Identification and Quantitation of Aqueous Single- and Multianalyte Solutions of the Isomers Ethylbenzene, m-, p-, and o-Xylene Using a Single Specifically Tailored Sensor Coating and Estimation Theory-Based Signal Processing

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Identification and Quantitation of Aqueous Single- and Multianalyte Solutions of the Isomers Ethylbenzene, $m$-, $p$-, and $o$-Xylene Using a Single Specifically Tailored Sensor Coating and Estimation Theory-Based Signal Processing

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Abstract

The isomer-specific detection and quantitation of \( m \), \( p \), and \( o \)-xylene and ethylbenzene, dissolved singly and as mixtures in aqueous solutions at concentrations from 100 to 1200 ppb by volume, is reported for a specifically designed polymer-plasticizer coating on a shear-horizontal surface acoustic wave (SH-SAW) device. The polystyrene-ditridecyl phthalate-blend coating was designed utilizing Hansen solubility parameters and considering the dipole moment and polarizability of the analytical targets and coating components to optimize the affinity of the sensor coating for the four chemical isomers. The two key coating sorption properties, sensitivity and response time constant, are determined by the (slightly different) dipole moments and polarizabilities of the four target analytes: as analyte dipole moment decreases, coating sensitivity increases; as analyte polarizability decreases, coating response time lengthens. Using the measured sensitivities and time constants for the targets, sensor signals were processed with exponentially weighted recursive-least-squares estimation (EW-RLSE) to identify (with near 100% accuracy) and quantify (with ± 5–7% accuracy) the isomers. This impressive performance was achieved by combining the specifically tailored, high-sensitivity coating and an SH-SAW platform (yielding a detection limit of 5 ppb for the analytes) and using the EW-RLS estimator, which estimates unknown parameters accurately even in the presence of measurement noise and for analytes with only minor differences in response. Identification of the xylene isomers is important for applications including environmental monitoring and chemical manufacturing.

KEYWORDS:
chemical isomers detection, xylene isomers, polymer-plasticizer blend coating, dipole moment, polarizability, chemical sensors, liquid-phase sensing

Direct liquid-phase sensing of small aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and \( m \), \( p \), \( o \)-xylene (BTEX) is of significant interest in environmental monitoring applications (1,2) due to their prevalence in the products of the petrochemical industry. Moreover, each of these chemicals is utilized for petrochemical applications for which there are no currently viable replacements or cost-effective substitutions. For example, \( p \)-xylene is a chemical precursor of polyethylene terephthalate (PET) that cannot be replaced by either \( m \)- or \( o \)-xylene. (3,4) Isomer-specific detection is an important process-control capability for a number of industrial chemical separations, a family of processes that amounts to approximately 15% of total global energy consumption. (5,6)

We recently reported the design of a set of sensor coatings made from a single polymer-plasticizer pair with different mixing ratios as a means to tailor the sensitivity to specific aromatic hydrocarbons such as BTEX. (7) We have also reported on sensor coatings made from a variety of commercial, off-the-shelf (COTS) polymers (8–11) and from other polymer-plasticizer blends. (12) A significant challenge in these investigations has been the limitation of the primary mechanism of detection in reversible liquid-phase chemical sensing, namely partially selective absorption into the bulk of the chemically sensitive coating. This approach, while relatively simple to implement, appears to be less than ideal for distinguishing between molecules of high chemical similarity due to their very similar physicochemical properties. For example, appropriately selected COTS polymer coatings enable differentiation of benzene and toluene, but fall short for distinguishing among the four isomers, ethylbenzene, \( m \)-, \( p \)-, and \( o \)-xylene. (8–11) We showed, however, that using polymer-plasticizer blends as sensor coatings significantly increased the sensitivity to each individual BTEX analyte and
also provided partial isomer selectivity, in particular, the capability to differentiate ethylbenzene from “total xylene” (the sum of its \( m \), \( p \), and \( o \) isomers).\(^{(7,12)}\) This result piqued our interest in the development of a sufficiently sensitive and BTEX-optimized chemical sensor coating to utilize this relatively simple approach to identify and quantify all three chemical isomers of xylene.

