baseline fluctuations (or baseline drift), on the other hand, are caused by slowly changing environmental conditions such as humidity, temperature, and pressure as well as trace amounts of contaminants. Baseline drift occurs rapidly compared to device drift and may occur over a period of several minutes. These fluctuations can contribute significantly to the measured response (output) of the devices. In a single sensor, baseline drift will lead to incorrect quantification of the analyte. However, in sensor arrays, baseline drift will add a random (although correlated among sensors) contribution to the steady-state features used in the identification process.

In order to reduce the effects of baseline drift, a difference measurement between the steady-state response and the baseline (before exposure) is used to quantify the analyte. This technique works well when the sensor responds rapidly such that the baseline does not have time to drift before the sensor's steady-state response can be measured. However, if the sensor response is slow, the baseline signal may drift during exposure. In this case, the difference measurement using the baseline response before analyte exposure will fail to eliminate the contributions of the drift that occurred during the time required for the response to reach steady state. A more accurate approach to this problem is to estimate the baseline signal at the instant that the steady-state measurement is recorded. If the baseline is estimated accurately, then the contribution of baseline drift to the sensor response can be eliminated. (It is noted that subtracting the baseline before exposure is a specific case of the more general baseline estimation approach. In this case, the implicit assumption is that the baseline is constant during exposure.)

In this paper, estimation theory is used to compensate for baseline drift in the response of chemical sensors. Several aspects of the drift problem are considered. For example, methods for estimating baseline drift are developed when the sensor response is very slow, when the sensor is irreversible, when baseline drift changes rate and even direction during the exposure, and even when the sensor parameters (sensitivity and response time) are unknown and must be estimated. The technique is online, as the drifting baseline is estimated and separated from the sensor signal as the data is collected. This makes it possible to perform baseline drift compensation without using a standard method such as interpolation or extrapolation, which requires the sensor response to first completely reach equilibrium. In the case of interpolation, the analyte must also be completely flushed from the sensor before performing baseline compensation, and thus before quantification. Furthermore, interpolation and extrapolation techniques may not be sufficiently accurate as they utilize information only from data gathered before the sensor is exposed to the analyte and after desorption, thus ignoring any information during the response that may be used
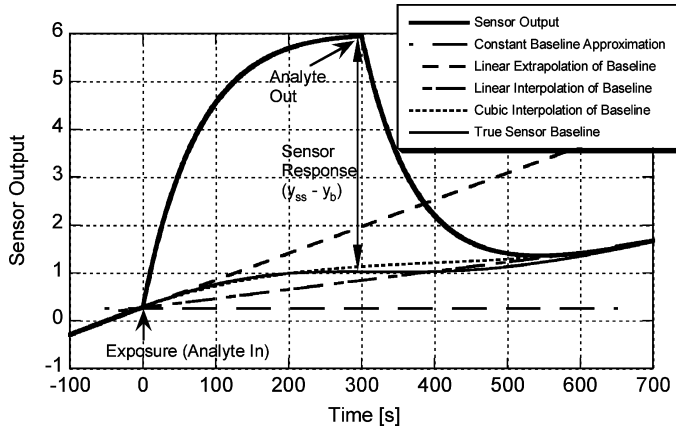
Fig. 1. Illustration of several baseline estimation techniques.

to estimate the baseline. Two different formulations of the proposed technique will be demonstrated. The choice of the selected formulation depends on the information available about the sensor device. An unknown input is considered first; this represents the practical case of analyte detection and quantification. Then, the more general case, in which the sensor parameters and the input are both unknown, is studied.

## II. BACKGROUND

### A. Baseline Correction Techniques

In order to reduce the contribution of the baseline to the sensor response, the baseline is often subtracted from the steady-state response. This is represented by

$$z = y_{ss} - y_b \tag{1}$$

where $y_{ss}$ is the sensor output measured at the steady state, $y_b$ is the sensor baseline, and $z$ is the measured difference response at the steady state. (It is noted that several other steady-state features can be used; often the physics of the sensor device determines the appropriate choice [2].) The sensor baseline should be measured at the same time that the steady-state response is measured (see Fig. 1). If this is not the case, drift that occurs during exposure may still contribute significantly to the measured difference response. Because it is difficult to directly measure the sensor baseline during exposure, it must be estimated using the information in the sensor output. Reference sensors can be used to try to measure the baseline signal [3]. However, because the reference sensor, by definition, has been modified so that it does not respond to the analyte, it likely does not have a baseline identical to that of the sensing line.

The techniques used to estimate the baseline during the sensor response often involve extrapolation or interpolation of the baseline using information obtained before the analyte comes into contact with the sensor and after the analyte has been completely flushed from the sensor. Extrapolation techniques have the advantage of requiring only the data obtained before the sensor is exposed to the analyte. Alternatively, interpolation can increase accuracy by using data obtained both before exposure and after the analyte has been flushed from the sensor (i.e., after desorption). However, this is done at the expense of the added time required for the analyte to be flushed from the sensor before the

baseline can be estimated and the overall response determined. Fig. 1 shows a typical sensor response superimposed on a fluctuating baseline as well as four possible techniques for estimating the baseline. In this case, cubic interpolation yielded the best estimate of the baseline and thus the best estimate of the true difference response (3% error compared to 4%, 14%, and 20% error for linear interpolation, constant baseline, and linear extrapolation, respectively). However, in order to use cubic interpolation, the baseline and the drift rate must be measured before exposure and after the analyte has been flushed from the sensor. In many cases, this will more than double the time required to quantify the analyte, because one must wait for desorption to be complete. Furthermore, interpolation is difficult to use if the sensor does not return to the baseline when the analyte is flushed from the system.

