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Design of Chemical Sensor Coatings Based on Blends of a Single Polymer-Plasticizer Pair for Detection of Single or Multi-Analyte Aqueous Solutions

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# Abstract:

The design of new, adaptable chemical sensor coatings using a single polymer-plasticizer pair for detection of single or multiple chemical compounds (e.g. BTEX) in aqueous solutions is presented. By modifying blend mixing ratios, the sensing characteristics of the coatings can be varied. Together with extraction of multiple sensing parameters (i.e. shear modulus, sensitivity, response time constant, etc.), this allows for more accurate analyte identification and quantification. Using a selected single polymer-plasticizer pair, several coatings were designed and used to build a sensor array. Sensing data indicates sufficient selectivity for unique identification of single analyte solutions. For solutions of multiple analytes and interferents, a different approach involving a single coated sensor characterized for all possible target chemicals and estimation theory-based multivariate signal processing was implemented. Results show accurate analyte identification and estimation of concentrations for multi-analyte solutions.

# INTRODUCTION

Direct chemical sensing in liquid phase allows for accurate quantification of many dissolved analytes, including non-volatile compounds. However, it requires new and innovative approaches to overcome various challenges, such as coating stability in water and sensitivity. Sensitivity of polymer-coated sensors in liquid phase is often low as partition coefficients for most coating/analyte pairs are lower in water than in air [1]. Selectivity of chemical sensors can also be poor for chemically similar analytes as is the case for benzene, toluene, ethylbenzene, and xylenes (BTEX compounds).

Sensor arrays work well for single analyte detection but are ineffective for solutions of two or more analytes [2]. Signal processing techniques can help overcome this inherent shortcoming through the use of multiple different coating sensing parameters.

Polymer coated sensor responses in liquid phase are typically significantly slower than responses in the gas phase, as analyte diffusion coefficients are much lower in liquid [3]. Slower responses are useful for signal processing, as in some cases slower responses can allow for detailed analysis of transient responses. This, in turn, can help reduce the number of coated sensors needed to form an array. This technique is also expected to work with gas phase measurements, provided that signal processing is able to track much more rapid sensor responses.

Polymer and polymer-plasticizer blend coated SH-SAW devices have been shown to be chemically sensitive and selective to some hydrocarbon compounds (i.e. BTEX) and are therefore the focus of this work. Polymer-plasticizer blends offer higher sensitivity than commercially available polymer coatings [4]. The sensing characteristics of polymer-plasticizer blend coatings can be tuned to vary sensitivity and selectivity of each coating/analyte pair of interest. By using a two-step approach involving formation of an array of coated sensors using a single polymer-plasticizer pair with a varied blending ratio, and multivariate signal processing using a single selected sensor from the array, both single and multi-analyte solutions can be accurately identified.

# EXPERIMENTAL

## Design of Sensor Coatings

Selection of an appropriate polymer for use as a sensor coating is critical to coating design. The chemical and/or physical properties (e.g., glass transition temperature, Hansen solubility parameters) of commercially available polymers often make them unsuitable for development of sensor coatings. The number of available polymers can be increased when considering the addition of a suitable plasticizer. Adding a plasticizer to an appropriately selected polymer can drastically improve the sensing characteristics of the resulting coating/s.

The glass transition temperature (Tg) of a polymer greatly influences the ability of the polymer to absorb target analytes. For example, a polymer with high affinity to selected target analytes may also have a high Tg, and therefore may be unsuitable for sensing due to a low sorption capacity (characteristic of a glassy polymer). By selecting a suitable plasticizer, the glass transition of a high Tg polymer can be reduced, and the resulting polymer-plasticizer blend may now have more suitable characteristics for sensing.

Hansen solubility parameters (HSPs) of coating constituents and target analytes should also be considered when selecting coating materials (if available). Selecting polymer and/or plasticizer with HSPs close to those of the target analyte will result in increased affinity between analyte and coating [4]. HSPs are directly related to forces present between molecules, specifically the intermolecular dispersion forces (δd), polar forces (δp), and hydrogen bonding forces (δh). HSPs are used to calculate a radius of solubility Ra for two materials as an indicator of solubility, given by equation 1 [5]. RED is calculated as the ratio of Ra to an experimentally determined radius of interaction R0 [5].

HSPs provide an accurate way of predicting affinity between chemical compounds as RED values directly indicate miscibility between the selected chemical compounds. RED values less than one indicate good miscibility between compounds. High affinity/good miscibility between coating components and target analytes can result in increased coating sensitivity and selectivity to those analytes.