In this paper, we report the characterization and analysis of a single sensor coating selected from a previously designed set of polymer-plasticizer blends, chosen for its high sensitivity and stability, for the unique identification and quantitation of the chemical isomers ethylbenzene and the xylenes dissolved singly and in multianalyte samples, directly in aqueous phase. Coating selection takes into account key relevant properties of both coating components and target analytes, including polarizability, dipole moment, and the combination of dispersion, polarity, and hydrogen bonding embodied in the Hansen solubility parameters. The result is a high affinity for the targeted isomers and, most importantly, differentiable sensor responses for all four target analytes, despite the significant similarities of these isomers. Small variations in coating transient responses to single-analyte solutions were quantified to extract the key sensing parameters, sensitivity and response time constant, for all target analytes. To manage these small differences reliably, even with noisy sensor signals, the polymer-coated shear-horizontal surface acoustic wave (SH-SAW) sensor responses were analyzed via estimation theory-based sensor signal processing to identify and estimate the concentrations of each analyte present in mixtures of ethylbenzene and the xylenes.

**Polymer Coatings for the Absorption of Isomers**

Detection of molecules with a very high degree of chemical similarity (e.g., chemical isomers such as ethylbenzene and the xylenes\(^{(8−11)}\)) presents a significant challenge in direct liquid-phase chemical sensing. This is especially true for the case of sensors utilizing partially selective thin films as their chemically sensitive interfaces, with the primary sensing mechanism being partially specific absorption of chemical analytes. In addition to often not being able to differentiate between chemical isomers, these sensors typically exhibit sensitivity to both target analytes and nontarget interferents.\(^{(10,13)}\)

In general, the physicochemical properties of each target analyte dictate the coating response to it, usually explained and characterized through cumulative parameters such as Hildebrand or Hansen solubility parameters.\(^{(14)}\) However, when analyte properties are highly similar (as is often the case with chemical isomers), using additional analyte and coating properties to characterize sensor responses may be necessary. The four isomers studied here differ in structure only in the position of a single methyl group, and Table 1 shows that several properties, such as boiling point and density, which for many sets of analytes prove useful in determining affinity, are virtually identical for these four compounds. Fortunately, variations in analyte polarizability and dipole moment offer hope that properly designed sensor coatings might provide measurable if small variations in responses to the four targets, in which case a sensor signal-processing technique that identifies targets using small, repeatable differences is necessary. If such a technique also works well with noisy signals, the overall method will be more robust for real-world sensing challenges.

<table>
<thead>
<tr>
<th>analyte</th>
<th>boiling point (K)</th>
<th>density at 298 K (g/cm(^3))</th>
<th>polarizability (\times 10^{24}) cm(^3)</th>
<th>dipole moment (\times 10^{18}) esu cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylbenzene</td>
<td>409.3</td>
<td>0.867</td>
<td>14.2</td>
<td>0.59</td>
</tr>
<tr>
<td>(m)-xylene</td>
<td>412.3</td>
<td>0.861</td>
<td>14.2</td>
<td>0.36</td>
</tr>
<tr>
<td>(p)-xylene</td>
<td>411.5</td>
<td>0.858</td>
<td>13.7</td>
<td>0.1</td>
</tr>
<tr>
<td>(o)-xylene</td>
<td>417.6</td>
<td>0.876</td>
<td>14.9</td>
<td>0.65</td>
</tr>
</tbody>
</table>
In addition to the analyte properties in Table 1, Hildebrand, Hansen, and other solubility parameters offer a convenient means of quantifying the affinity of two materials (i.e., polymer/plasticizer or coating/analyte) for one another. This involves the calculation of a relative energy difference \( RED \) for each coating/analyte pair using a calculated radius of interaction \( R_a \) and an experimentally determined radius of solubility \( R_0 \) \((14)\)

\[
RED = \frac{R_a}{R_0}
\]

where \( RED < 1 \), \( RED \approx 1 \), and \( RED > 1 \) indicate good affinity/miscibility, borderline miscibility, and poor affinity/immiscibility, \((14)\) respectively. A detailed description of the method by which \( R_a \) is calculated is presented elsewhere. \((12)\)

