SAW ARRAYS USING DENDRIMERS AND PATTERN RECOGNITION TO DETECT VOLATILE ORGANICS

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Chemical sensor arrays eliminate the need to develop a high-selectivity material for every analyte. The application of pattern recognition to the simultaneous responses of different microsensors enables the identification and quantification of multiple analytes with a small array. Maximum materials diversity is the surest means to create an effective array for many analytes [1], but using a single material family simplifies coating development.

Dendrimeric polymers, or dendrimers, are attractive for such arrays because they contain chemically tailorable endogenous and exogenous binding sites, in addition to tunable permeability and other physical properties [2]. Dendrimers, prepared by repetitive branching, have three anatomical features: a central core, repetitive branch units, and terminal functional groups. Dendrimers are synthesized by adding repetitive branch units to the molecule one layer, or generation, at a time in iterative growth steps. Here we report the successful combination of an array of six dendrimer films with mass-sensitive SAW (surface acoustic wave) sensors to correctly identify 18 organic analytes over wide concentration ranges, with 99.5% accuracy. The set of materials for the array is selected and the results evaluated using Sandia’s Visual-empirical Region of Influence (VERI) pattern recognition (PR) technique [3,4].

We evaluated eight dendrimer films and one self-assembled monolayer (SAM) as potential SAW array coatings [5]. The region of the SAW delay line between transducers is first modified by a 200 nm-thick Au film, followed by a self-assembled monolayer of mercaptoundecanoic acid (MUA) [1,2]. Chemical diversity is imparted to the dendrimers through bulk-phase coupling of appropriate terminal functional groups with the primary-amine-terminated dendrimer surface. Next, reaction of the dendrimers’ few remaining unfunctionalized amines with the MUA monolayer yields amide-linked dendrimer films on the SAW devices.

Design and fabrication of SAW devices and the measurement system have been described elsewhere [1,5]. The 97-MHz ST-quartz SAW delay lines provide short-term frequency stability of ca. 0.3 Hz, yielding a detection limit of 100 pg/cm².

The 18 organic analytes we examined were: cyclohexane, n-hexane, i-octane, kerosene, benzene, toluene, chlorobenzene, carbon tetrachloride, trichloroethylene, methanol, n-propanol, pinacolyl alcohol, acetone, methyl isobutyl ketone, dimethylmethylphosphonate, diisopropylmethylphosphonate, tributylphosphate, and water. These analytes include multiple examples from several chemical classes.

We analyzed the SAW/dendrimer array data using the VERI PR technique [3,4], a newly-developed multivariate analysis method based on an empirical model of human cluster perception. VERI analysis correctly treats arbitrarily complex sensor response distributions, and automatically determines the multivariate decision thresholds necessary to produce appropriate class volume shapes for the array responses to any chemical analyte. Appropriate class volume shapes are needed to obtain correct estimates of the chemical recognition performance of sensor arrays and to achieve the most effective discrimination against unknown analytes (i.e., those not in the training set). VERI leave-one-out analysis quantitatively compares the chemical recognition performance of alternative choices of sensor films, and thus finds the optimal subset of a group of films for a set of target analytes. These results enable quantitative array-element selection comparisons not possible with principal-component analysis [3,4]. Inclusion of modeled sensor response degradation into the VERI leave-one-out analysis provides a comparison of the robustness of array responses for different film combinations.

Thus, the ability of an array to distinguish different analytes using VERI PR hinges upon choosing an array of sensors, the response of each constituting an axis in multi-dimensional space, such that each analyte is represented by a cluster of points that is geometrically distinct from the clusters for all other analytes. By choosing the best set of 6 coatings (5 dendrimers and one methyl-terminated SAM), we achieved 99.5% accuracy in identifying all of the compounds listed above over the 0.25 — 50% of pSa concentration range. This accuracy is maintained even with the addition to the calibration data of sensitivity losses of as much as 8% for any or all of the 6 sensors. The distributions of responses are quite complex, and are not easily converted into any of the simple forms needed for statistical-based pattern-recognition (PR) analysis.

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References
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