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Karthick Sothivelr  
*Marquette University*

Florian Bender  
*Marquette University, florain.bender@marquette.edu*

Fabien Josse  
*Marquette University, fabien.josse@marquette.edu*

Antonio J. Ricco  
*Stanford University*

Edwin E. Yaz  
*Marquette University, edwin.yaz@marquette.edu*

*See next page for additional authors*

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**Authors**

Karthick Sothivelr, Florian Bender, Fabien Josse, Antonio J. Ricco, Edwin E. Yaz, Rachel E. Mohler, and Ravi Kolhatkar

Marquette University

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# Detection and Quantification of Aromatic Hydrocarbon Compounds in Water Using SH-SAW Sensors and Estimation-Theory-Based Signal Processing

Karthick Sothivelr

Department of Electrical and Computer Engineering, Marquette University, Milwaukee, Wisconsin

Florian Bender

Department of Electrical and Computer Engineering, Marquette University, Milwaukee, Wisconsin

Fabien Josse

Department of Electrical and Computer Engineering, Marquette University, Milwaukee, Wisconsin

Antonio J. Ricco

Department of Electrical Engineering, Center for Integrated Systems, Stanford University, Stanford, California

Edwin E. Yaz

Department of Electrical and Computer Engineering, Marquette University, Milwaukee, Wisconsin

**Rachel E. Mohler**

Chevron Energy Technology Company, 100 Chevron Way, Richmond, California

**Ravi Kolhatkar**

Chevron Energy Technology Company, 3901 Briarpark, Houston, Texas

## Abstract

This work investigates a sensor system for direct groundwater monitoring, capable of aqueous-phase measurement of aromatic hydrocarbons at low concentrations (about 100 parts per billion (ppb)). The system is designed to speciate and quantify benzene, toluene, and ethylbenzene/xylenes (BTEX) in the presence of potential interferents. The system makes use of polymer-coated shear-horizontal surface acoustic wave devices and a signal processing method based on estimation theory, specifically a bank of extended Kalman filters (EKFs). This approach permits estimation of BTEX concentrations even from noisy data, well before the sensor response reaches equilibrium. To utilize estimation theory, an analytical model for the sensor response to step-changes, starting from clean water, to mixtures of multiple analytes is first formulated that makes use of both equilibrium frequency shifts and response times (for individual analyte), the latter being specific for each combination of coated device and analyte. The model is then transformed into state-space form, and the bank of EKFs is used to estimate BTEX concentrations in the presence of interferents from transient responses prior to attainment of equilibrium. Samples used in the experiments were either manually mixed in the laboratory or taken from real monitoring sites; they contained multiple chemically similar analytes with concentrations of individual BTEX compounds in the range of 10–2000 ppb. The estimated BTEX concentrations were compared to independent gas chromatography measurements and found to be in very good agreement (within about 5–10% accuracy), even when the sample contained multiple interferents such as larger aromatic compounds or aliphatic hydrocarbons.

## KEYWORDS:

chemical sensors, SH-SAW sensors, sensor signal processing, estimation theory, groundwater monitoring, BTEX/benzene, in situ

Environmental monitoring is crucial to safeguard the environment and the public from hazardous chemicals (1) such as volatile organic compounds (VOCs). VOCs can originate from a variety of sources such as vehicle emissions, industrial and laboratory processes, and cigarette smoke, but a major source is accidental releases of gasoline from underground storage tanks (USTs) into groundwater. (1-4) Such accidental releases can go unnoticed for extended periods of time unless specific measures are taken to monitor the areas surrounding USTs. (1) As of 2014, in the US there were over 570 000 active USTs, all regulated by the Environmental Protection Agency (EPA). (5) Currently, USTs are only inspected at 2–3 year intervals, and groundwater samples have to be collected at the monitoring wells and transported to a laboratory for analysis. (5) Existing practice requires personnel to manually collect the samples from the sites, which can be costly, and send them to another location for off-site analysis. (1) Moreover, the integrity of the collected sample can be easily compromised during collection, transportation, storage, and analysis, an overall process that often spans multiple days. (1) In short, the current monitoring method is time-consuming, labor intensive, and costly, rendering the continuous or frequent monitoring of USTs highly impractical.

A need clearly exists to develop an in situ sensor system that is more accurate, rapid, and comparatively inexpensive for long-term monitoring of groundwater: improved management of hydrocarbon-impacted sites will require frequent analysis to provide better documentation of temporal changes in concentrations, from

which spatial concentration changes can sometimes also be inferred. Such a system would also enhance and improve the real-time assessment of the efficacy of remediation measures. The sensor system should be capable of identifying and quantifying the hazardous compounds present in groundwater near USTs in an automated manner and, given the need for high accuracy in estimating analyte concentrations under field conditions, the system needs to include a capable signal-processing unit.

Of the many compounds present in gasoline, benzene, toluene, ethylbenzene, and xylenes (BTEX) are of particular concern due to their relatively high solubilities in water and their hazard potential. (6-9) The EPA maximum contaminant levels of BTEX compounds in drinking water are in the low ppb ( $\mu\text{g/L}$ ) to low ppm ( $\text{mg/L}$ ) range. (8) BTEX compounds are present in crude oil as well as its refined products and therefore serve as good indicators of fuel and oil releases. (6) Benzene is of particular importance due to its carcinogenicity and relatively higher water solubility. Thus, it is crucial, and in some cases a legal obligation, to determine the concentration of benzene in groundwater. Also, among the BTEX compounds, benzene has the lowest polymer/water partition coefficients due to having the highest water solubility, (9-11) generally resulting in lower benzene sensitivities using polymer-coated sensor devices.

The task of identifying and quantifying aromatic hydrocarbons such as the BTEX compounds, particularly benzene, is challenging, not only because of the low relevant concentrations, but also due to the chemical similarity of these compounds as a group, as well as the presence of other similar aromatic compounds in groundwater. (12) One particular complicating factor is that the number of chemical isomers increases as the numbers of carbon atoms and substituent locations around the aromatic ring increase. For example, within the substituted-benzene family, toluene is the only seven-carbon isomer, but ethylbenzene and the three xylenes are all eight-carbon chemical isomers. Due to their fairly similar physicochemical properties, and depending as well on the nature of the sensor used, the isomers often exhibit about the same sensitivity and response time. Additional interferents may also be present in groundwater, including dissolved salts, particles and sediments, humic acid, dissolved gases, aliphatic hydrocarbons, ethers, esters, and so forth.