By varying the mixing ratio of an appropriately selected plasticizer and polymer the sensing properties (sensitivity, response time constant, device loss) of coatings can be varied. It is noted that the frequency shift response for polymer coated SAW-based sensors indicates both mass loading and viscoelasticity contribution. Viscoelastic contributions are due to the polymer shear storage modulus G' and shear loss modulus G''. Hence, in addition to frequency shift (i.e. sensitivity) and response time constant, coating loss can also be used as a sensing parameter. Changes in coating loss (viscoelastic properties of the coating) are due to further softening/plasticization of the coating. During the sorption process, the polymer matrix undergoes softening, thus a reduction in shear modulus [6]. These changes in shear modulus can be determined by observing the corresponding changes in coating loss. Shown in Figure 1 are the loss changes of polymer-plasticizer blend coatings in air versus in water. As plasticizer concentration in the blend is increased, the resultant coating is observed to soften further and a corresponding change in coating loss is observed.

[Figure 1 - 
Plot of change in coating loss (dB) from in air to in liquid (water) for several plasticizer concentrations. Notice that as plasticizer concentration increases, so does the loss when moving from air to water.
](https://ieeexplore.ieee.org/mediastore_new/IEEE/content/media/8787960/8808173/8808686/post1-p4-post-large.gif)

**Figure 1** Plot of change in coating loss (dB) from in air to in liquid (water) for several plasticizer concentrations. Notice that as plasticizer concentration increases, so does the loss when moving from air to water.

The polymer selected for this work is polystyrene (PS), as its HSPs are a good match for benzene and other chemically similar compounds (see table 1) [4]. This is expected, as the styrene monomer contains a phenyl ring and is highly chemically similar to BTEX compounds.

**Table 1**Differences between HSPs of 1st and 2nd compound (Δδ, in units of MPa0.5), with quadratic sum Ra and normalized RED values.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 1st | 2nd | **∆δd** | **∆δp** | **∆δh** | **Ra** | **RED** |
| Benzene | PS | -0.2 | -4.5 | -0.9 | 4.61 | 0.54 |
| Toluene | PS | -0.6 | -3.1 | -0.9 | 3.44 | 0.40 |
| Ethylbenzene | PS | -0.8 | -9.9 | -1.5 | 4.47 | 0.52 |
| Xylenes | PS | -1 | -3.5 | 0.2 | 4.04 | 0.47 |

The plasticizer Ditridecyl Phthalate (DTP) was selected based on previous work with another phthalate-based plasticizer, Diisooctyl Phthalate (DOP) [7]. DOP-PS coatings showed good sensitivity to BTEX compounds, but DOP’s small molecular weight (390.56 g/mol) resulted in observable plasticizer leaching, hence coating instability. As DTP has a significantly larger molecular weight (530.82 g/mol), higher permanence in the coating is achieved, resulting in excellent coating stability over a much longer period of time.

Varying mixing ratio of coating components can result in slight variations in the characteristics of the resultant coatings, which will lead to increased selectivity to target analyte for sensor arrays. However, the above is not obvious, as varying mixing ratios along with selection of an appropriate plasticizer, a tradeoff in coating properties must be achieved. The efficiency of a plasticizer is in direct conflict with its permanence, as can be seen in Figure 2 (shown with a third property, compatibility) [8]. The higher permanence of DTP is achieved at the cost of lower plasticizer efficiency but is remedied by increasing plasticizer concentration.

[Figure 2 - 
Diagram of tradeoffs between plasticizer properties and associated material properties of each [8].
](https://ieeexplore.ieee.org/mediastore_new/IEEE/content/media/8787960/8808173/8808686/post2-p4-post-large.gif)

**Figure 2** Diagram of tradeoffs between plasticizer properties and associated material properties of each [8].

Variation of plasticizer concentration can only be done within a certain range (unique for each plasticizer-polymer pair) as dictated by the chemical and physical properties of polymer and plasticizer. For this work, plasticizer percentage was varied to create coatings with a range of 22%-35% weight/weight plasticizer to polymer. This range was experimentally determined to give stable coatings for the selected polymer-plasticizer pair DTP and PS. Concentrations lower than 22% w/w plasticizer resulted in coatings which were too glassy, or poor absorbers of analyte. Concentrations higher than 35% w/w plasticizer resulted in coatings with poor long-term stability.