It is noted that estimation of the baseline may not be necessary for sensors that respond rapidly. If the sensor responds rapidly, the baseline, which is slowly changing in nature, does not have time to substantially change before the sensor reaches equilibrium. Thus, one can simply measure the baseline response before the sensor is exposed to the analyte and use it as an estimate of the baseline at steady state. Conversely, the baseline may change significantly over the course of a slow response. In those cases, the drift rate and even the drift direction are likely to change. As a result, standard baseline correction techniques are not sufficient for sensors with a relatively long response time. However, by treating the baseline as a state variable, estimation theory can be used to estimate the baseline using all available data, without waiting until after desorption.

### B. Estimation Theory

In this paper, a state estimation technique (Kalman Filtering) will be used to perform baseline correction. This section contains a brief overview of some of these estimation techniques. The Kalman filtering approach is used for two important reasons. First, it can be performed online, as measurements are obtained. Second, it has low memory and computational requirements making it suitable for implementation on relatively simple microcontrollers. This is important for small, portable, and cost effective sensor devices that can detect, in real time, the presence of dangerous chemicals even in the presence of baseline drift.

Consider a system of the form

$$\mathbf{x}_{k+1} = f(\mathbf{x}_k, \mathbf{u}_k, \mathbf{v}_k) \tag{2a}$$
$$\mathbf{y}_k = h(\mathbf{x}_k, \mathbf{w}_k). \tag{2b}$$

The state vector $\mathbf{x}_k$ can be estimated by measuring the output (vector) of the system, $\mathbf{y}_k$. The control input vector $\mathbf{u}_k$ is assumed known, and the process noise $\mathbf{v}_k$ and measurement noise $\mathbf{w}_k$ have zero means and covariance matrices of $Q$ and $R$, respectively. If (2a) and (2b) are linear, the Kalman filter [4], [5] can be used to estimate the state variables. However, for a nonlinear system, one common approach is to perform a Taylor series expansion about the current state estimate. This leads to the extended Kalman filter (EKF) when only the linear terms are used [5]–[7] and the second-order extended Kalman filter (SOEKF) [8] when the terms of order less than or equal to two are used.

Extended Kalman filtering consists of starting with an initial estimate of the state vector, $\hat{\mathbf{x}}_0^- = E\{\mathbf{x}_0\}$, and the covariance

of the error in the estimate, $P_0^-$. (Note that $\hat{\mathbf{x}}$ is used to represent the state estimate and the superscript "minus" represents the estimate/error covariance before updating the estimate using information from the measurement, whereas a superscript "plus" will be used to represent the estimate/error covariance after updating the estimate with the measurement). After each measurement is made, the state estimates are updated based on the newly acquired information using the following equations:

$$\hat{\mathbf{x}}_k^+ = \hat{\mathbf{x}}_k^- + P_k^- C_k^T \left( C_k P_k^- C_k^T + G_k R G_k^T \right)^{-1}$$
$$\times \left[ \mathbf{y}_k - h \left( \hat{\mathbf{x}}_k^-, 0 \right) \right] \quad (3a)$$
$$P_k^+ = P_k^- - P_k^- C_k^T \left( C_k P_k^- C_k^T + G_k R G_k^T \right)^{-1} C_k P_k^-. \quad (3b)$$

After the measurement update is completed, the state estimate and error covariance must be updated in time using the system model

$$\hat{\mathbf{x}}_{k+1}^- = f \left( \hat{\mathbf{x}}_k^+, \mathbf{u}_k, 0 \right) \quad (3c)$$
$$P_{k+1}^- = A_k P_k^+ A_k^T + F_k Q F_k^T \quad (3d)$$

where matrices $A_k$, $C_k$, $F_k$, and $G_k$ are defined as

$$A_k = \left. \frac{\partial f}{\partial \mathbf{x}} \right|_{\substack{\mathbf{v}_k=0 \\ \mathbf{u}_k \\ \mathbf{x}_k = \hat{\mathbf{x}}_k^+}} \quad (4a)$$

$$C_k = \left. \frac{\partial h}{\partial \mathbf{x}} \right|_{\substack{\mathbf{w}_k=0 \\ \mathbf{x}_k = \hat{\mathbf{x}}_k^-}} \quad (4b)$$

$$F_k = \left. \frac{\partial f}{\partial \mathbf{v}} \right|_{\substack{\mathbf{v}_k=0 \\ \mathbf{u}_k \\ \mathbf{x}_k = \hat{\mathbf{x}}_k^+}} \quad (4c)$$

$$G_k = \left. \frac{\partial h}{\partial \mathbf{w}} \right|_{\substack{\mathbf{w}_k=0 \\ \mathbf{x}_k = \hat{\mathbf{x}}_k^-}}. \quad (4d)$$

The above formulation of the extended Kalman filter can also be used as a parameter estimator for linear systems [9]. This is very useful if one of the parameters of the system (for example, the absorption time constant of a sensor) is unknown and must be estimated along with the states of the system. In a later section, this technique will be used to perform baseline correction while simultaneously estimating the baseline. The Kalman filter allows one to correct the estimate of the baseline in real time as the sensor response samples are being collected.