While \( RED \) is often used to characterize the affinity of a given coating/analyte pair, it only serves as an indicator of affinity as reflected by miscibility. When the individual affinities of a sensor coating to highly similar target analytes need to be quantified, as for ethylbenzene and the xylenes, additional properties of the coating and target analytes must be considered. The polymer polystyrene (PS) was selected as the base polymer because of its good affinity for aromatic hydrocarbons (polystyrene is, effectively, an alkane-chain backbone with a benzene ring pendant on every other backbone carbon). In addition, the dipole moment \((0.181 \text{ D}) \((15)\) and polarizability \((12.8 \times 10^{-24} \text{ cm}^3) \((16)\) of PS indicate that it is highly nonpolar and thus an excellent choice for detection of relatively nonpolar analytes in aqueous environments. In particular, a coating made from such a polymer would be anticipated to be sensitive to the small differences among the dipole moments and polarizabilities of the isomers of interest. However, polystyrene is glassy at room temperature \((T_g = 95–105 \degree \text{C}) \((17)\) and thus requires the addition of a plasticizer to reduce the \( T_g \) so that the polymer is rubbery at low frequencies, on the time scale of analyte absorption, \((18)\) to enable response on a reasonable time scale. The plasticizer ditridecyl phthalate was selected primarily for its good miscibility with PS and the target analytes as well as its relatively high molecular weight, helping to ensure negligible leaching of the plasticizer into the contacting aqueous media. \((19)\)

To help visualize the affinities described above between coating components and analytes, Figure 1 shows the PS and DTP molecules along with one example analyte molecule (\(p\)-xylene). The black dashed lines indicate the locations of aromatic rings (e.g., the benzene ring in the styrene monomer), and the red lines indicate the locations of ethyl and methyl groups. Coating components with structural similarities to the target analytes were intentionally selected to follow the principle of “like dissolves like.” In the case of the alkyl groups, this concerns mainly the known high miscibility between hydrocarbons with low polarities, while for the aromatic rings, additional interactions have been reported (“pi-stacking”). \((20)\) Note that while \(p\)-xylene is used here as an example, each isomer will show similar (though slightly different) affinity, as indicated by the analyte dipole moment and polarizability data in Table 1. To determine differences in coating responses to each isomer (i.e., sensitivity and response time), the coating/analyte partition coefficient, \( K \), a measure of the affinity of the coating to each analyte, can be used to capture these differences. In cases where the response of a coated acoustic wave sensor is dominated by mass loading, the magnitude of the response (and hence the sensitivity) is directly proportional to the partition coefficient and to the sum of the linear solvation energy relationship (LSER) factors, a linear combination of several coating and analyte properties. In the present case, the terms of interest, which are directly affected by the analyte and coating dipole moments and polarizabilities, are \( s \pi_2 \text{H} \) and \( r \pi_2 \text{H} \), where the coefficients \( s \) and \( r \) are related to the coating properties and \( \pi_2 \text{H} \) and \( \pi_2 \text{H} \) are related to the analyte properties, respectively. \((21,22)\) The minor variations in dipole moment and polarizability among the four isomers are expected to directly affect the partition coefficients of the coating, leading to small, yet measurable, variations in sensitivity and response time for each isomer.
Figure 1. Repeat unit of polystyrene along with formulae of ditridecyl phthalate and p-xylene. Black arrows indicate possible interactions between 6-membered aromatic rings; red arrows indicate alkyl groups.

Shown in Table 2 are the differences in Hansen solubility parameters (HSPs), the calculated $R_a$, and the resulting RED for each coating/analyte pair. Note that the calculated REDs for $p$- and $o$-xylene are very similar, indicating that the effects of polarizability and dipole moment (Table 1) will be critical to differentiable analyte responses.

