Investigating Molecular Size Variations In Thin Film Chemical Vapor Sensors

Thesis by

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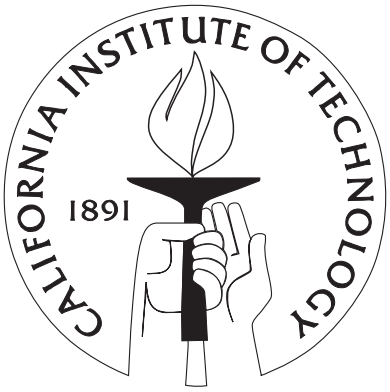
for the Degree of

Doctor of Philosophy



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To my mother, who said “Oh, they’ll pay *you*? You should totally do it!”

Acknowledgments

These last couple of months have been tumultuous. My family, and indeed, my entire social network have been there, in strength, and I can never repay that collective debt. Before getting to particular people, I must thank and send all my love to my family. I also must extend thanks to my thesis committee, and finally, to the USFS and NPS for helping me retain my sanity through my graduate career.

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Abstract

Vapor sensing arrays composed of broadly responsive, chemically sensitive detectors have been explored for many years. They have been used in fields ranging from good quality control, to environmental monitoring and explosives detection, to disease diagnostics. All of these tasks require high sensitivity and fine discrimination ability. As new challenges arise, the ability to understand the performance and improve the availability of array components becomes paramount.

This work details progress in gaining greater understanding of certain chemical substrates used in sensor arrays. Specifically, arrays using insulator/carbon black composite sensors have been prepared using either polymer or non-volatile small organic molecules as the insulating, chemically sensitive component. The crystallinity of the small molecules as compared to the polymers was determined to cause the differing formulation requirements between the polymers and the small molecules.

Additionally, arrays of sensors composed of varying molecular weights of a given polymer were examined. Very low molecular weights of polystyrene, a high glass transition temperature polymer, exhibited improved behavior and response times compared to higher molecular weights. Finally, arrays composed of varied length carboxylic and dicarboxylic acids were studied. Of these two homologous series, the arrays composed of carboxylic acids provided better discrimination than did those composed of dicarboxylic acids, suggesting the utility of sensor materials containing multiple accessible functional groups.

These studies, taken together, suggest several new ways to increase the number of compounds and chemical functionalities available to use in chemical vapor sensors. Increased sensor choice allows construction of more broadly responsive and finely discriminating sensor arrays, thereby increasing the general utility of composite vapor sensor arrays.

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Chapter 1

Introduction

sensor, n. — A device giving a signal for the detection or measurement of a physical property to which it responds.

Oxford English Dictionary [1]

1.1 Sensors

Throughout human history, people have relied on sensors. Chief among these, never out of vogue, are those comprising our sensory system. Eyes function as light detectors, transducing photons into electrical signals. Our ears do the same for sound waves, and our skin for such things as temperature or mechanical pressure. The brain receives all these electrical signals, and processes the raw data.

As understanding of the physical world grew, so too did our use of sensors in tools. Liquid thermometers detect temperature and transduce it via calibrated thermal expansion. Compasses rely on the magnetic properties of metals to sense the directionality of the planet's magnetic field. Barometers sense changes in air pressure, transduced through changing height of a column of liquid. Sensors are how we know the things we know.

We are surrounded by sensors in our everyday lives, rarely cognizant of their ubiquity. Every system with a remote control contains an infrared sensor. Car and refrigerator doors contain simple mechanical-electrical sensors to determine if a door is open or closed — transduced into a circuit closing, and a light turning on. Elevators sense your presence on their threshold, airplane systems sense the cabin pressure, and gas pumps sense when your tank is full. Sensors are increasingly how our systems know what *they* know, as well.

1.2 Cross Reactive Sensor Arrays

One particular sensor system, studied since the early 1980s, is a vapor-detecting sensor array. Modelled in some ways after the mammalian olfactory system, and because it can be used to "smell" the environment around it, such systems have been colloquially labelled as "electronic noses." In such arrays, each sensor produces a distinct but not deterministic response to an input — exposure to a vapor, such that a given analyte activates multiple sensors, and a given sensor responds to multiple analytes.[2] This is similar to the mammalian olfactory system, in which the olfactory epithelium is studded with odorant receptors (ORs). Each OR is active towards a variety of odorants, and a given odorant likewise activates multiple ORs.[3] However, a mammalian system has hundreds of distinct receptor types (mice have over one thousand different expressed ORs,[4] while humans have around 350[5]), with thousands of copies each. In comparison, array sizes of 10–20 distinct detectors are common in laboratory use, with each additional sensor slightly improving overall discrimination ability, but also adding further noise (Figure 1.1).[6]

In both systems, however, the pattern response from the complete system is passed