## III. THEORY

### A. Modeling the Sensor Response

When exposed rapidly to an analyte of ambient concentration, $C_{\text{amb}}(t) = C_{\text{max}} u_s(t)$, most sensors will respond rapidly at first and then slow as they reach equilibrium. This type of response can, in many cases, be effectively modeled by an exponential rise to a steady state governed by a single time constant, $\tau_s$. In this case, the sensor response due to exposure of analyte is given by

$$y(t) = s\gamma C_{\text{max}} \left[ 1 - \exp\left( -\frac{t}{\tau_s} \right) \right] u_s(t) \quad (5)$$

where $s\gamma$ is the sensitivity of the sensor ($s$ represents the sensitivity of the sensor platform, whereas $\gamma$ is the ability of the

polymer coating to absorb the analyte, similar to the partition coefficient). If (5) does not accurately fit the response and the dynamics of the chemical/physical processes that cause the sensor to respond are known, then the equations for the specific sensor should be used. Some examples for which (5) may not be adequate include sensors for which absorption is rate limited by Fickian diffusion within the chemically sensitive coating [10], chemical sensors that undergo multilayer adsorption [11], and polymer-coated microcantilever sensors operating in the static mode [12].

Most sensor systems are implemented with a microcontroller for which the sensor outputs are sampled at discrete time instants. For that reason, a difference equation must be obtained whose solution to a step input satisfies (5) for $t = kT$, where $T$ is the sampling rate. (The discrete-time Kalman filter is chosen because the sensor output is sampled at discrete time instances.) One possible discrete-time, state-space system is

$$C_{k+1} = (1 - T/\tau_s)(\gamma C_{\text{amb},k} - C_k) + C_k \quad (6a)$$
$$y_k = sC_k \quad (6b)$$

where $C_k$ is the concentration (or amount) of the sorbed analyte at $t = kT$. The discrete-time model represented by (6a) and (6b) has been successfully employed in order to predict the steady state of the sensor response well before equilibrium using the EKF [13], [14].

As previously indicated, baseline drift is generally caused by a slowly changing environmental condition such as temperature, humidity, or the presence of trace amounts of contaminants. Because the drift is, by nature, quite slow, it is noted that the baseline signal will appear linear in time spans on the order of a few sampling times. Thus, two states are defined to represent the baseline drift. The drift rate $\lambda_k$ is added to the current baseline signal $b_k$ at each sampling instant. This yields the following two state equations, which represent the linear drift

$$\lambda_{k+1} = \lambda_k + z_k \quad (7a)$$
$$b_{k+1} = \lambda_k + b_k \quad (7b)$$

where a drift rate disturbance $z_k$ has been added to account for the possibility of the baseline drift changing rate or even changing direction over a relatively long time span.

The output of the sensor is then a combination of signal due to sorption of analyte, the baseline signal, and the noise in the system. Adding measurement noise and process noise to (6a), one obtains a state-space system for which baseline drift is explicitly modeled as

$$\bar{C}_{k+1} = (1 - T/\tau_s)\bar{C}_k + T/\tau_s (u_k - u_{k+\Delta}) + v_k \quad (8a)$$
$$\lambda_{k+1} = \lambda_k + z_k \quad (8b)$$
$$b_{k+1} = \lambda_k + b_k \quad (8c)$$
$$y_k = d\bar{C}_k + b_k + w_k. \quad (8d)$$

In the above equations, $y_k$ is the measured output of the sensor, $\bar{C}_k$ is the absorbed analyte concentration normalized by the total analyte concentration that will be absorbed at equilibrium, $\gamma C_{\text{max}}$, and $ds\gamma$ is the steady-state response. The goal of baseline compensation is to separate the baseline signal from the signal due to analyte exposure, i.e., to determine $d\bar{C}_k$. This process will be performed using the (extended) Kalman

filter for two different cases depending on the type of information known about the sensor. In each, it will be assumed that the input to the system $C_{\mathrm{amb},k}$ is a rapidly applied step in concentration (along with a rapid flush). Therefore, $C_{\mathrm{amb},k}$ can be replaced with $C_{\max}(u_k - u_{k+\Delta})$ where $\Delta$ is the sample at which the analyte is flushed from the system. This would be a valid assumption if the analyte to be analyzed is collected over a period of time and then presented rapidly to the sensor. Once the sensor reaches equilibrium, the analyte could be flushed from the system using the reference solution. For environmental monitoring, this process could then be repeated at regular time intervals. This repeated collection, rapid exposure, and purge process was proposed to track baseline instabilities for sensors that respond rapidly, such that the baseline does not drift significantly during exposure [1].

