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Detection and Quantification of Multi-Analyte Mixtures Using a Single Sensor and Multi-Stage Data-Weighted RLSE

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Abstract:

This work reports the development and experimental verification of a sensor signal processing technique for online identification and quantification of aqueous mixtures of benzene, toluene, ethylbenzene, xylenes (BTEX)

and 1, 2, 4-trimethylbenzene (TMB) at ppb concentrations using time-dependent frequency responses from a single polymer-coated shear-horizontal surface acoustic wave sensor. Signal processing based on multi-stage exponentially weighted recursive least-squares estimation (EW-RLSE) is utilized for estimating the concentrations of the analytes in the mixture that are most likely to have produced a given sensor response. The initial stages of EW-RLSE are used to eliminate analyte(s) that are erroneously identified as present in the mixture; the final stage of EW-RLSE with the corresponding sensor response model representing the analyte(s) present in the mixture is used to obtain a more accurate quantification result of the analyte(s). The success of this method in identifying and quantifying analytes in real-time with high accuracy using the response of just a single sensor device demonstrates an effective, simpler, lower-cost alternative to a sensor array that includes the advantage of not requiring a complex training protocol.

SECTION I. Introduction

The objective of this work is to demonstrate an alternative to the use of sensor arrays for multi-analyte detection, namely smart analysis of the time-dependent frequency shift transient from a single polymer-coated shear-horizontal surface acoustic wave (SH-SAW) sensor. Polymer-based chemical sensors often show only limited selectivity in real-world applications because, unlike biosensors, their partial selectivity leads to interaction with many analytes or analyte classes. This lack of selectivity exacerbates the challenge of correctly identifying and quantifying target analytes in a mixture of compounds.

The most common approach to achieve adequate selectivity in polymer-based chemical sensing is to use an array of partially selective sensors with chemically diverse sensor coatings selected for a particular application [1]. All the sensors in the array respond to most if not all analytes in the probed environment, but the pattern of responses from the sensors provides a unique fingerprint for each analyte or group of analytes [1]. The sensor-array approach to detect and quantify target analytes is often facilitated by dimension reduction and pattern-recognition techniques including linear-discriminant analysis, principal-component analysis, and cluster analysis. This approach works well for single and binary analyte samples or pre-defined mixtures. However, as the complexity of the mixture increases, the approach produces inaccurate detection and quantification results. Other drawbacks include potential misclassification, which is particularly likely if the chemical diversity (“chemical orthogonality”) and partial selectivity of the sensor coatings is insufficient; this problem is exacerbated if only one sensing parameter per sensor is used for classification, as is often the case. Given all the drawbacks of chemical sensor arrays, there is a pressing need to develop novel advanced signal processing approaches that can overcome challenges in chemical sensing for in-situ applications.

In this work, a multi-stage exponentially weighted recursive least-squares estimation (EW-RLSE) technique that utilizes two sensing parameters (i.e. response-time constant and steady-state amplitude) for the online identification and quantification of multi-analyte mixtures using the transient frequency-shift response of polymer-coated SH-SAW sensors is investigated. EW-RLSE is implemented in series (multiple stages) to obtain a more accurate result. The proposed technique can identify and quantify n analytes in a mixture, provided the characteristic response time constants and sensitivities of the analytes are known. Moreover, the approach could also be used to eliminate analytes that are erroneously identified as present in a mixture.

SECTION II. Proposed Signal Processing Procedure

The EW-RLSE technique used in this work is described in [2]. The purpose of EW-RLSE is to estimate the equilibrium frequency shifts resulting from the various analytes in the mixture, $f_{\infty,i}$ that collectively produced the measured total frequency-shift transient response. The concentrations of the analytes present in the mixture can then be determined based on the estimated equilibrium frequency shift and measured sensitivity (from single-analyte sensor responses) for each analyte. In this technique, initial estimation of $f_{\infty,i}$ is performed

using EW-RLSE and the n-analyte sensor response model. If erroneous analyte detection(s) are identified from the initial estimation step, the estimation process is repeated using the appropriate sensor response model (i.e. a sensor response model for analytes less than n) and EW-RLSE to obtain more accurate analyte quantification. This is because the estimated concentration(s) associated with erroneously detected analyte(s) can greatly influence the quantification result obtained for the analyte(s) that are present in the mixture. Thus, by repeating the estimation using EW-RLSE with the corresponding sensor response model for the analyte(s) identified to be in the mixture, more accurate quantification can be obtained. Note that erroneous analyte detections are identified based on the estimated concentrations of the analytes: if the estimated concentration of a particular analyte is negative or lower than a threshold value (i.e. the measured detection limit for that analyte), the concentration of the analyte is assumed to be zero and the estimation is repeated. The proposed approach is summarized in Fig. 1.