<table>
<thead>
<tr>
<th>analyte</th>
<th>coating</th>
<th>$\Delta\delta_d$, MPa$^{1/2}$</th>
<th>$\Delta\delta_p$, MPa$^{1/2}$</th>
<th>$\Delta\delta_h$, MPa$^{1/2}$</th>
<th>$R_a$, MPa$^{1/2}$</th>
<th>RED</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylbenzene</td>
<td>DTP-PS</td>
<td>0.13</td>
<td>4.17</td>
<td>1.20</td>
<td>4.4</td>
<td>0.51</td>
</tr>
<tr>
<td>$m$-xylene</td>
<td>DTP-PS</td>
<td>0.13</td>
<td>2.17</td>
<td>-0.2</td>
<td>2.2</td>
<td>0.26</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>DTP-PS</td>
<td>0.33</td>
<td>3.77</td>
<td>-0.5</td>
<td>3.9</td>
<td>0.45</td>
</tr>
<tr>
<td>$o$-xylene</td>
<td>DTP-PS</td>
<td>0.13</td>
<td>3.77</td>
<td>-0.5</td>
<td>3.7</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*30% DTP by weight in PS polymer film; HSPs of this coating were estimated as the percentage-weighted sum of the HSPs of two coating components.

Materials and Methods

A single sensor coating has been selected for this work from among the set of previously designed coatings. (7) Polystyrene (35,000 g/mol) was purchased from Sigma-Aldrich, and DTP (530.8 g/mol) was purchased from Scientific Polymer Products. Chloroform, used as a solvent to cast the coating layer, was purchased from Sigma-Aldrich (purity > 99.5%). The coating solutions were prepared as weight/weight ratios of 30% plasticizer to 70% polymer and then of 7% polymer-plasticizer blend to 93% solvent to achieve the desired coating thickness. The resulting coating solution was sealed to prevent solvent evaporation, stirred overnight, and then sonicated for a minimum of 4 h to ensure uniformity of the solution.

The sensor device selected for this work is a 36-degree-rotated Y-cut, X-propagating lithium tantalate (LiTaO$_3$) SH-SAW device, known for its efficient operation in liquid environments. (23) The device uses a dual delay-line configuration to conduct differential measurements that minimize the impact of small temperature variations on the results. A detailed description of the operation of this device can be found elsewhere. (23)

The cleaning procedures for sensor devices and glass slides (acting as sensor analogs for coating thickness characterization) have been described in detail. (7) Following proper cleaning, coatings were deposited onto the
surface of each sensor device and analogue via spin coating at 5000 rpm, followed by baking for 1 h at 60 °C to
evaporate the solvent and remove internal stress from the coatings. Thickness was characterized using an α-
Step IQ surface profilometer and was measured to be $h = 1.30 \pm 0.03 \mu\text{m}$ using the conditions specified above.

Coating characterization for each target analyte was performed using single-analyte solutions of each isomer in
degassed ultrapure DI water. Ethylbenzene, $m$-, $p$-, and $o$-xylene were purchased from Sigma-Aldrich with
purities of >99.5%, >99%, >99%, and >98%, respectively. Solutions of 5 parts-per-million (ppm) by volume target
analyte in DI water were prepared and stirred for at least 4 h before dilution to target concentrations between
100 ppb and 1.2 ppm.

Coated devices were mounted in a liquid flow cell for single- and multianalyte measurements, conducted using a
microflow peristaltic pump (Ismatec Reglo Digital MS-CA4/12–100), a vector network analyzer (Agilent E5061B),
and switch-control unit (Agilent 34980A). A gas chromatography-photoionization detector (GC-PID; Defiant
Technologies FROG-4000) was used to independently confirm the concentration of each analyte solution, with
an associated measurement error of 7%. (24) The experimental setup, measurement procedures, and transient
response analysis (both for single- and multianalyte solutions) are described in further detail
elsewhere. (7,11) For the analysis, sensor responses to single-analyte and multianalyte samples were modeled
as a single exponential curve and as a sum of exponential functions, respectively. (11)

Results and Discussion

Single-Analyte Characterization

In previous work, sensor coatings made from poly(isobutylene) (PIB) provided adequate sensitivity to identify
benzene and toluene but did not permit differentiation of ethylbenzene and total xylene. (8–11) This deficiency
was addressed by designing polymer-plasticizer blend coatings with significant increases in sensitivity, providing
measurable differences between the responses of the analytes of interest. (7,12) Building on those results, the
present work relies upon a single, highly sensitive sensor coating with estimation-theory-based signal processing
to better elucidate minor differences in the sensing parameters extracted from sensor transient responses.