### B. Case 1: Sensor Parameters Known

In this case, it will be assumed that the sensor transient response parameters are known, but the input $C_{\max}$ is unknown. This corresponds to the case of detection and quantification of a (bio)chemical analyte. Here, the steady-state response $d$ is unknown, but can be estimated by defining it as a state variable [9], [13], [14]. Once estimated, this term can be used to find the ambient concentration using the known sensitivity. With the new state variable, $d_k$ (the steady-state response $d$ is now represented as $d_k$ because this parameter can change as different concentrations are injected into the system), the system used to simultaneously estimate the steady-state response while performing online baseline compensation becomes

$$\bar{C}_{k+1} = (1 - T/\tau_s)\,\bar{C}_k + T/\tau_s\,(u_k - u_{k+\Delta}) + v_k \quad (9a)$$
$$\lambda_{k+1} = \lambda_k + z_k \quad (9b)$$
$$b_{k+1} = \lambda_k + b_k \quad (9c)$$
$$d_{k+1} = d_k + \delta_k \quad (9d)$$
$$y_k = d_k \bar{C}_k + b_k + w_k, \quad (9e)$$

which involves a nonlinear measurement equation. Here, $\delta_k$ is a disturbance that accounts for the possibility that the steady-state response, $d_k$, changes. This is usually not a factor during a single exposure because $C_{\max}$, and thus, the steady-state response should remain constant for a single exposure. However, when multiple exposures are run continuously, the drift rate and baseline should "carry over" to the next exposure, whereas the $d_k$ does not. For this reason, the disturbance term, $\delta_k$, can be defined as zero except at the beginning of each new exposure. At this point, it has a high variance, representing the uncertainty in the steady-state value of the next exposure.

The EKF could be used to estimate the four state variables in this system. However, by reformulating the problem, it is possible to still use the Kalman filter. Equations (9a)–(9d) can be used to rewrite (9e), thus eliminating the sorbed analyte concentration from the state variables. The modified state equations are given by

$$\lambda_{k+1} = \lambda_k + z_k \quad (10a)$$
$$b_{k+1} = \lambda_k + b_k \quad (10b)$$
$$d_{k+1} = d_k + \delta_k \quad (10c)$$
$$y_k - (1 - T/\tau_s)\,y_{k-1} = (1 - T/\tau_s)\,\lambda_k + T/\tau_s b_k$$
$$+ T/\tau_s d_k u_{k-1} + w'_k. \quad (10d)$$

Here, the fact that $\lambda_{k+1} \approx \lambda_k$ and $d_{k+1} = d_k$ (except for the first sample of a new exposure), has been used. For this reason, the above model does not hold for the first sample of a new exposure. Thus, this first measurement, $y_k - (T/\tau_s)y_{k-1}$, should not be used to correct any of the estimates (the estimates should still be updated). Note that because of the reformulation, the covariance matrix of the process noise $Q$ has the form

$$Q_k = \begin{bmatrix} \sigma_z^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{\delta,k}^2 \end{bmatrix} \quad (11)$$

and is time-varying because $\sigma_{\delta,k}^2$ is large only at the start of a new exposure and is zero otherwise.

### C. Case 2: Sensor Parameters Unknown

When the sensor parameters and the input are unknown, they must all be estimated. In this case, the state vector is augmented with the two parameters to be estimated ($d$ and $\tau_s$). This leads to the nonlinear system described by

$$\bar{C}_{k+1} = (1 - T/\tau_{s,k})\,\bar{C}_k + T/\tau_{s,k}\,(u_k - u_{k+\Delta}) + v_k \quad (12a)$$
$$\lambda_{k+1} = \lambda_k + z_k, \quad (12b)$$
$$b_{k+1} = \lambda_k + b_k \quad (12c)$$
$$d_{k+1} = d_k + \delta_k \quad (12d)$$
$$\tau_{s,k+1} = \tau_{s,k} + \alpha_k \quad (12e)$$
$$y_k = d_k \bar{C}_k + b_k + w_k. \quad (12f)$$

A bank of several EKFs can be used to estimate the five states of the system. The bank of EKFs are combined to form a Gaussian Sum Filter as presented in [15], [16]. Initially, each of the EKFs are given the same weight, i.e.,

$$w_{p,0} = \frac{1}{n_e} \quad (13)$$

where $n_e$ is the number of individual estimators being used and the subscript $p$ is used to indicate the weight of the $p$th EKF in the filter bank. During the measurement update, the estimator weights are also updated by evaluating how well the measurement compares to each EKF's estimate of the measurement, $\hat{\mathbf{y}}_{p,k}$. This is done using the individual EKF's estimate of the measurement and its estimate of the error covariance in the measurement. The normal density function is then used to estimate the likelihood of the measurement given the EKF's estimates. This yields the weight update equations given by

$$w_{p,k} = \frac{1}{c}\,|S_{p,k}|^{-\frac{1}{2}}$$
$$\times \exp\left\{ -\frac{1}{2}\,[\mathbf{y}_k - \hat{\mathbf{y}}_{p,k}]^T\,[S_{p,k}]^{-1}\,[\mathbf{y}_k - \hat{\mathbf{y}}_{p,k}] \right\} w_{p,k-1}$$
$$(14a)$$