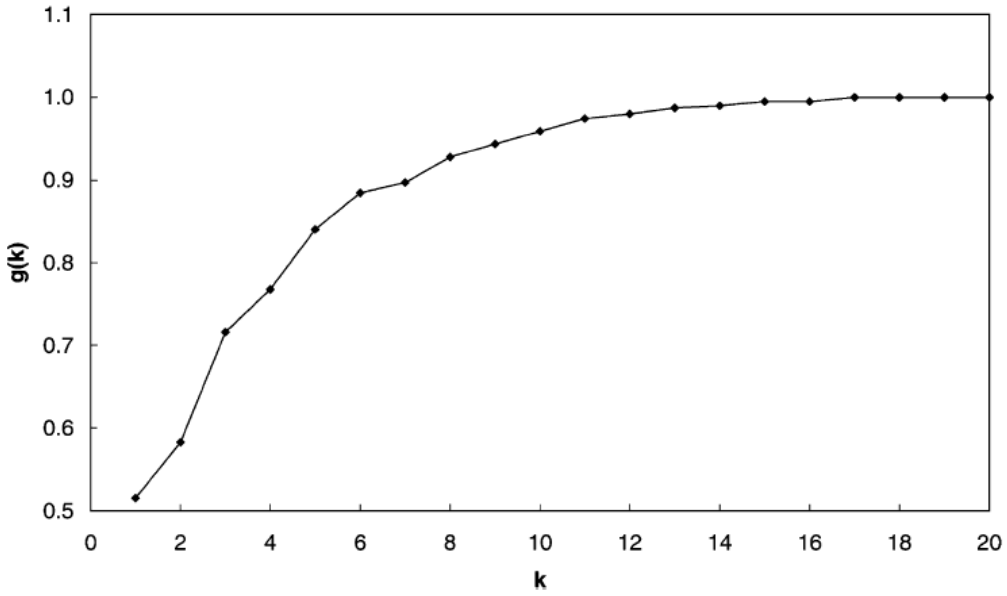

Figure 1.1: Classification performance — g(k) — vs. array size k for a polymer/CB composite sensor array. For each value of k in the range $1 \leq k \leq 20$, an exhaustive search of all possible k-detector combinations from a 20-detector array was performed to identify the array having k detectors that had the best classification performance for each of 21 tasks. For each task, the classification performance for any k-detector array was then compared to that of the full 20-detector array. No combination of k detectors does strictly better than g(k) relative to the full 20-detector array on all 21 tasks.[6]

along to the controlling system (brain or computer) for further processing; analyte determination, discrimination, quantification, or any other tasks. Cross reactive sensor arrays of this type have found use in such fields as food quality control,[7–10] environmental monitoring,[11,12] explosives detection,[13,14] and disease diagnostics.[15–17]

1.3 Sensor Types

A variety of sensor modalities have been used in vapor-detecting sensor arrays, some of the most notable being surface acoustic wave[9,13,18] and bulk acoustic wave detectors,[19,20] semiconducting metal oxide sensors,[10,21] microcantilevers,[22–24] conducting polymers,[7,25–28]

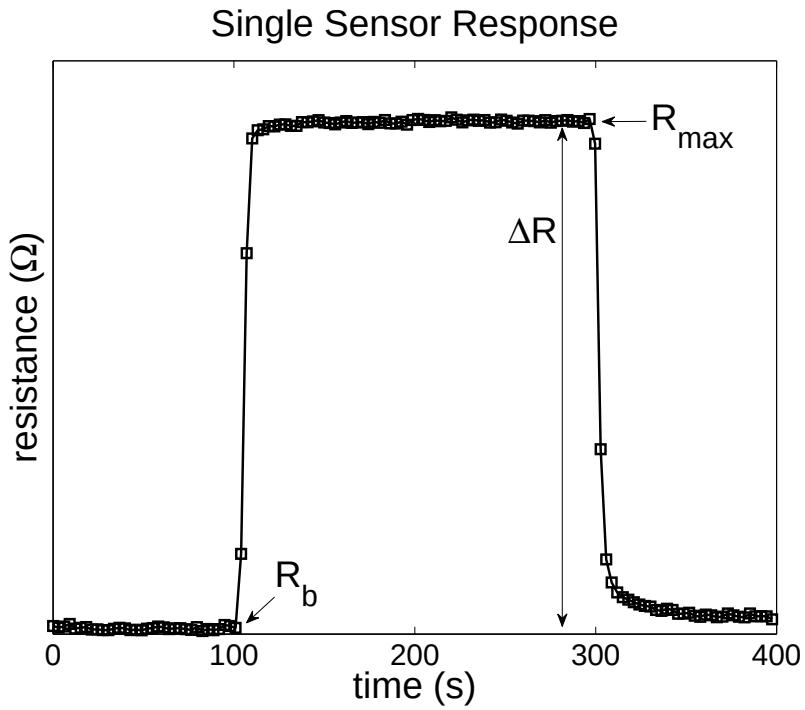

Figure 1.2: Resistance change of a poly(ethylene oxide)/carbon black composite sensor to a 200 second exposure to 2 ppth of chloroform vapor, at an overall flow rate of 2.5 L min^{-1}. R_{b} is the baseline resistance of the sensor, R_{max} the maximum resistance reached during exposure, and ΔR is the difference between the two. Raw data are shown; the absolute change in resistance displayed is around 60 ohms.