The selected 30% DTP-PS polymer-plasticizer blend coating exhibits excellent sensitivity to all BTEX
analytes, (7) including total xylene. The extracted sensing parameters, sensitivity and response time constant,
for this coating interacting individually with each of the target analytes are shown in Table 3. Our experiments
showed that over the concentration range studied, sensitivity and response time are independent of
concentration. In addition, an RMS noise level of 8.9 Hz was measured for this coating, corresponding to a
detection limit of 5 ppb or less of absorbed analyte (xlenes), and indicating satisfactory performance at very
low analyte concentrations. Note that measurements as low as 20 ppb have been recorded for this coated
device, close to the calculated limit of detection.

Table 3. Average Sensitivity and Response Time Constant of 30% DTP-PS Coating for Each Target Analyte

<table>
<thead>
<tr>
<th>analyte</th>
<th>sensitivity (Hz/ppm)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylbenzene</td>
<td>3700 ± 250</td>
<td>325 ± 16</td>
</tr>
<tr>
<td>$m$-xylene</td>
<td>6170 ± 650</td>
<td>316 ± 25</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>7680 ± 450</td>
<td>370 ± 6</td>
</tr>
<tr>
<td>$o$-xylene</td>
<td>4110 ± 620</td>
<td>244 ± 19</td>
</tr>
</tbody>
</table>

*Values are averages of 10 < $n$ < 20 measurements; standard deviation is indicated after “±”; coating
thickness $h = 1.3 \mu\text{m}$.

An inverse relationship between coating sensitivity and analyte dipole moment (Table 1) was noted for $m$-, $p$-, and $o$-xylene: as analyte dipole moment decreases, coating sensitivity increases. Thus, both ethylbenzene and $o$-
xylene, with similarly high dipole moments, show relatively low sensitivities. This result follows the coating design criteria: both DTP and PS are relatively nonpolar and thus favor the absorption of nonpolar analytes, especially in aqueous-phase sensing where the analytes partition between the polar aqueous phase and the nonpolar sensor coating. This is in line with previous results, (7) wherein we reported this coating’s insignificant sensitivity to the very polar ethanol (1.66 D) (25) and exceptionally high sensitivity to the nonpolar n-heptane (0.0 D). (26) The sensitivity results in Table 3 also indicate that the coating/analyte partition coefficient, $K$, is highest for $p$-xylene.

Also apparent in Tables 2 and 3 is the relationship between analyte polarizability and response time constant: $p$-xylene, the least polarizable, displays the slowest response, followed by $m$-xylene and ethylbenzene, with identical polarizabilities and similar response time constants, then $o$-xylene, with the highest polarizability and fastest response. The rate-limiting factor for analyte sorption in liquid-phase sensing can be either diffusion of the analyte through the aqueous phase (particularly at very low analyte concentrations), diffusion through the polymer matrix (more typical at higher concentrations, or when analyte and coating interact more strongly), or a convolution of the two; the concentration-independent time constants observed here are consistent with diffusion either through the polymer coating or the aqueous phase being rate limiting. Response time constants may therefore increase if the sensitivity to an analyte increases to the point that diffusion slows. More typically for physisorptive processes, diffusion in both aqueous and coating phases slows with molecular size (i.e., location of alkyl groups around the benzene ring), leading to a longer response time. At first, this does not appear to be the case for ethylbenzene, which unexpectedly shows a response time constant similar to $m$-xylene, despite their different sensitivities. This deviation is potentially explained by the steric hindrance caused by its ethyl group in comparison to the relative locations of the methyl groups in the three xylene isomers: $o$-xylene is most compact (most highly polarizable, see Table 1) due to its two methyl groups’ close proximity; $m$-xylene is next, with both methyl groups on “the same half” of the benzene hexagon, closely followed by ethylbenzene, with a more elongated shape but only one pendant alkyl group; followed by $p$-xylene, the least polarizable isomer, due to its pendant alkyl groups being as far as possible from one another across the aromatic ring. Note that ethylbenzene is also the only compound among these four chemical isomers that is not planar, with the ethyl group lying preferentially perpendicular to the plane of the benzene ring. (27) The fact that ethylbenzene and $m$-xylene have identical polarizability, but the latter is slightly more compact in shape, would lead us to predict that its response time constant should be slightly shorter, which is indeed the case.