where

$$S_{p,k} = C_{p,k} P_{p,k}^- C_{p,k}^T + R_{p,k} \quad (14b)$$
$$\hat{\mathbf{y}}_{p,k} = h\left( \hat{\mathbf{x}}_{p,k}^- \right) \quad (14c)$$

and $c$ is a normalization constant so that the sum of all the weights is equal to one. The estimates from each EKF can then be combined using

$$\hat{\mathbf{x}}_k^+ = \sum_{p=1}^{n_e} w_{p,k} \hat{\mathbf{x}}_{p,k}^+ \tag{15a}$$

$$P_k^+ = \sum_{p=1}^{n_e} w_{p,k} \left( P_{p,k}^+ + \left[ \hat{\mathbf{x}}_{p,k}^+ \right] \left[ \hat{\mathbf{x}}_{p,k}^+ \right]^T \right) - \left[ \hat{\mathbf{x}}_k^+ \right] \left[ \hat{\mathbf{x}}_k^+ \right]^T \tag{15b}$$

which are the mean and covariance of a Gaussian mixture model with component means $\hat{\mathbf{x}}_{p,k}^+$, component covariance matrices $P_{p,k}^+$, and component weights $w_{p,k}$. The disturbance terms in (12d) and (12e) should be utilized in a manner similar to the one described in the previous section, taking nonzero values only at the beginning of a new exposure. In this case, the process noise covariance matrix takes the form

$$Q_k = \begin{bmatrix} \sigma_{v'}^2 & 0 & 0 & 0 & 0 \\ 0 & \sigma_z^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_{\delta,k}^2 & 0 \\ 0 & 0 & 0 & 0 & \sigma_{\alpha,k}^2 \end{bmatrix} \tag{16}$$

and is again time-varying.

## IV. CHEMICAL SENSOR DATA

As previously stated, the techniques will be demonstrated on both simulated data, for which the true baseline signal and response due to analyte exposure are known, and on experimental data collected during the detection of organophosphate pesticides using a guided SH-SAW sensor platform.

The simulated data was produced using the model in (8a)–(8d) with a measurement noise covariance of $225\ \text{Hz}^2$ and a process noise that represented fluctuations of approximately 2% about the nominal ambient concentration. Responses were produced for two different baselines. One for which the drift is rather slowly changing, and a second for which the drift follows a sinusoidal function.

The polymer coated SH-SAW sensor data used in this paper was originally reported in [14]. Poly(epichlorohydrin) (PECH), chloroform (99.8%), methanol (99%), acetone (99%), and phosmet were purchased from Sigma-Aldrich (Milwaukee, WI) and used as supplied in the experiments [14]. The $36°$ YX-LiTaO$_3$ guided SH-SAW device is used in this work as the sensing platform. The devices are fabricated with 10/80-nm-thick Cr/Au split finger pairs interdigital transducers (IDTs) having a periodicity of 40 $\mu$m, which corresponds to an operating frequency of $\sim$103 MHz for the uncoated device. The delay lines have a metallized path to eliminate acoustoelectric interaction with the load. PECH solutions were prepared by dissolving appropriate amounts of the polymer in chloroform to make 2.1 %wt PECH. The polymer solutions were spin-coated on the device surface (over the IDTs and the delay path) and allowed to dry in a desiccator (room temperature of 22 °C) for at least 12 h to obtain an approximate thickness around 1 $\mu$m. Thickness calibration was performed using thickness-shear mode (TSM) resonators in conjunction with the Sauerbrey equation [17]. However, it is noted that the calibration results only in an approximate thickness, as Sauerbrey's equation is not valid for viscoelastic layers [18], [19].

At the molecular level, phosmet is a polar analyte with molecular weight and size of 317.3 amu, 311.58 $\overset{\circ}{\text{A}}^3$. Phosmet is slightly soluble in water but more soluble in methanol, hence the analytes are first dissolved in methanol and then diluted with Milli-Q deionized water (13–14 M$\Omega$ cm) to obtain an aqueous methanol solution. Since water is not the primary solvent, the weight fraction definition for concentration (ppm) is used in this work. The equation used in preparing analyte solutions is given by

$$C_{\text{analyte,ppm}} = \frac{m_{\text{analyte}}}{m_{\text{analyte}} + m_{\text{solvent}} + m_{\text{H}_2\text{O}}} \times 10^6 \tag{17}$$

where $m_{\text{analyte}}$, $m_{\text{solvent}}$, and $m_{\text{H2O}}$ is the mass of analyte, solvent (methanol), and water in grams, respectively.

A typical run started by pumping the reference solution (dilute aqueous methanol solution) through the flow cell at 0.2 mL/min. This flow rate limited the hydrodynamic coupling between the flowing liquid and the crystal surface, but was still fast enough to flush the entire cell in less than five minutes. This ensured that the sensor would see a "step" in analyte concentration that is much faster than the dynamics of the analyte sorption into the polymer coating. After pumping the reference solution through the flow cell until the output was stable, an analyte solution was pumped into the system for detection by the sensor. After reaching equilibrium, the reference solution was again pumped through the system to flush the flow cell and cause the analyte to desorb from the coating. This was repeated periodically for different concentrations. The data shown in this paper corresponds to exposures of two different PECH-coated SH-SAW devices to approximately 5, 10, and 15 ppm of phosmet in the reference solution. Because absorption of the organophosphate from the solution is quite slow, the responses take a long time to reach equilibrium and can drift by a considerable amount during that time making baseline correction necessary.