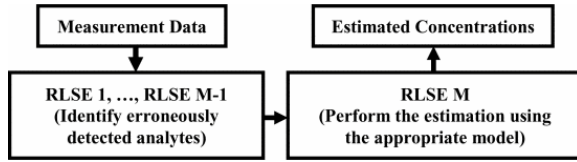


Fig. 1. Block diagram of multi-stage EW-RLSE for online identification and quantification of multiple analyte mixtures.

Note that the use of EW-RLSE for estimating equilibrium frequency shifts requires an accurate analytical model that describes the response of the SH-SAW sensor to the multi-analyte samples. This model follows directly from the model of single-analyte samples and binary mixtures of analytes, which has been discussed in detail in a previous publication [3]. The sensor response model to a mixture of n analytes can be represented by the following equation:

$$\Delta f_k = \begin{bmatrix} m_k^{(1)} & \dots & m_k^{(n)} \end{bmatrix} \begin{bmatrix} f_{\infty,1} \\ \vdots \\ f_{\infty,n} \end{bmatrix} + w_k = H_k \theta + w_k \quad (1)$$

where Δf_k is the measured frequency shift, $m_k^{(i)}$ is the normalized concentration of analyte i absorbed at time step k , and w_k is measurement noise with variance σ_w^2 . Note that $H_k = [m_k^{(1)} \dots m_k^{(n)}]^T$ is a vector of known signals (regressor) that can be determined at every time step, k using

$$m_{k+1}^{(i)} = \left(1 - \frac{T_S}{\tau_i}\right) m_k^{(i)} + \frac{T_S}{\tau_i} u_{s,k}, \quad (2)$$

and $\theta = [f_{\infty,1} \dots f_{\infty,n}]^T$ is a vector of unknown parameters that need to be estimated using EW-RLSE. In (2), τ_i is the response time constant for a given analyte/coating combination, $u_{s,k}$ is the unit step function, and T_S is the sampling period.

SECTION III. Results and Discussion

The proposed technique was demonstrated for the detection and identification of multi-analyte mixtures of benzene, toluene, ethylbenzene, xylenes (BTEX) and 1, 2, 4-trimethylbenzene (TMB) using the time-transient frequency shift response of a single polymer-coated SH-SAW sensor. The frequency transients were either obtained from SH-SAW sensors coated with 0.6 – μm poly(epichlorohydrin) (PECH) or 0.8 – μm poly(isobutylene) (PIB). For reference, analyte concentrations were also measured using a gas chromatograph-photoionization detector (GC-PID) system. The threshold values used for signal processing are

100 ppb (benzene), 50 ppb (toluene), 30 ppb (sum of ethylbenzene and xylenes), and 10 ppb (TMB), which in each case is the measured detection limit of the respective compound.

A sample result is shown in Fig. 2. Measured and estimated frequency shifts are in good agreement, resulting in estimated analyte concentrations within $\pm 10\%$ of actual concentrations. Note that the analytes in the mixture can be identified and quantified accurately in just half the time required for the response to reach steady state.

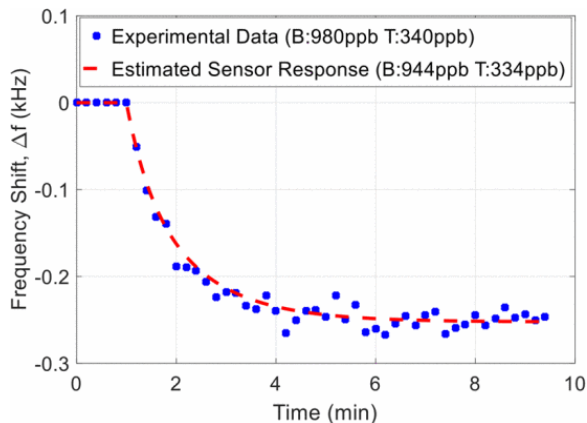


Fig. 2. Measured response of a SH-SAW sensor coated with $0.6 \mu\text{m}$ PECH to a binary mixture of benzene (b) and toluene (t). Also shown (red dashed line) is the frequency shift transient estimated using the proposed technique. The actual and estimated analyte concentrations are shown in the inset.

Table I shows sample results obtained using the multi-stage EW-RLSE technique, demonstrating its ability to identify and quantify mixtures of BTEX and TMB at ppb concentrations using measured frequency responses from only a single polymer-coated SH-SAW sensor. This demonstrates that the proposed technique is a viable alternative to chemical sensor arrays for multi-analyte detection and quantification, reducing cost and complexity while eliminating the training process.

Table I. Identification and quantification results obtained using multi-stage ew-rlse and frequency transient data, compared to analyte concentrations in the mixture measured using gc-pid

Actual Concentrations (in ppb)				Estimated Concentrations (in ppb)			
B	T	EX	TMB	B	T	EX	TMB
0	360	0	0	0	359	0	0
980	340	0	0	944	334	0	0
620	0	1260	0	660	0	1242	0
0	640	0	0	0	631	0	0
0	0	370	0	0	0	367	0

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