Existing techniques to detect and quantify BTEX compounds include spectroscopy and gas chromatography, (13, 14) which can be configured for the necessary identification and quantitation, and which work well for off-site analysis. These methods are, however, relatively impractical for use as field-deployed (in particular, “down-well”) systems due to their total system size and complexity, as well as the typical need for challenging sample preparation procedures.

We believe a better approach to on-site BTEX monitoring is to use a sensor array in which each sensor has a different, partially chemically selective coating. (15) When the sensors, coatings, and operating parameters are properly designed and selected in such a system, the overall array response to a particular analyte is unique. Chemical sensor arrays can be based on a range of sensing platform technologies, a number of which have been used to directly detect petroleum products in soil and water. (6, 11, 12, 16-25) Analyte identification based on arrays of partially selective sensor responses is often facilitated by pattern-recognition techniques, (26) including linear-discriminant analysis, principal-component analysis, and  $k$ -nearest-neighbor algorithms.

Using a sensor array to perform analyte identification and quantification does, however, have potential drawbacks, two of the most important being longer processing time and misclassification. Data dimensionality and complexity, and hence the necessary processing resources and time, all increase with the number of sensors in the array. Misclassification errors are particularly likely if the chemical diversity (“chemical orthogonality” (27)) and partial selectivity of the available sensor coatings is insufficient, and/or if only one sensing parameter per sensor is used for classification, as is often the case. By increasing the number of sensing parameters per sensor used for classification, more reliable results are attainable and an effective sensor array can be constructed with fewer sensors, with attendant reductions in system cost, complexity, and size.

For the example of BTEX analysis, our experience is that the use of equilibrium sensor responses alone for classification purposes in the absence of a sufficient number of chemically diverse sensing films can result in unacceptable rates of misclassification. (11) Adding a second measured parameter to the classification process provides additional chemically specific information, such as the characteristic transient response time when a step change in concentration occurs. The added information can dramatically improve the identification and quantification of BTEX compounds, provided each selected sensing film exhibits significantly different response-time behavior for the various analytes. (12)

In this paper, a capable sensor system is presented that makes use of an array of SH-SAW (shear-horizontal surface acoustic wave) devices, coated with partially selective polymers and matched with customized signal processing based on estimation theory, in order to detect and quantify BTEX compounds in the presence of interferents typically found in groundwater. While we have previously shown the promise of SH-SAW sensor arrays to detect BTEX compounds in aqueous environments in the absence of such interferents, (6, 11, 12) here we report significant progress in combining these responses—both time-transient and signal-amplitude data for each element of the array—with estimation theory in order to detect and quantify BTEX compounds with greater reliability, improved chemical selectivity, even in the presence of interferents, higher quantitative accuracy, shorter time to collect the response data (using methods that do not require equilibrium to be attained before reporting a result), and shorter data processing time. In fact, we show for this application that estimation theory, particularly the bank-of-extended-Kalman-filters (EKF) approach, allows analyte detection and quantification in near-real time. Importantly, this use of estimation theory is only possible because the sensor responses can be modeled analytically: in the relevant concentration range, this was confirmed for the SH-SAW sensor responses, which are modeled easily with only a few assumptions. (12, 28)

## Experimental Details

Sensor responses analyzed in this work were collected using a 36° YX-LiTaO<sub>3</sub> guided SH-SAW device as the sensing platform. (11, 12, 29, 30) Devices were fabricated with 10/80 nm-thick Ti/Au interdigital transducers (IDTs) using a multielectrode design (30) that produces an operating frequency for the third harmonic SH-SAW of 103 MHz for polymer-coated devices. The sensor platform uses a dual-delay-line configuration, one used as the sensor and the other as a reference to measure and correct for changes in temperature, pressure, and other parameters unrelated to sorption of the analyte of interest. Both delay lines include a metalized path between the IDTs to minimize acoustoelectric interactions with the load (here, the contacting ambient environment and its constituents). In this study, the sensing line was coated with sorbent polymer coatings that interact with the analytes of interest; polymers studied include poly(ethyl acrylate) (PEA), poly(epichlorohydrin) (PECH), and poly(isobutylene) (PIB), all purchased from Sigma-Aldrich, St. Louis, MO. The polymers were deposited on the sensing line from solution in toluene (PEA) or chloroform (PECH, PIB) by spin coating and baking for 15 min at 55 °C, resulting in thicknesses of 1.0 μm for PEA, 0.6 μm for PECH, and 0.8 μm for PIB. It was found that the baking step is necessary to ensure repeatability of the sensor responses. Reference lines were coated with poly(methyl methacrylate) (PMMA) (Scientific Polymer Products, Ontario, NY) and baked for 120 min at 180 °C, resulting in a glassy, nonsorbent coating so that the reference line does not absorb appreciable amounts of analyte (i.e., it is chemically insensitive) at the concentrations of interest. BTEX analytes were purchased from Sigma-Aldrich, had purities of at least 98.5%, and were diluted to the appropriate concentration with deionized (DI) water or groundwater. Groundwater and light nonaqueous phase liquid (LNAPL) samples were provided by Chevron Corporation from groundwater monitoring wells in California. Concentrations are reported in parts per million or per billion by weight. The following interferents, commonly found in groundwater at accidental release sites, were tested in the experiments: *n*-heptane, 1,2,4-trimethylbenzene, MTBE (methyl-*tert*-butyl ether), and ethanol. The interferents were all purchased from Sigma-Aldrich and had purities of ≥ 98%, except ethanol which was denatured and had ≥ 90% purity.