and various colorimetric indicators (such as metalloporphyrins).[13,29,30]

One specific approach, and that explored in this thesis, uses sensors comprised of intermixed regions of a conducting material mixed with an insulating organic material. Exposure to an analyte produces detectable changes in the resistance of sensor films cast from these mixtures (Figure 1.2). Conducting materials are often carbon black,[15,31,32] but have also included carbon nanotubes[33] or metal nanoparticles.[34,35] Insulating phases have included polymers,[15,31,32] dendrimers,[36] ligands on metal nanoparticles,[34,35] and non-volatile small organic molecules (SM).[37] All experiments described in this thesis rely on polymer- or SM/carbon black composite films.

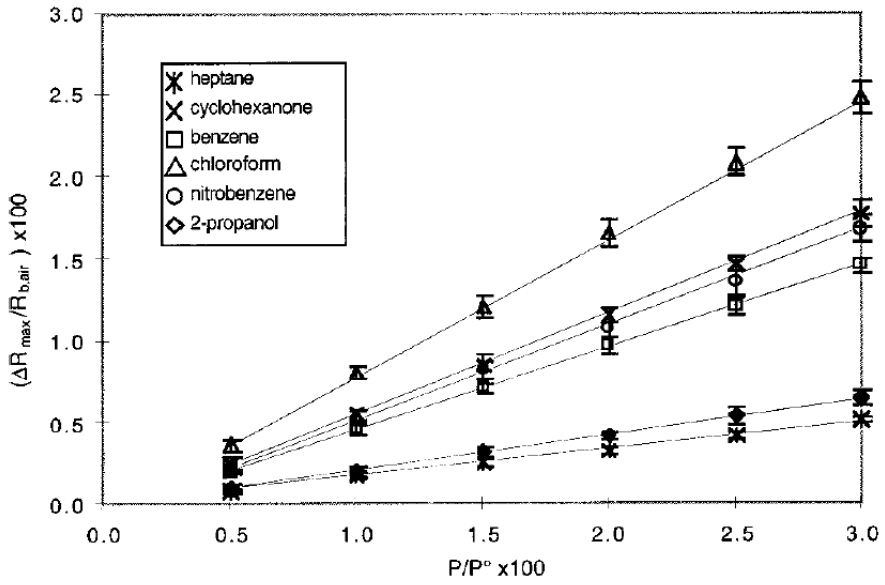

Figure 1.3: Average relative differential resistance responses of a poly(butadiene)/CB composite sensor upon exposure to various analytes, at analyte concentrations ranging from $P/P^0 = 0.005$–0.03, in air, demonstrating linearity of response with respect to analyte concentration.[38]

Polymer/CB composite sensors have been extensively characterized.[6,26,31,32,36–39] Upon exposure to an analyte vapor, some fraction of the vapor sorbs into the film, controlled by the activity coefficient of each particular vapor/solid combination. As the analyte diffuses through the film and comes into equilibrium with the sensor, the volume of the sensor film increases. This swelling increases the average interparticle distance of the carbon black, thereby increasing the overall resistance of the film.[39] Removal of the analyte vapor from the exposure stream allows the sensor to return to its baseline size and resistance. The resistive sensor responses have been shown to be linear with analyte concentration and additive with response to multiple analytes (Figures 1.3 and 1.4).[38] Response times of the films have also been characterized,[40] as have effects of temperature[41] and spatial orientation.[42,43]