## Setup and Procedure

The sensors chosen for this work are 36° YX LiTaO3 Shear Horizontal-Surface Acoustic Wave (SH-SAW) devices [9]. Each sensor is coated with a polymer-plasticizer blend by spin coating. A thickness of 1.3 ± 0.05µm was selected for all coatings and verified with a surface profilometer. Coated devices are housed in individual liquid flow cells for exposure to analyte solutions. The transient responses of coated devices to analyte solutions were observed by first exposing the coating to DI water, followed by analyte solution. Coated device responses (frequency shifts) were recorded using a network analyzer. Flow rate of all liquid samples was a constant 7µL/s. Analyte concentration (for both single and multi-analyte solutions) was independently verified by a Gas Chromatography-Photoionization Detector (GC-PID).

Selectivity of the formed sensor array for BTEX compounds has been analyzed using principal component analysis (PCA). Sensing parameters used for analysis were sensitivity and average response time constant for each coating/analyte pair, extracted from single-analyte transient responses. Coatings made from commercially available polymers were found to be unsuitable to uniquely identify ethylbenzene from xylenes, as coating parameters for these analytes have been similar/identical. Coatings made from designed polymer-plasticizer blends are shown below to be capable of unique detection of each BTEX analyte; a significant improvement from previously investigated coatings.

To demonstrate that limitations associated with sensor array selectivity are not insurmountable, multivariate sensor signal processing is used with a single coated sensor to identify multi-analyte BTEX solutions. A technique based on estimation theory using recursive-least-squares estimation and modeling of sensor transient responses has been selected for analysis of multi-analyte solutions. Using sensitivity and response time constant data extracted from single analyte responses (as was used for PCA), the program is able to accurately identify and estimate the concentrations of BTEX solutions of single or multiple analytes. This is useful as real-world samples typically contain multiple chemically similar analytes, which sensor arrays are not able to analyze with accuracy.

# RESULTS

Transient responses of coated sensors to single analyte solutions of BTEX compounds have been used to extract coating sensitivity and response time constant for each coating/analyte pair. Extracted sensing parameters are summarized in tables 2 and 3; values denote averages from n > 10 measurements for each coating/analyte pair.

**Table 2**Sensitivities for each coating/analyte combination studied (in Hz/ppm by weight). Coating compositions given as % DTP plasticizer in polystyrene.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **% DTP** | **B. Sens.** | **T. Sens.** | **E. Sens.** | **X. Sens** |
| 22% | 250±10 | 830±50 | 2470±300 | 4220±480 |
| 30% | 490±30 | 1220±50 | 2680±200 | 5650±480 |
| 32% | 520±20 | 1390±40 | 3520±230 | 5680±730 |
| 33.5% | 510±20 | 1390±30 | 3820±190 | 5140±400 |
| 35% | 530±30 | 1370±50 | 2930±130 | 5080±310 |

**Table 3**Response time constants (τ; in s) for each coating in the sensor array to each BTEX analyte.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ***% DTP*** | ***τ(B)*** | ***τ(T)*** | ***τ(E)*** | ***τ(X)*** |
| 22% | 74±6 | 144±4 | 365±9 | 424±7 |
| 30% | 46±3 | 125±5 | 311±22 | 430±8 |
| 32% | 38±2 | 108±3 | 336±9 | 407±17 |
| 33.5% | 42±3 | 125±4 | 338±28 | 430±11 |
| 35% | 48±3 | 127±3 | 366±23 | 410±22 |

Extracted coating parameters are used as inputs for a MatLab based PCA program. Results show significant cluster separation, including between ethylbenzene and xylenes clusters. This indicates good array selectivity to each BTEX analyte including ethylbenzene and xylenes, which were previously indistinguishable from one another using commercially available polymer coatings. Coating sensitivities (see Table 2) show similarity for some coating/analyte pairs. Array selectivity is significantly improved via the inclusion of response time constant data in analysis. Selectivity between ethylbenzene and xylenes should be expected for the studied polymer-plasticizer blend coatings, as significant differences are observed in coating parameters for these analytes. This data supports the findings from PCA, indicating the highly increased selectivity of the designed polymer-plasticizer blend coatings.

For visualization of array selectivity, sensing parameters of several coatings are shown in a radial plot (Figure 3). Sensitivities (normalized to the sensitivity of the 22% DTP-PS coating for each coating/analyte pair) and response time constants (in units of 100 seconds) are shown for selected coatings. Notice that while some ratios of sensitivities are similar, large differences in response time constants are observed, indicating good separation in agreement with PCA results.