Sensor data were collected using a network analyzer (Agilent E5061B, Santa Clara, CA) and a switch/control system (Agilent 34980A) to switch between the two SH-SAW delay lines (sensing, reference) on each device. In order to provide an independent measurement of BTEX concentrations for the aqueous LNAPL solutions, a portable GC-PID (gas chromatograph-photoionization detector) system was used (Defiant Technologies FROG-4000, Albuquerque, NM). In some cases, analyte concentrations were further confirmed using GC-MS (gas chromatography–mass spectroscopy). LNAPL samples were prepared by placing the LNAPL above DI water in a separatory funnel for 3 days to create a saturated aqueous solution, which was further diluted with either DI water or groundwater for the respective experiments to yield concentrations of 1 ppm or less for each BTEX compound. PTFE tubing, PTFE valves, and PTFE sealed glass vials were used throughout the experiments, and headspace in the sample vials was kept negligible to minimize loss of the volatile analytes; actual sample concentrations as seen by the sensor was determined by the subsequent GC-PID measurements, as indicated above. Experiments were performed by placing the SH-SAW sensor inside a flow cell (designed in our laboratory (31)); solutions were drawn through the flow cell by a peristaltic pump (IDEX Ismatec Reglo Digital MS, Oak Harbor, WA). All the solutions were pumped at a sample flow rate of 7  $\mu\text{L/s}$  to minimize hydrodynamic forces from the flowing fluid. A reference solution (DI water or groundwater) was drawn through the cell to obtain a stable baseline output signal before introducing the analyte (LNAPL dissolved in DI water or groundwater, respectively) into the flow cell. Note that for downhole operation in the field, this reference sample can be conveniently generated by removing BTEX compounds from a sample of groundwater using, e.g., activated charcoal. For groundwater samples, filtration was first performed to remove sediments and other physical interferents in the sample, before pumping these samples into the flow cell. After the sensor signal reached the equilibrium response to the analyte, the reference solution was pumped again through the system to flush the flow cell and cause the analyte(s) to desorb from the polymer coating on the sensor. This process was repeated periodically for different analyte samples and concentrations. The above procedures are well described in the literature. (11, 12, 29, 30) Measurements were conducted at a constant temperature of  $22 \pm 0.1$  °C. The experiments were performed using samples containing either a single BTEX analyte, two BTEX compounds, or (diluted) LNAPL, the last being dissolved either in DI water or groundwater and containing BTEX compounds as well as chemical and physical interferents.

## Modeling the Sensor Response

The present work focuses on the detection and quantification of BTEX compounds in the presence of interferents using estimation theory. In order to fully understand and model the SH-SAW sensor response to aqueous mixtures of multiple BTEX compounds, it is first necessary to characterize the sensor responses to single analytes.

### Model of Single-Analyte Sensor Response

Using the experimental technique described above, data for single-analyte sensor responses were collected. Typical SH-SAW responses to single-analyte samples are shown in Figure 1. (12) Based on such responses for BTEX compounds, the response to a step change in analyte concentration in the 0–10 ppm range is well modeled using a single exponential fit

$$\Delta f(t) = \Delta f_0 [1 - e^{-t/\tau}]$$

(1)

where  $\Delta f_0$  is the equilibrium frequency shift,  $\tau$  is the response time constant, and  $\Delta f(t)$  is the frequency shift as a function of time. (6, 12) Fitting the sensor response to eq 1 yields a characteristic value of  $\tau$  for each coating/analyte combination. Experimental results show  $\tau$  to be independent of analyte concentration in the range of interest and, for a given sensor coating, it therefore can be used to identify the analyte. The single-

analyte experiments also provide sensitivities (Hz of frequency shift per ppm-by-mass of analyte concentration) for each combination of sensor coating and BTEX compound, which, like the response times, are independent of concentration (and hence the equilibrium frequency shifts can be conveniently used to determine analyte concentration(s)). As chemical isomers, ethylbenzene and the three xylenes are found to have nearly identical values for their response times and sensitivities; therefore, no attempt was made to distinguish between them. The average values of response time constants and sensitivities for various coating/analyte combinations are listed in Tables 1 and 2. (6, 12)

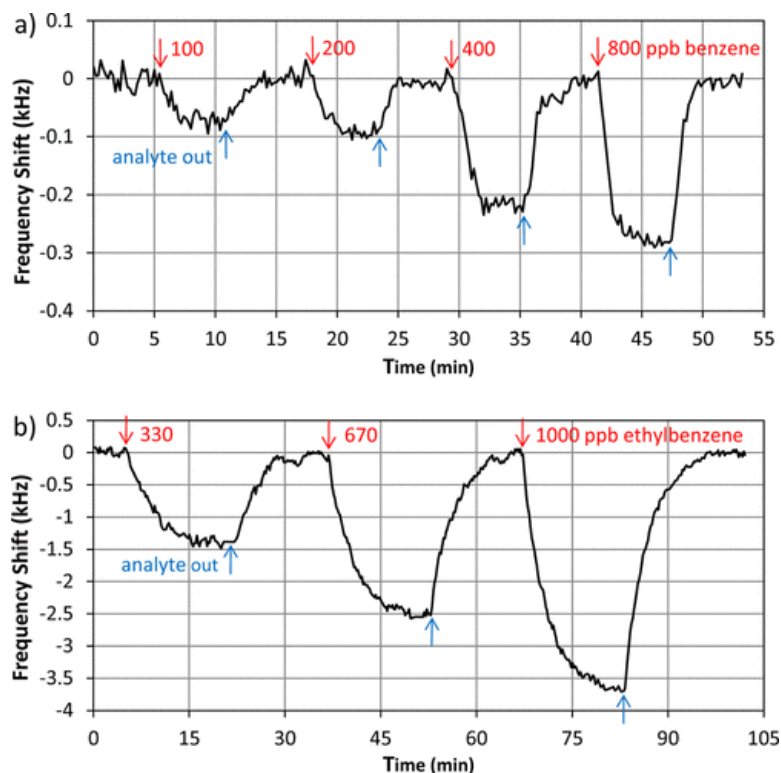


Figure 1. (a) Response of a SH-SAW sensor coated with 1.0  $\mu\text{m}$  PEA, alternating between DI  $\text{H}_2\text{O}$  and various step concentration changes of benzene in water (concentrations are indicated in the graph). (b) Response of a SH-SAW sensor coated with 1.0  $\mu\text{m}$  PEA to various concentrations of ethylbenzene in water.

Table 1. Measured Mean Response Times,  $\tau$  (in s), for Three Different Polymer Coatings to Various BTEX Analytes, Together with Their Standard Errors ( $n = 5$ )

polymer	$\tau_{\text{benzene}}$	$\tau_{\text{toluene}}$	$\tau_{\text{ethylbenzene}}$
1.0 $\mu\text{m}$ PEA	36.1 ( $\pm 10.0$ )	76.7 ( $\pm 6.0$ )	204 ( $\pm 4.5$ )
0.6 $\mu\text{m}$ PECH	26.5 ( $\pm 8.4$ )	77.6 ( $\pm 2.8$ )	175 ( $\pm 13$ )
0.8 $\mu\text{m}$ PIB	29.3 ( $\pm 7.8$ )	84.2 ( $\pm 6.5$ )	245 ( $\pm 14$ )