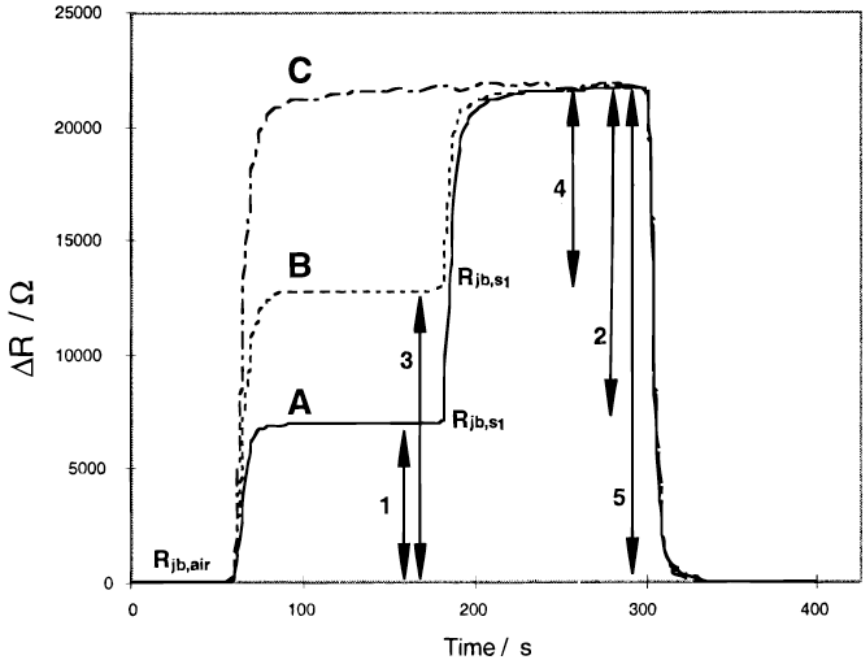

Figure 1.4: Differential resistance response for a poly(ethylene-co-vinyl acetate)/CB composite sensor. A) Exposure to benzene at $P/P^0 = 0.02$, followed by exposure to both benzene and chloroform, each at $P/P^0 = 0.02$. B) Exposure to chloroform at $P/P^0 = 0.02$, followed by exposure to both benzene and chloroform, each at $P/P^0 = 0.02$. C) Simultaneous exposure to benzene and chloroform each at $P/P^0 = 0.02$.[38]

1.4 Sensor Goals

All of this body of work has been aimed towards making better sensor arrays — that is, ones both more broadly responsive, sensitive, and finely discriminating. It has been seen that a given broad polymer/CB sensor array has better discriminatory ability towards gross chemical classes (alcohols, aromatics, etc.) than it has towards physical differences such as molar volume or dipole moment.[44] Similarly, it has been seen that similarities in polarity and functional groups between polymers and analytes creates clear responses.[6,45,46] However, specifically chosen sets of sensors have been shown to perform such difficult discrimination tasks as separating H_2O from D_2O,[6] or distinguishing between an enantiomeric

Analyte	MW (g/mol)	P^0 (kPa, 25 °C)	mp (°C)	bp (°C)	ρ (g/ml, 20 °C)	μ (D)	ε (20 °C)
hexane	86.18	20.2	-95.4	68.7	0.6548[a]	0	1.89
heptane	100.20	6.09	-90.6	98.4	0.6837	0	1.92
toluene	92.14	3.79	-94.9	110.6	0.8669	0.38	2.38[b]
chloroform	119.38	26.2	-63.6	61.1	1.4832	1.04	4.81
ethanol	46.07	7.87	-114.1	78.2	0.7893	1.69	25.30
isopropanol	60.10	6.02	-89.6	82.3	0.7855	1.58	20.18
ethyl acetate	88.11	12.6	-83.6	77.1	0.9003	1.78	6.08

[a] Density at 25 °C
[b] Permittivity at 23 °C

Table 1.1: Listing and physical characteristics of all analytes used in these studies. Values are: molecular weight, melting point, boiling point, density, dipole moment, and the permittivity (dielectric constant).[48]

pair of vapors.[47] As time passes, new challenges in detection continue to arise, notably in cases such as landmine detection, involving very low vapor pressure compounds.

Sensors can often be selected for a particular task, and iterative optimization of a given array can often improve performance. Work has also been done on computationally assisted array selection.[46] Towards all these ends — specific selection of sensors, and the construction of the broadest, most sensitive array possible — we must expand both our set of available sensors and our understanding of how they work. This will yield wider selection, and better comprehension of when and how to select amongst them.

1.5 Outline of This Thesis

This work seeks to address these issues by exploring certain size-related properties of the insulating organic materials used in composite vapor sensors. All the studies presented use one set of analyte vapors; these molecules and some of their physical quantities are pre-

sented in Table 1.1. Previous work has demonstrated the use of small organic molecules in CB composite sensors, and determined them to have notably different formulation requirements than polymer/CB composites. This work compares libraries of polymer/CB and small molecule/CB sensors and determines that the formulation differences stem from the crystallinity of the small molecule materials (Chapter 2). Additionally, varied weight polymers are studied to determine the effects of size and viscosity differences in sensor performance. It is determined that in the case of a high glass transition polymer, sensor response times are greatly improved when using very low weights of that polymer (Chapter 3). Finally, two related homologous series of small molecules, over a range of lengths, are used as sensors. Greater discrimination ability is seen using materials that have increased access to multiple functional groups (Chapter 4). Increased utility of small molecules as sensor substrates, and improved access to many high glass transition temperature polymers, should improve the quality of composite vapor sensor arrays.

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