[Figure 3 - 
Radial plot showing selected response time constants and ratios of sensitivities of coatings in the sensor array (response time constant values divided by 100 for scale) indicating selectivity of the array.
](https://ieeexplore.ieee.org/mediastore_new/IEEE/content/media/8787960/8808173/8808686/post3-p4-post-large.gif)

**Figure 3** Radial plot showing selected response time constants and ratios of sensitivities of coatings in the sensor array (response time constant values divided by 100 for scale) indicating selectivity of the array.

Careful selection of coatings for sensor array design is important, as ratios of sensitivity between coatings significantly contribute to the selectivity of the formed array. While ratios of sensitivity to benzene among coatings remain relatively similar, those of toluene, ethylbenzene, and xylenes vary significantly from coating to coating. For example, ratios of sensitivity to ethylbenzene and xylenes differ greatly between the 35% DTP-PS coating and 30% DTP-PS coating with respect to the 22% DTP-PS coating. This further supports the conclusion that the designed polymer-plasticizer blend coatings presented are indeed able to separate responses to ethylbenzene from those of xylenes.

For analysis of multi-analyte solutions, one coating has been selected from the array (30% DTP-PS) for testing. Using extracted sensing parameters, the estimation program is able to provide accurate identification and estimation of analytes present in solutions of single or multiple analytes. Figure 4 presents a sample sensor absorption response and response curve estimated by the program for a three-analyte solution of BTE. Note how the estimated response (shown as a dashed red line) closely tracks the experimentally obtained transient response, indicating a good fit to the model.

[Figure 4 - 
Response of SH-SAW device coated with 30% DTP-PS (h = 1.3µm) to multi-analyte BTE solution, introduced at t = 1 min. Shown are the measured and estimated responses obtained using EW-RLSE model.
](https://ieeexplore.ieee.org/mediastore_new/IEEE/content/media/8787960/8808173/8808686/post4-p4-post-large.gif)

**Figure 4** Response of SH-SAW device coated with 30% DTP-PS (h = 1.3µm) to multi-analyte BTE solution, introduced at t = 1 min. Shown are the measured and estimated responses obtained using EW-RLSE model.

Table 4 shows actual sample concentrations (as measured by GC-PID), estimated concentrations, and the percentage difference between estimated and actual concentrations for the curve shown in Figure 4. Low error in estimated values as compared to actual concentrations indicates high accuracy in quantifying concentrations of chemically similar analytes in a mixed solution.

**Table 4**Actual analyte concentrations, as measured by GC-PID system, and concentrations estimated using MS-EW-RLSE with percent difference for sensor response shown in Figure 5. Note that in this sample xylenes is estimated below the detection limit of the sensor, indicated by ~0 concentration.

|  |  |  |  |
| --- | --- | --- | --- |
| **Analyte** | **Actual Conc.** | **Est. Conc.** | **% Diff.** |
| Benzene | 590 ppb | 531 ppb | 10% |
| Toluene | 470 ppb | 450 ppb | 4% |
| Ethylbenzene | 250 ppb | 237 ppb | 5% |
| Xylenes | 0 ppb | ~0 ppb | N/A |

Figure 5 shows preliminary measured and estimated concentrations for data collected using the selected coated sensor, indicating that estimation of concentrations is accurate across several measurements. While more data collection is needed, preliminary results support the finding that polymer-plasticizer blend coatings are highly selective, including to ethylbenzene and xylenes unlike previously explored coatings.

[Figure 5 - 
Plot of estimated versus actual concentrations of BTEX analytes for several transient responses, shown with ideal line. Data shown falls close to the ideal line, indicating low error in each estimated result.
](https://ieeexplore.ieee.org/mediastore_new/IEEE/content/media/8787960/8808173/8808686/post5-p4-post-large.gif)

**Figure 5** Plot of estimated versus actual concentrations of BTEX analytes for several transient responses, shown with ideal line. Data shown falls close to the ideal line, indicating low error in each estimated result.

# CONCLUSION

A combined approach utilizing a sensor array and a single selected sensor with multivariate signal processing has been shown to overcome some selectivity issues inherent to chemical sensing. The plasticizer DTP was shown to form sensitive and stable sensor coatings when blended with PS. Sensing characteristics of coatings have been varied to form a sensor array from a single polymer-plasticizer pair. Selectivity of the array is high, thus allowing unique identification of single-analyte BTEX solutions. Preliminary estimation results using polymer-plasticizer blend coatings show promise in identifying and estimating multi-analyte BTEX solutions, which will further improve by using a third sensing parameter, the device loss. Work characterizing polymer-plasticizer blend coating responses to common interferents (i.e. trimethylbenzene, naphthalene, etc.) is ongoing for real-world sensing applications of aqueous samples.

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