Sample transient response curves for each target analyte scaled to 1 ppm analyte concentration are shown in Figure 2 to visualize the data in Table 3. Note that while the absorption responses show similar shapes, unique sensing parameters for each isomer are observed, indicating that unique identification of each isomer is possible with this coating. This is a result not previously possible, as sensor coatings made from COTS polymers do not, in our experience, display the sensitivity required to detect such small variations in coating responses. It is also noted, as shown in Figure 3, that the desorption time constant is identical to the absorption time constant for each isomer, thus allowing for the possible use of the less-noisy time constant in the data processing or providing two opportunities to measure the same value per sorption event, providing improved accuracy.
Figure 2. Measured sample absorption responses of the 30% DTP-PS \((h = 1.3 \text{ µm})\) coating to (blue) ethylbenzene, (red) \(m\)-xylene, (purple) \(p\)-xylene, and (green) \(o\)-xylene. Each analyte is introduced at the time denoted by the arrow.

Figure 3. Measured absorption and desorption responses of the 30% DTP-PS \((h = 1.3 \text{ µm})\) coating to \(p\)-xylene (A), \(o\)-xylene (B), ethylbenzene (C), and \(m\)-xylene (D), scaled to 1 ppm analyte concentration. Analyte is introduced at the time denoted by the blue arrow, and pure DI water is introduced to flush the analyte from the coating at the time indicated by the red arrow. Note that the desorption responses are nearly identical to the absorption responses in each case, allowing for their interchangeable use if required.

Sensor Signal Processing for Detection and Identification of Chemical Isomers in Multianalyte Samples

Previously, exponentially weighted recursive-least-squares estimation (EW-RLSE) was developed to estimate the concentrations of several analytes in mixture solutions by modeling transient responses as sums of single exponentials. \(^{11}\) We subsequently reported the unique identification of ethylbenzene and total xylene (1:1:1 mixtures of \(m\)-, \(p\)-, and \(o\)-xylene, treated as a single analyte) using this method. \(^{7}\) The assumption that the absorption of one analyte did not interfere with that of any others was key. This approach is critical here, as treating each xylene isomer as an individual analyte in liquid-phase sensing is challenging and requires a signal-processing technique appropriate for small variations in extracted sensing parameters. A further benefit of EW-RLSE is the accurate estimation in the presence of significant measurement noise: the responses in Table 3 show that sensitivities and response time constants can be extremely close and hence could be difficult to distinguish in noisy data.

The above framework requires that the total concentration of the mixture in the coating at time \(t\) be the sum of the concentrations of each individual \((i\text{th})\) analyte, \(C_i(t)\), as would be measured in a single-analyte response; thus, a multianalyte sensor response can be modeled by the sum of the individual frequency shifts for individual analytes.
\[ \Delta f(t) = \sum_{i=1}^{4} \alpha_i f_{\infty,i} \left[ 1 - e^{-t/\beta_i \tau_i} \right] u_s(t) \]

(2)

where \( \Delta f(t) \) is the total frequency shift as a function of \( t \), \( f_{\infty,i} \) is the equilibrium frequency shift for each individual analyte, \( \tau_i \) is the response time constant of each analyte for the selected coating, and \( u_s(t) \) is the unit step function. In eq 2, the constants \( \alpha_i \) and \( \beta_i \) represent the respective effects of the dipole moment and polarizability of each analyte.