## V. RESULTS AND DISCUSSION

Here, results of baseline correction will be shown for each of the two cases (unknown analyte concentration and unknown sensor parameters). For each case, the baseline compensation technique is applied first to simulated data, for which the true baseline is known. This makes it possible to compare the estimated baseline and estimated response due to analyte sorption to the true baseline and true response due to analyte sorption. The technique is then applied to polymer-coated SH-SAW sensor data during the detection of aqueous solutions of the organophosphate, phosmet. In the case of actual sensor data, there is no "true" baseline to compare to; however, the results demonstrate the technique's ability to perform on real sensor data for which there may be some mismatch between the model used during the implementation of the Kalman filter and the true physical system of the sensor device.

Fig. 2(a) and (b) shows the results of baseline compensation technique on simulated data assuming that the sorption time constant is known (i.e., case 1). Each response shows a different type of drift (a slowly changing baseline and a sinusoidal baseline). For the two responses [(a) and (b)], the Kalman filter was
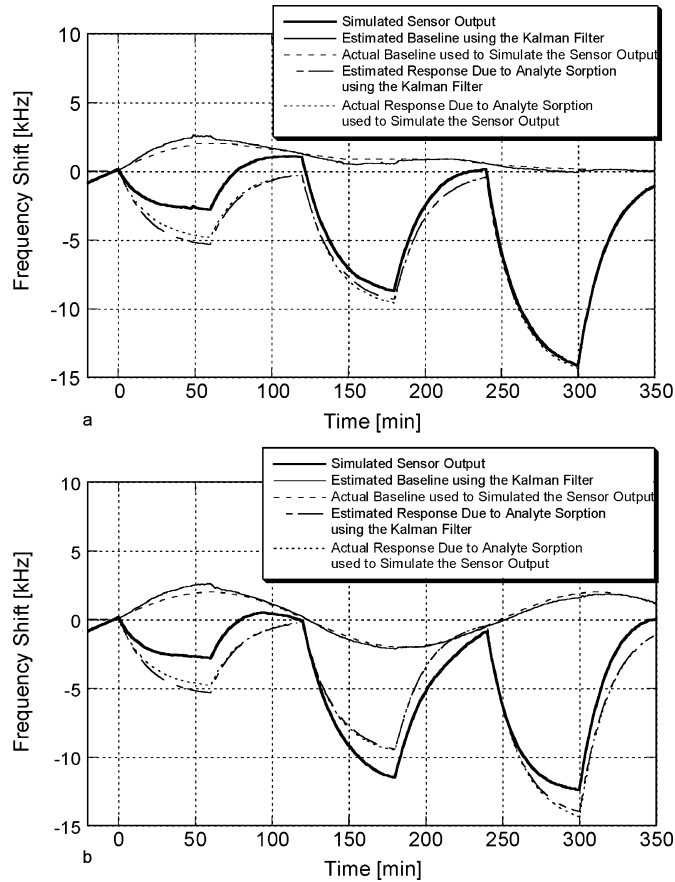
Fig. 2.   Online baseline compensation using the Kalman filter demonstrated on simulated sensor data. This is an example of case 1, where it is assumed that the sorption time constant is known.
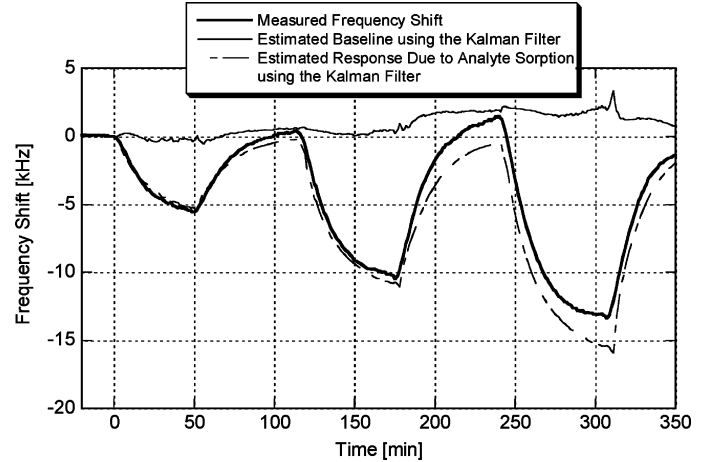


Fig. 3.   Baseline compensation using the Kalman filter performed on data collected from a PECH-coated SH-SAW sensor during the detection of phosmet. This is an example of case 1, where it is assumed that the sorption time constant is known.