Table 2. Measured Mean Sensitivities,  $\sigma$  (in Hz/ppm), for Three Different Polymer Coatings to Various BTEX Analytes, Together with Their Standard Errors ( $n = 5$ )

polymer	$\sigma_{\text{benzene}}$	$\sigma_{\text{toluene}}$	$\sigma_{\text{ethylbenzene}}$
1.0 $\mu\text{m}$ PEA	244 ( $\pm 27$ )	690 ( $\pm 160$ )	2240 ( $\pm 460$ )
0.6 $\mu\text{m}$ PECH	109 ( $\pm 9$ )	435 ( $\pm 25$ )	1450 ( $\pm 240$ )
0.8 $\mu\text{m}$ PIB	63 ( $\pm 5$ )	344 ( $\pm 43$ )	1670 ( $\pm 10$ )



In order to analytically model the sensor responses to single-analyte samples of BTEX compounds, it was assumed the responses obey Henry's law as demonstrated previously. (6, 11, 12) Usually, when the sensor is exposed to a step change in the ambient concentration of an analyte, the sensor responds rapidly at first with the rate of change of the signal changing more slowly as the coating and analyte approach equilibrium. The process of analyte absorption for the case of a single-analyte sample can be fit by a first-order model described by

$$\dot{C}(t) = -\frac{1}{\tau}C(t) + \frac{K_{p-w}}{\tau}C_{amb}(t)$$

(2a)

and

$$\Delta f(t) = -aC(t)$$

(2b)

where  $C(t)$  is the concentration of analyte in the coating at time  $t$ ,  $C_{amb}(t)$  is the ambient analyte concentration at time  $t$  (which for these experiments remains constant due to the constant flow of fresh analyte solution throughout the measurement),  $\tau$  is the response time constant for a given analyte/coating combination,  $K_{p-w}$  is the polymer/water partition coefficient for a given analyte/coating pair,  $\Delta f(t)$  is the frequency shift observed at time  $t$ , and  $a$  is the or equilibrium sensitivity, which is a function of the sensor platform, the sensor coating, and the analyte. (28) Equation 2b represents the measured SH-SAW device frequency shift for the single-analyte system at time  $t$ . Solving the differential eq 2a yields an exponential time dependence with decay time  $\tau$ , which, when substituted into eq 2b, yields a single exponential expression in the form of eq 1, with  $\Delta f_0 = aC(\infty)$ .

### Model of the Multiple-Analyte Sensor Response

The model of single-analyte sensor response can readily be extended to multianalyte responses. We have shown previously (6, 12) that sensor responses to binary analyte mixtures are well modeled by dual exponential fits and that the total equilibrium frequency shift in response to a binary mixture is the sum of the frequency shifts for the individual analytes (i.e.,  $\Delta f = \Delta f_1 + \Delta f_2$ ). Figure 2 depicts the responses of a SH-SAW sensor to a binary mixture of BTEX analytes and to the individual analytes that comprise it. (12) Figure 2 confirms that the sensor response for the binary mixture can be modeled using a dual-exponential fit given by

$$\Delta f(t) = \Delta f_1[1 - e^{-t/\tau_1}] + \Delta f_2[1 - e^{-t/\tau_2}]$$

(3)

where  $\tau_1$  and  $\tau_2$  represent the response time constants of analyte 1 and analyte 2, respectively, and  $\Delta f_1$  and  $\Delta f_2$  represent the equilibrium frequency shifts of analyte 1 and analyte 2, respectively.

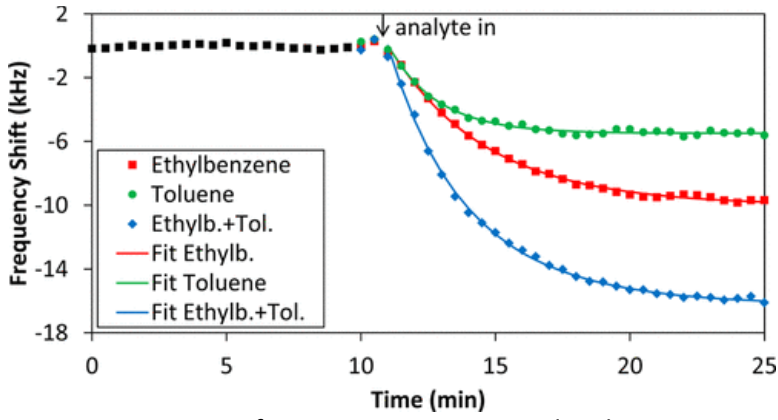


Figure 2. Response of a SH-SAW sensor coated with 1.0  $\mu\text{m}$  PEA to toluene (10 ppm), ethylbenzene (10 ppm), and their binary mixture (10 ppm of each component). Experimental response data (dots) are modeled with single- and dual-exponential fits (solid lines) for single analytes and the binary mixture of analytes, respectively.

Based on the same assumptions, the sensor response to a mixture containing  $n$  analytes can be modeled using  $n$  exponential terms

$$\Delta f(t) = \sum_{i=1}^n \Delta f_i [1 - e^{-t/\tau_i}]$$

(4)

where  $\Delta f_i$  and  $\tau_i$  are the equilibrium frequency shift and the response time constant, respectively, associated with the  $i$ th analyte. If the sensitivities of each analyte in the mixture are known, the concentration of each analyte in the mixture can be extracted.

The generic analytical model for the sensor response to a mixture of  $n$  analytes can be obtained by making two major assumptions: First, the mixture obeys Henry's law, from which it can be inferred that for a dilute mixture of multiple soluble species, the sorption of any given species into the polymer does not affect the sorption of the other species in any way. Free partitioning of analytes between polymer and aqueous phase is inferred, including the implication that the sorption process is fully reversible at room temperature (i.e., only physisorption occurs). Based on our experimental observations, Henry's law is valid for analyte concentrations in the range of 0 to at least 10 ppm depending on the analyte. (6, 11, 12) Moreover, Henry's law implies that the concentration of the mixture in the coating at any time  $t$  is simply the sum of the concentrations of the individual analytes:  $C_{\text{mixture}}(t) = C_1(t) + C_2(t) + \dots + C_n(t)$  for any time  $t$ , where  $C_i(t)$  represents the concentration of each analyte in the mixture as it would be measured in a single-analyte response. The process of analyte absorption can then be assumed to be first order (similar to the model of single-analyte sensor response). The second assumption is that the equilibrium frequency shifts are also mutually independent: the frequency shift due to the mixture at any time  $t$  is the sum of the frequency shifts due to each analyte in the mixture at that time. Based on these two assumptions, the sensor response to a mixture of the  $n$  analytes can be represented by

$$\dot{C}_i(t) = -\frac{1}{\tau_i} C_i(t) + \frac{K_{p-w,i}}{\tau_i} C_{\text{amb},i}(t)$$

(5a)

and

$$\Delta f(t) = - \sum_{i=1}^n a_i C_i(t)$$

(5b)

where all the variables are as previously defined, with subscript  $i = 1, 2, \dots, n$  referring to each analyte in the mixture.