Identifying and quantifying isomers with high similarity via very similar sensor responses requires reliable treatment of small variations, including possible corrupting noise. EW-RLSE is well suited, weighting the most recent data more heavily (exponentially so) to accelerate convergence and accurately estimate unknowns. To apply EW-RLSE, the multianalyte sensor response is rearranged to (11)

\[ y_k = \Delta f_k = \sum_{i=1}^{4} f_{\infty,i} x_k^{(i)} + w_k = x_k^T C + w_k \]

(3)

Equation 3 is a general discretization of eq 2, where \( y_k \) represents the measured data, \( \Delta f_k \) represents the discretized total frequency shift, \( x_k \) is a set of normalized concentrations of absorbed analytes at time \( t = kT \) (where \( T \) is the sampling period), \( w_k \) is the actual measurement noise, and \( C = [f_{\infty,1} f_{\infty,2} f_{\infty,3} f_{\infty,4}]^T \) is a vector of unknown parameters (equilibrium frequency shifts) that are to be estimated. From here, the estimated output \( \hat{y}_k \) can be expressed as

\[ \hat{y}_k = x_k^T \hat{C}_k \]

(4)

with \( \hat{C}_k \) defined as the estimate of the unknown parameters at discrete times \( kT \). EW-RLSE extracts identification from the responses of such closely related chemicals by the amplification factor introduced by the exponential weight, highlighting the small differences, enabling proper identification. This factor, \( 1/\lambda \), is introduced in the estimate of the unknown parameters, \( \hat{C}_k \), allowing minimization of an exponentially weighted least-squares cost function (11)

\[ \hat{C}_k = \hat{C}_{k-1} + P_{k-1} x_k (x_k^T P_{k-1} x_k + \lambda^2 \sigma_w^2)^{-1} e_k \]

(5)

where \( 0 < \lambda \leq 1 \) is called the forgetting factor, \( x_k \) vector components are the normalized concentrations of absorbed analytes at time instant \( k \), \( \sigma_w^2 \) is the measurement (sensor) noise variance, \( (x_k)^T \) denotes the transpose of the vector \( x_k \), and \( e_k \) denotes the measurement estimation error, defined as the difference between the measured data and estimated data at time \( k \).

The matrix \( P_{k-1} \), which is the covariance of the parameter estimation error, is found from the following Riccati difference equation (11)
\[ P_k = \frac{1}{\lambda^2} \left[ P_{k-1} - P_{k-1} x_k (x_k^T P_{k-1} x_k - \lambda^2 \sigma_w^2)^{-1} x_k^T P_{k-1} \right] \]

(6)

In order for the parameter estimate \( \hat{\theta}_k \) to converge to its actual value, the convergence of the solution \( P_k \) of the Riccati equation is needed, since \( P_k \) measures the uncertainty in the value of the estimated parameters. From the convergence theory of such Riccati equations, (28) it is known that the observability Gramian must be of full rank to guarantee convergence, which in this case reduces to \( \mathcal{O} = \sum_{k=1}^{4} L L^T \), where

\[
L = \begin{bmatrix}
    x_k^T & \frac{1}{\lambda} x_k^T & \frac{1}{\lambda^2} x_k^T & \frac{1}{\lambda^3} x_k^T \\
\end{bmatrix}^T
\]

(7)

Since elements of \( x_k^T \) may be very close to one another due to the similarity of the properties of isomers, multiplication of the second to fourth rows of the \( L \) matrix by \( \lambda^{-1}, \lambda^{-2}, \) and \( \lambda^{-3} \), respectively, amplifies their differences, guaranteeing the nonsingularity/full-rank property of the observability Gramian. This results in the superior response, which shows successful identification of the isomers by this estimator.

Multianalyte Characterization

Using the approach described above, the responses of the 30% DTP-PS polymer-plasticizer-coated device were used to identify and quantify multianalyte mixtures of ethylbenzene and the three xylenes. A typical result (Figure 4) demonstrates excellent agreement between the measured data (dots) and the estimated transient sensor response (dashes) to a mixture of the four isomers.