set up using $R = 40$ and $\sigma_z^2 = 0.5$ and the known model parameter $\tau_s = 20$ min. In this case, the steady-state value $d_k$ is unknown and must be estimated. In Fig. 2 the estimated baseline and estimated response due only to the analyte compare well with the actual baseline and actual response due to the analyte that were used to simulate the response. The Kalman filter requires an initial estimate of $d_k$, but is relatively insensitive to the value used. In Fig. 2 the initial estimate of $d_k$ was 75% more than the actual value for the first exposure. After the first exposure the current estimate of the steady-state response was carried over to the next exposure (i.e., the initial estimate was 50% less than the actual value for the second exposure and 33% less than the actual value for the third exposure). The respective errors in estimating the response due to analyte sorption are less than 10%, 3%, and 3% for each of the two figures. In all cases, this is still far less error than if no baseline compensation was performed. Note that Fig. 2(a). shows that linear interpolation performs reasonably well for the last two analyte exposures and cubic interpolation performs well in all cases; however, as shown in Fig. 2(b), the performance of linear interpolation is poor when the baseline drift changes direction during the experiment and cubic interpolation fails to capture some of the information. Furthermore, it is important to remember that the Kalman filtering technique is estimating the baseline as the sensor response samples are being collected. Thus, it is not nec-

essary to wait until the entire sensor response has been collected (and the original baseline is reestablished) as in the interpolation techniques. This reduces the time required to estimate the baseline and calculate the response due to analyte sorption.

The results in Fig. 3 show the online baseline correction technique applied to experimentally obtained sensor data as a poly(epichlorohydrin) (PECH)-coated SH-SAW sensor is exposed to aqueous concentrations of 5, 10, and 15 ppm of phosmet. It is noted that what appeared to be a saturation effect in the 15 ppm exposure was in fact caused by baseline drift and compensated for with the Kalman filter technique. Though the true baseline and response due to analyte sorption is unknown in Fig. 3, the result demonstrates that the technique works on real sensor data. However, in some cases the estimated baseline seems to "jump" when the analyte is injected into the system and also when the flush cycle begins. This may be caused by model mismatch between the mathematical model of the sensor system and the actual physical system. Remember that it was assumed that the ambient concentrations "seen" by the sensor can be represented by step functions. This, of course, is not possible, and the true ambient concentration will rise over some finite time, approximately the time required to flush the cell. In the flow system used to collect the data in these experiments, the time required to flush the cell is around 5 min.

To estimate the baseline when the transient response parameters (in this case, the sorption time constant) are not known, a bank of five EKFs in the Gaussian Sum arrangement [15], [16] was used. Each EKF was initialized with the same steady-state response as in the previous case, when it was assumed that the sorption time constant was known. However, each estimator was initialized with a different sorption time constant (15, 20, 25, 30, and 35 seconds for EKF 1–5, respectively). Again, the filter was implemented using $R = 40$ and $\sigma_z^2 = 0.5$. Fig. 4(a) and (b) shows that, even when the sorption time constant is not known, this baseline compensation technique is capable of accurately estimating the baseline, the steady-state response, and the sorption time constant. Additionally, the same technique was applied to the PECH-coated SH-SAW data during an exposure to
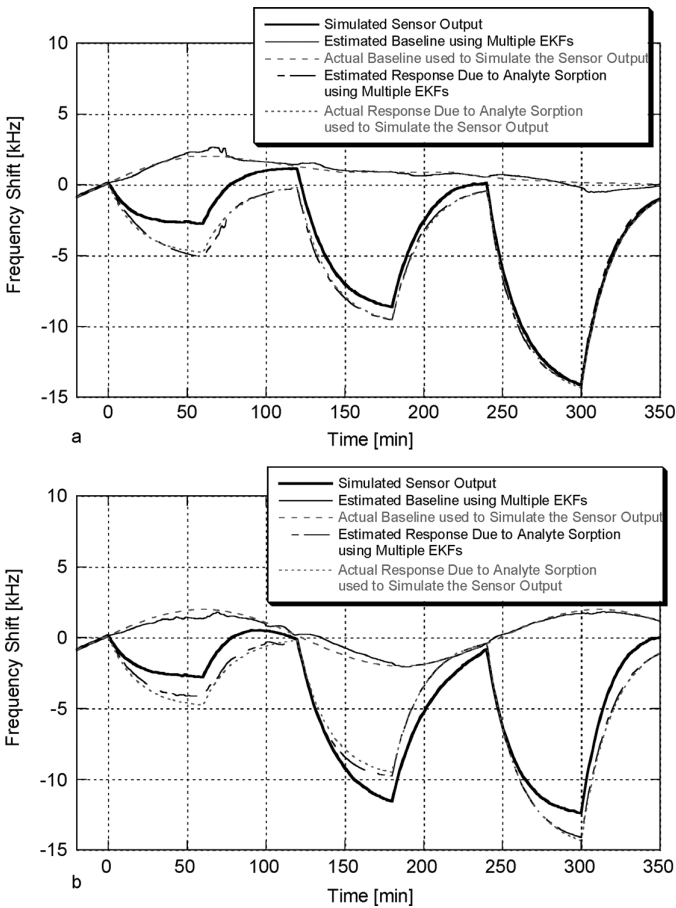
Fig. 4. Online baseline compensation using a bank of Extended Kalman Filters demonstrated on simulated sensor data. This is an example of case 2, where it is assumed that the sorption time constant is not known and must also be estimated.
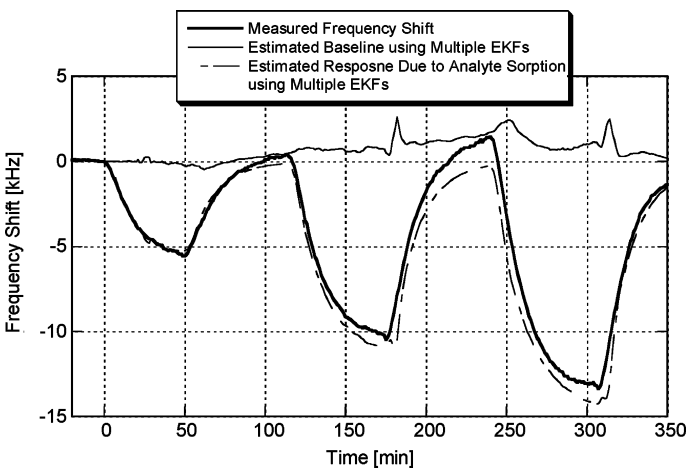