In order to use the generic model of eq 5 to detect and quantify target analytes in the presence of interferents, the following assumptions are made: first, that there can be an unknown number of interferents present together with the target analytes; second, that the sensor response(s) due to these interferents does not dominate the response(s) due to the target analytes. From experimental observations for BTEX in groundwater (see Results section), we find that the interferents either have slower response time constants or lower sensitivities than the four target analytes. In other applications, this condition often can be met by using appropriate sorbent coatings, i.e., coatings with significantly larger partition coefficients for the analytes than interferents. When the selected coatings and the set of interferents are such that the time-dependent absorption for all the interferents is relatively similar, a simple approach is to represent their combined response by a single exponential term. In such cases, eq 5 can be used to represent the sensor response of  $n - 1$  target analytes ( $i = 1, 2, \dots, n - 1$ ) and the collection of interferents ( $i = n$ ).

From experiments with the polymer coatings listed above and several of the interferents found in released oil and fuel (details in the Results section), their contributions to the sensor response indeed do *not* dominate those of the BTEX compounds, and/or these interferents are found to have response time constants significantly longer than those of the BTEX compounds. The fact that ethylbenzene and the three xylenes are chemical isomers means that, in applying eq 5, their combined response can be represented by a single exponential term. Thus, the subscripts  $i = 1, 2, 3$  represent the target analytes benzene, toluene, and the combination of the four C8 isomers, respectively, and the subscript  $i = 4$  represents the combined response due to the interferents in the mixture. Figure 3 shows a measured typical response of an SH-SAW sensor to the water-soluble fraction of LNAPL in groundwater.

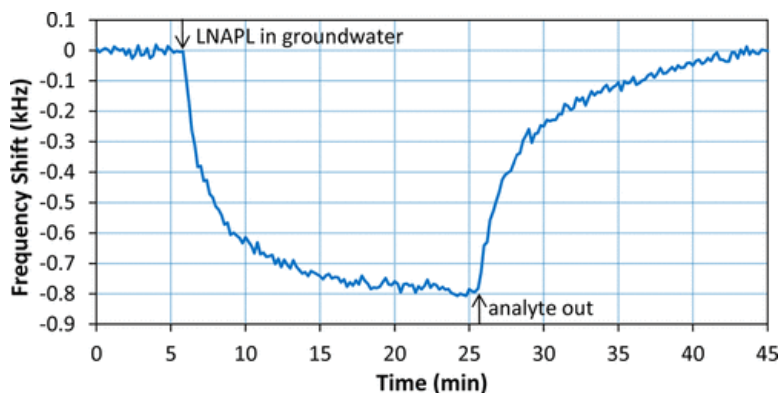


Figure 3. Measured response of a SH-SAW sensor coated with 0.6  $\mu\text{m}$  PECH to the water-soluble fraction of LNAPL in groundwater. Concentration of BTEX compounds in the sample: 506 ppb benzene, 661 ppb toluene, 3 ppb ethylbenzene, and 44 ppb xylenes. Note that water-soluble compounds other than BTEX are also present in LNAPL and do contribute to the sensor response.

## Application of the Model to SH-SAW Sensor Responses

The model above was used to develop an estimation-based theory for the detection and quantification of BTEX compounds in the presence of interferents. For that purpose, the sensor response model of the multianalyte mixture (eq 5) has to be normalized, discretized, and converted into state-space form. Equation 5 was normalized by dividing by  $K_{p-w,i}C_{\max,i}$  (where  $C_{\max,i}$  represents the equilibrium ambient concentration). By defining new variables as

$$m_i(t) = \frac{C_i(t)}{K_{p-w,i}C_{\max,i}}$$

(6a)

$$u_i(t) = \frac{C_{\text{amb},i}(t)}{C_{\max,i}}$$

(6b)

and

$$\alpha_i = -a_i K_{p-w,i} C_{\max,i}$$

(6c)

the following normalized equations are obtained:

$$\dot{m}_i(t) = -\frac{1}{\tau_i} m_i(t) + \frac{1}{\tau_i} u_i(t)$$

(7a)

and

$$\Delta f(t) = \sum_{i=1}^4 \alpha_i m_i(t)$$

(7b)

where, for analyte  $i$ ,  $m_i(t)$  represents the normalized concentration absorbed at time  $t$ ,  $\alpha_i$  is the equilibrium frequency shift, and  $u_i(t)$  represents the step in concentration for the transition from clean water to the sample (for  $t < 0$ ,  $C_{\text{amb},i}(t) = 0$ ; for  $t > 0$ ,  $C_{\text{amb},i}(t) = C_{\max}$ ). Because sensor data are collected at discrete-time instants (i.e.,  $t = kT_s$ , where  $T_s$  is the sampling period and  $k$  is a non-negative integer), it is necessary to transform the continuous time-normalized model of the sensor response (eq 7) into a discrete-time model. Using Euler's first-order forward method, eq 7 becomes

$$m_{i,k+1} = (1 - S_i)m_{i,k} + S_i u_{i,k} + v_k$$

(8a)

and

$$\Delta f_k = \sum_{i=1}^4 \alpha_i m_{i,k} = w_k$$

(8b)

where  $S_i$  is the absorption rate constant (i.e.,  $S_i = T_s/\tau_i$ ). The terms  $v_k$  and  $w_k$  are added to represent the process and measurement noise, respectively, which are likely to be present in the system. It is assumed that both process and measurement noise are white noise (uncorrelated in time) and also that they are uncorrelated with each other.