Figure 4. Experimentally obtained transient response (blue dots) of SH-SAW device coated with 30% DTP-PS coating to a 4-analyte aqueous solution of 150 ppb ethylbenzene (estimated: 143 ppb), 440 ppb \( m \)-xylene (estimated: 407 ppb), 440 ppb \( p \)-xylene (estimated: 405 ppb), and 420 ppb \( o \)-xylene (estimated: 413) together with the estimated sensor response using EW-RLSE (red dashed line), which closely tracks experimental results, demonstrating accurate estimation.

Several measurements were conducted with mixtures of ethylbenzene and the three xylenes at concentrations from low ppb to low ppm. Results in Figure 5 are compared to the concentrations determined using GC-PID, by which method analyte concentrations are determined with an average error of ±7%. (24) The estimated concentrations lie in close proximity to the ideal line, with an average deviation of about ±7% for ethylbenzene,
±5% for m-xylene, ±7% for p-xylene, and ±6% for o-xylene. Unique identification of each xylene isomer, both in single-analyte and mixture solutions, was achieved, a result previously impossible using conventional polymer coatings. Given the 7% measurement error of the GC-PID, its measured concentrations are in excellent agreement with those estimated.

Figure 5. Actual analyte concentrations versus estimated analyte concentrations from sensor responses using EW-RLSE processing for several aqueous solutions of ethylbenzene and the three xylenes, shown with an ideal line. Dashed lines indicate ± 10% analyte concentration. Actual analyte concentrations were determined to be ± 7% using GC-PID. The closer the data falls to the ideal line, the more accurate the estimate.

Conclusions
The analytical capability of a sensor system has been investigated, which includes an SH-SAW sensor device coated with a specifically designed polymer-plasticizer blend coating whose response is analyzed using estimation theory-based sensor signal processing. The result of this analysis is the identification and quantification of single- or multianalyte solutions of the chemical isomers ethylbenzene, m-, p-, and o-xylene directly in the liquid phase. While separation of these chemical isomers is not the focus of this work, unique detection and sensing can provide a foundation for a fast and accurate method of identification. This relatively simple approach identifies the targeted analytes efficiently, which could save significant time and energy during chemical manufacturing or environmental monitoring. Using exponentially weighted recursive-least-squares estimation, the concentrations of four-analyte mixtures of chemical isomers were estimated to ≤ 7% average error for each individual analyte. In each mixture sample, all analytes were successfully identified and estimated, a result that has yet to be reported in the field of direct liquid-phase chemical sensing using acoustic wave-based sensors.

This impressive performance utilized a sensor coating that blends the plasticizer ditridecyl phthalate with polystyrene for high sensitivity to aromatic hydrocarbons in water, with good stability. Coating sorption properties, namely sensitivity and response time constant, are significantly impacted by analyte dipole moment and polarizability. While COTS polymer sensor coatings may suffice for many chemical sensing applications, challenges such as identifying chemical isomers can benefit from bespoke design and tailoring of sensor coatings based on physical parameters and chemical structures of coating components and analytes. Likewise, while the use of one sensing parameter such as SH-SAW equilibrium frequency shift may suffice in some cases, challenging applications may necessitate a multivariate sensing approach with capable signal processing. The reproducible analyte-to-analyte variations in the extracted sensing parameters of this coating (30% DTP-PS blend) are the foundation of unique identification, but they must be combined with an appropriate method like EW-RLSE to reliably identify and accurately quantify multianalyte solutions. The presented approach can also be applied to other isomer systems and, even in the presence of chemical interferents, provided that the designed coating shows distinguishable responses to the isomer system and/or interferents. In the presence of interferents, eqs
2, and 3 can be appropriately modified to account for their responses. It should be noted that the coating may also be designed to have low or no affinity for some interferents, and hence would contribute to the selectivity of the sensor system. This approach has been shown for a number of interferents in a previous work. (7)

Notes
The authors declare no competing financial interest.

References