Fig. 5. Baseline compensation using a bank of Extended Kalman Filter performed on data collected from a PECH-coated SH-SAW sensor during the detection of phosmet. This is an example of case 2, where it is assumed that the sorption time constant is not known and must also be estimated.

TABLE I
COMPARISON OF THE ERRORS BETWEEN THE TRUE SENSOR RESPONSES DUE TO ANALYTE EXPOSURE AND THE CALCULATED RESPONSES USING THE KALMAN FILTER (KF)-BASED ESTIMATION TECHNIQUE AND THE TWO INTERPOLATION (LINEAR AND CUBIC) TECHNIQUES. CASE 1: SENSOR DYNAMICS KNOWN; CASE 2: SENSOR DYNAMICS UNKNOWN

**Comparison of Baseline Correction Techniques**

| Analyte Exposure | Steady-state response kHz | KF-based estimation (case 1) kHz - %err | KF-based estimation (case 2) kHz - %err | Linear Interpolation kHz - %err | Cubic Interpolation kHz - %err |
|---|---|---|---|---|---|
| 1 | 4.8 | 5.3  11.1% | 4.2  13.3% | 2.7  46.7% | 4.2  13.3% |
| 2 | 9.5 | 9.4  1.1% | 9.8  3.2% | 11.2  17.9% | 9.8  3.2% |
| 3 | 14.3 | 14.0  2.1% | 14.1  1.4% | 11.8  17.5% | 13.1  8.4% |

exposure and the calculated responses using the Kalman-filter-based estimation technique and the two interpolation (linear and cubic) techniques.

## VI. SUMMARY AND CONCLUSION

A real-time online technique for baseline drift compensation was demonstrated. Two cases were investigated. The first case is applicable for the detection and quantification of chemical analytes (i.e., when the sensor parameters are known but the input unknown). The second case is applicable when the identity of the analyte is unknown and the various target analytes have a wide range of sorption time constants into the polymer coating (the sensor sorption time constant, sensitivity, and the ambient analyte concentration are all unknown).

The technique was demonstrated on sensors for which the analyte sorption is reversible. The presented baseline compensation technique is online. The results obtained during sorption, and thus the recovered differential response, do not depend on whether or not the sensor returns to the baseline. The technique could be modified in order to perform baseline compensation on sensors for which the response does not return to the original baseline or even for one-time-use sensors. In this case, the Kalman filter technique could be applied when the sensor is exposed to the analyte. This would perform baseline compensation during sorption so that the response due to the analyte can be recovered, and the differential response measured. If the sensor can still be utilized, the Kalman filter algorithm could then be stopped and reinitialized with the new baseline after the analyte has been flushed from the system.

The demonstrated techniques can be also used in conjunction with previously presented techniques that use the (extended) Kalman filter to estimate a sensor's steady-state response well before the equilibrium is achieved [13], [14]. This allows for the rapid analyte quantification even in the presence of baseline drift. The presented baseline compensation technique will reduce the number of false alarms caused by sensor drift and, if coupled with a technique to decrease quantification time, will allow faster detection and rapid response to the presence of environmental contaminants.

The technique presented has several advantages over the typical interpolation/extrapolation techniques that have been illustrated throughout this paper. The present technique uses information during analyte exposure to estimate the "hidden" baseline signal; this leads to improved accuracy, especially when

phosmet. These results are shown in Fig. 5. This technique is capable of simultaneously estimating the baseline, steady-state response, and sorption time constant. However, it can be sensitive to mismatch between the model and the actual physical system due to flow dynamics as the analyte is injected. Table I compares the errors between the true sensor responses due to analyte

compared to constant or linear extrapolation techniques which only use information measured from the baseline before analyte exposure. In some cases, interpolation techniques can exhibit accuracy comparable to the presented technique. However, the reduction in time required to determine the baseline response and thus the response due to the analyte is an advantage of the present technique. Because the technique is online, the data collected at time $t$ is used to correct the estimate of the baseline at time $t$. The presented technique reduces the time required to quantify the analyte by eliminating the time needed to wait for desorption; this is compatible with other techniques being investigated to reduce the time needed to estimate the sensor's steady-state response [13], [14]. Finally, it is possible to apply this technique to sensor responses which do not return to their original baseline. Sensor responses of this type typically preclude the use of interpolation techniques.

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