The unknown parameters that need to be estimated in the model defined by eq 8 for successful quantification of BTEX compounds in the presence of interferents include the equilibrium frequency shifts (i.e.,  $\alpha_i$ ,  $i = 1, 2, 3, 4$ ), the absorption rate constant of the fourth analyte (i.e.,  $S_4$ ), and the normalized concentration of the fourth analyte (i.e.,  $m_{4,k}$ ). Note that the normalized concentration is related to the absorption rate constant. In order to facilitate the estimation process, eq 8 is converted into state-space form by assigning state variables to the unknown parameters

$$\begin{bmatrix} x_k^{(1)} \\ x_k^{(2)} \\ x_k^{(3)} \\ x_k^{(4)} \\ x_k^{(5)} \\ x_k^{(6)} \end{bmatrix} = \begin{bmatrix} S_4 \\ m_{4,k} \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{bmatrix}$$

(9)

and the resulting discrete-time state-space form is as follows:

$$x_{k+1} = f(x_k, u_k, v_k) = \begin{bmatrix} x_{k+1}^{(1)} \\ x_{k+1}^{(2)} \\ x_{k+1}^{(3)} \\ x_{k+1}^{(4)} \\ x_{k+1}^{(5)} \\ x_{k+1}^{(6)} \end{bmatrix} = \begin{bmatrix} x_k^{(1)} \\ (1 - x_k^{(1)}) x_k^{(2)} + x_k^{(1)} u_{1,k} + v_k \\ x_k^{(3)} \\ x_k^{(4)} \\ x_k^{(5)} \\ x_k^{(6)} \end{bmatrix}$$

(10a)

and

$$y_k = h(x_k, u_k, w_k) = x_k^{(3)} m_{1,k} + x_k^{(4)} m_{2,k} + x_k^{(5)} m_{3,k} + x_k^{(6)} x_k^{(2)} + w_k$$

(10b)

Equation 10b is specifically referred to as the output equation. From eqs 10a and 10b, it can be seen that the state-space representation is a nonlinear model. Therefore, a nonlinear estimator has to be used to estimate the unknown parameters; the state estimates are denoted as  $\hat{x}_k$ . Discrete-time EKF was used to estimate the unknown parameters, requiring the nonlinear system to be linearized using a Taylor series expansion about the current state estimate,  $\hat{x}_k$ . The result of linearization and the generalized expressions of the terms are used to define the following EKF algorithm

$$\hat{x}_{k+1} = f(\hat{x}_k, u_k, \bar{v}) + A_k P_k C_k^T (C_k P_k C_k^T + G_k W_k G_k^T)^{-1} [y_k - h(\hat{x}_k, u_k, \bar{w})]$$

(11a)

and

$$P_{k+1} = A_k P_k A_k^T + F_k V_k F_k^T - A_k P_k C_k^T (C_k P_k C_k^T + G_k W_k G_k^T)^{-1} C_k P_k A_k^T$$

(11b)

where

$$A_k = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ -\hat{x}_k^{(2)} + u_{B,k} & (1 - \hat{x}_k^{(1)}) & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad F = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$C_k = [0 \quad \hat{x}_k^{(6)} \quad m_{1,k} \quad m_{2,k} \quad m_{3,k} \quad \hat{x}_k^{(2)}]$$

and

$$G = [1]$$

In eq 11, the term  $P_k$  represents the error covariance matrix and  $(\cdot)^T$  denotes a matrix transpose. This EKF algorithm can be applied to perform the estimation of the unknown parameters, which, in turn, allows for the quantification of the detected analytes of interest.

The above EKF algorithm starts with an initial estimate of the state vector,  $\hat{x}_0$  (i.e., the state variables) and the error covariance matrix,  $P_0$ . The initialization of the state vector,  $\hat{x}_0$ , requires initializing the unknown parameters in eq 9; based on this initial estimate of the state vector,  $\hat{x}_0$ , the initial error covariance,  $P_0$  is set. If the initial value of the state vector,  $\hat{x}_0$ , is completely unknown, an educated guess is made and a value set for the initial state estimate,  $\hat{x}_0$ , and the initial error covariance,  $P_0$ , is set to a large value. After each measurement of a new data point, the state estimates and error covariance are updated based on this acquired information. The update process is repeated recursively until the unknown parameters converge to a particular value. Using this algorithm, the equilibrium frequency shift for each detected BTEX compound can be estimated, enabling the concentrations of the detected BTEX compounds to be extracted by dividing the estimated equilibrium frequency shift of each BTEX compound by its corresponding average sensitivity. The EKF algorithm can be implemented by a microcontroller or readily available software packages. Supporting Information on the actual derivation of the EKF equations is available.

## Results and Discussion: Detection and Quantification of BTEX Compounds

Here, results are reported for the detection and quantification of BTEX compounds in groundwater in the presence of interferents using the above-formulated sensor signal-processing model and measured SH-SAW sensor responses. Using the discrete-time state-space models (eqs 10 and 11) with measured frequency shifts as a function of response time from each coated sensor for LNAPL samples collected at a series of discrete-time instants (i.e., at each sampling period), the estimation of the unknown parameters (BTEX concentrations vs time) was performed using EKF. Since the state-space model is highly nonlinear (it includes bilinear terms), a bank of several EKFs with different initial estimates was used to estimate the six states of the system in order to obtain more accurate results. (32-37) The working principle of a bank of EKFs is very similar to that of a single EKF, except that the sensor response is processed simultaneously by several EKF estimators in parallel, each using different initial conditions, and the estimates from the filter are combined in order to generate the final estimates of the states at each instant of time. (32)

For the present application, initial conditions of each EKF were based on likely concentration ranges of individual BTEX compounds that could be present in an LNAPL sample: typically, in the 10 to 2000 ppb range. The corresponding range of equilibrium frequency shifts for each BTEX compound was determined by multiplying the concentration range by the average sensitivity for the respective BTEX compound. The range of equilibrium frequency shifts was then used to initialize all the filters in the bank. The estimates obtained from all the EKFs are combined using weights, which are updated recursively using each EKF's estimate of the error covariance in the measurement as well as its estimate of the measurement. The filters that produce the smallest error covariance are given the most weight. In order to combine the estimates from all the filters, the weight of each filter is multiplied by its corresponding estimate, and the resulting products are added to produce an average estimate of the unknown parameters.

In order to test the validity of the formulated signal processing model, which accounts for chemical interferents, the coated sensors were exposed to four different compounds selected to represent the classes of interferents commonly encountered in groundwater at release sites. No significant response to ethanol was found up to concentrations of 100 ppm. For MTBE, a very low sensitivity was found ( $\sim 1$  Hz/ppm). Since this compound is usually present at low concentrations, its effect on the sensor response can also be neglected. For 1,2,4-trimethylbenzene and *n*-heptane, high sensitivities ( $>1$  kHz/ppm) and long response times were found. The high sensitivities indicate that, normally, these compounds cannot be ignored even at the low concentrations commonly encountered. However, since their response times are longer than those of the BTEX compounds, they can be conveniently modeled by the last ( $i = 4$ ) term in eq 8b. The same is expected to hold true for other larger aromatic or aliphatic compounds.

A large number of measurements of SH-SAW sensor responses to BTEX-containing samples were made; their estimated concentration results, using a bank of EKFs, are summarized graphically at the end of this section. A pair of representative estimation results are presented here in detail to illustrate the overall process. Figure 4 and Table 3 present such results for a SH-SAW sensor coated with  $0.6 \mu\text{m}$  PECH to a LNAPL sample (in groundwater) including 197 ppb of benzene, 241 ppb of toluene, and 16 ppb of ethylbenzene and xylenes in the presence of typical interferents (as indicated by GC-PID and GC-MS). Figure 4 shows excellent agreement between the measured data points and the estimation, calculated by substituting the estimated equilibrium frequency shifts and corresponding time constants into eq 4 (with  $n = 4$ ). Note that this estimation technique allows the unknown parameters to be calculated well before the sensor response reaches equilibrium. In practice, it is found that the time for quantification has to be longer than the response times of all BTEX compounds (see Table 1). Using the sensitivities of BTEX compounds (Table 2), their concentrations are extracted by dividing the estimated equilibrium frequency shift for each compound by its corresponding average sensitivity. As summarized in Table 3, the estimated concentrations of BTEX compounds are in very good

agreement with the actual concentrations: less than 15% difference on average. The actual concentration of BTEX compounds refers to measurements using a portable GC-PID. Table 3 also shows that the percentage difference between the actual and estimated concentrations of ethylbenzene and xylenes (EX) is relatively high compared to those of benzene and toluene, but the absolute difference is just 3 ppb, which is lower than the estimated detection limit for this analyte/coating combination (about 10 ppb). It is to be expected that in this low concentration range, the signal noise will limit the accuracy of the concentration estimation.

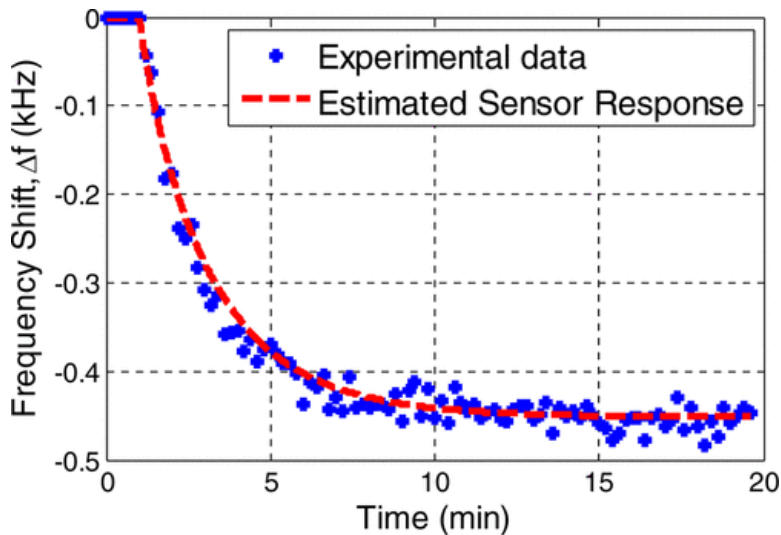


Figure 4. Measured response of a SH-SAW sensor coated with 0.6  $\mu\text{m}$  PECH to a LNAPL sample in groundwater containing 197 ppb of benzene, 241 ppb of toluene, 16 ppb of ethylbenzene and xylenes, and an unknown number and concentration of interferences. Also shown is the estimated sensor response curve plotted using the estimated sensor parameters.

Table 3. Estimated Concentrations of BTEX Compounds Obtained using the Measurement Data of a LNAPL Sample in Groundwater<sup>a</sup> Compared to Actual Concentrations

	concentrations (ppb)		
analyte of interest	actual	estimated	% difference
benzene	197	219	11
toluene	241	220	9
ethylbenzene and xylenes	16	19	19

<sup>a</sup>Collected using a SH-SAW device coated with 0.6  $\mu\text{m}$  PECH.

Figure 5 and Table 4 show another estimated result obtained using the response of a SH-SAW sensor, in this case coated with 0.8  $\mu\text{m}$  PIB, to a LNAPL sample (in DI water) including 610 ppb of benzene, 874 ppb of toluene, and 154 ppb of ethylbenzene and xylenes, and various interferences present in LNAPL. In Figure 5, the estimated sensor response curve shows excellent agreement with the measured data points, hence the estimated equilibrium frequency shifts should be close to the actual values. The equilibrium frequency shifts are then used to extract the concentrations of BTEX compounds; the results, listed in Table 4, are in very good agreement with the actual concentration values (less than 5% difference on average). Better agreement is not expected due to the error (5–10%) of the GC-PID instrument used to measure the absolute concentrations. (38) For this example, the estimation method enabled the BTEX analytes to be quantified in less than half the time required for the sensor response to reach equilibrium.



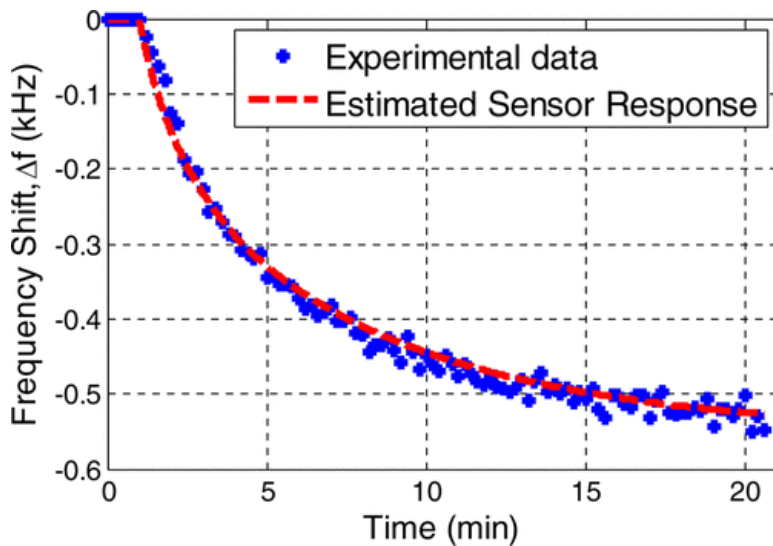


Figure 5. Measured response of a SH-SAW sensor coated with 0.8  $\mu\text{m}$  PIB to a LNAPL sample in DI water containing 610 ppb of benzene, 874 ppb of toluene, 154 ppb of ethylbenzene and xylenes, and various interferences. Also shown is the estimated sensor response curve plotted using the estimated sensor parameters.

Table 4. Estimated Concentrations of BTEX Compounds Obtained using the Measurement Data<sup>a</sup> of a LNAPL Sample in DI Water Compared to Actual Concentrations

	concentrations (ppb)		
analyte of interest	actual	estimated	% difference
benzene	610	597	2
toluene	874	919	5
ethylbenzene and xylenes	150	154	3

<sup>a</sup>Collected using a SH-SAW device coated with 0.8  $\mu\text{m}$  PIB.

As indicated above, a large number of measurements were made from multiple LNAPL samples diluted in groundwater or DI water, with BTEX concentrations ranging from low ppb to low ppm levels, and the estimation-based signal processing technique was applied. The results from these tests are summarized in Figure 6, which includes estimates obtained using SH-SAW sensors coated with 0.6  $\mu\text{m}$  PECH (Figure 6a) and 0.8  $\mu\text{m}$  PIB (Figure 6b). Most of the estimated concentration values in Figure 6 lie quite close to the ideal line (slope of one), meaning that the estimates are in very good agreement with the actual concentrations in the various samples. The relative percentage errors between estimated and actual concentrations (relative to the actual concentration over all tested identical dilutions of a given sample) were calculated and are shown in the legend boxes of Figure 6. Overall, the relative percentage error between the estimated and actual concentrations of BTEX compounds is less than 15%; for benzene, it is less than 10%. The error of the estimates could be further improved by reducing measurement noise and increasing the number of filters in the EKF bank.

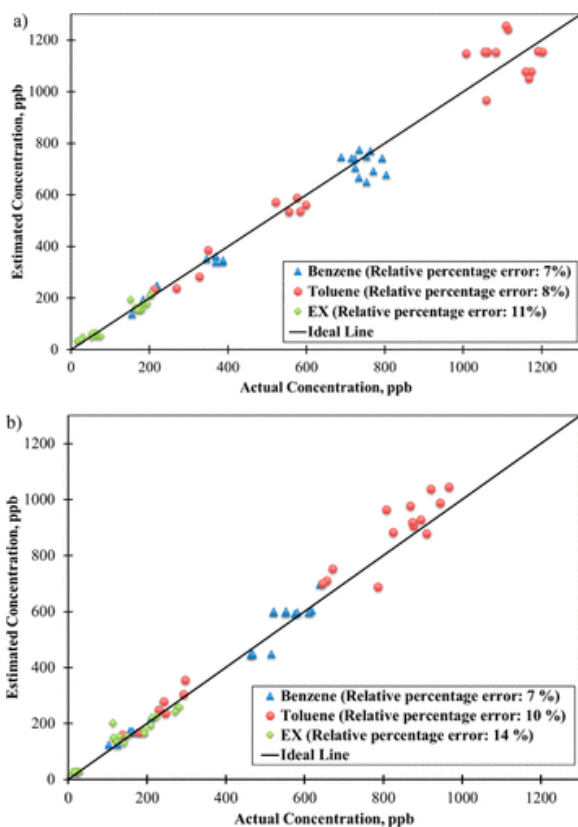


Figure 6. Estimated versus actual concentrations of BTEX compounds in multiple LNAPL solutions in DI water obtained using estimated responses of a SH-SAW sensor coated with (a) 0.6  $\mu\text{m}$  PECH and (b) 0.8  $\mu\text{m}$  PIB. The insets in the figures show the average relative percentage error between the estimated and actual concentrations of BTEX compounds. The lines have a slope of 1: the closer a point is to the line, the more accurate the estimate.

The results summarized by Figure 6 demonstrate the potential of estimation-based sensor signal processing to rapidly detect and quantify mixtures of BTEX compounds at ppb concentrations in the presence of interferents. This is realized using multiple sensing parameters, namely, the characteristic time transients as well as equilibrium frequency shifts. This technique enables the use of a sensor array with a small number of devices (2 to 3); choosing appropriate coatings provides identification redundancy and improved detection limits and accuracy, the last by averaging the results from all sensors in the array to yield the best estimated value.

## Summary and Conclusions

The analytical capability of a sensor system has been investigated that combines polymer-coated SH-SAW sensor responses with signal processing using estimation theory for the purpose of detection and quantification of BTEX compounds in water in the presence of interferents. Based on experimental results, models for the sensor responses to single-analyte samples and mixtures of multiple analytes were developed, utilizing both the equilibrium frequency shifts and the response time constants. A state-space model for the quantification of BTEX compounds in the presence of interferents was formulated. Because the model is highly nonlinear, a nonlinear estimator, specifically a bank of EKFs, was used to estimate the response parameters. The model was tested using measured responses of polymer-coated SH-SAW sensors to LNAPL samples in water. Our method accurately quantifies BTEX compounds in these samples, with most results falling within  $\pm 10\%$  of the concentrations measured independently using a GC-PID. In particular, the estimated concentrations for benzene, toluene, and ethylbenzene-plus-xylenes fall within  $\pm 7\%$ ,  $\pm 10\%$ , and  $\pm 14\%$ , respectively, of the

concentration from GC-PID measurements. These results indicate the ability of the formulated sensor signal processing method to tolerate the presence of interferents in the LNAPL samples in the quantification of BTEX compounds. A number of interferents present in the mixtures, i.e., *n*-heptane, 1,2,4-trimethylbenzene, MTBE, and ethanol were found not to affect the estimated results. These interferents, tested separately with the selected coatings and found to have low sensitivity and/or longer response times with the coatings, were accounted for in the model as a group. Concentrations of benzene in water down to 100 ppb were easily detected and quantified with the present system. Attempts to detect benzene in water around 50 ppb or lower showed reduced accuracy due to the smaller signal-to-noise ratio of the response of the coated sensors utilized. Effort is ongoing to investigate stable coatings with lower detection limits in aqueous environments.

It is important to point out that the quantification of BTEX compounds in LNAPL solutions was performed in real-time as the data were collected. This was achieved with very good accuracy in less than half the time required for the sensor response to reach equilibrium. A major advantage of the signal-processing method demonstrated here is that it can be implemented using a microcontroller, which will enable the development of a small, portable, cost-effective sensor system for field use, including in confined spaces like groundwater monitoring wells. While the signal processing method was applied here to polymer-coated SH-SAW sensors, many other chemical sensor platforms could be used for a range of measurement applications and, in some scenarios, in the presence of interferents, provided the sensor responses can be modeled analytically. Possible alternative sensor platforms include MEMS-based sensors (e.g., microcantilevers), optical chemical sensors, chemiresistors, other types of acoustic wave-based sensors, and various solid-state devices. Finally, note that the proposed method also enables the use of a sensor array with a smaller number of devices (2 to 3 in this case), with appropriate coatings still necessary for redundancy, better accuracy by averaging, and improved detection limits.

## Supporting Information

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## Notes

The authors declare no competing financial interest.

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