Chapter 6

Transient Chemical Signal Processing

In this chapter, signal processing that supports an alternative method of chemical discrimination is presented. Rather than focusing on the steady-state response of a heterogeneous array of chemical sensors, this method relies on temporal differences among sensors in these same arrays. The rate at which a particular chemical reacts with the chemical sensor surface can vary not only among different chemicals but across the variables of a heterogeneous array. This information can be useful for many chemical discrimination tasks and for decreasing the response time required to accurately recognize of a particular chemical. If the signal processing can determine a pattern for a particular chemical before an array of chemical sensors has reached steady-state, the effective response time of the system decreases. Since many microelectronic chemical sensors have slow response times due to diffusion-limited reactions between the chemical and the sensor itself, this method of chemical discrimination can be especially valuable in systems where early warning and real-time recognition of chemicals is critical. Steady-state information and related signal processing can then serve to confirm the temporal chemical discrimination information and to determine the final concentration of a chemical of interest.

The system described in this chapter captures the temporal nature of chemical reactions with tin-oxide chemical sensors. This temporal information is stored in a binary representation or pattern that is distinguishable among chemicals. The sensor array used for generating these particular patterns is heterogeneous, with each sensor in the array operating at a different temperature. This system has been able to distinguish carbon monoxide from other chemicals in less than 5 seconds, which is a fraction of the typical time (tens of seconds) required for a tin-oxide sensor to reach steady-state. Response times in integrated, thin-film sensors are shorter (ms) than the response times of the discrete sensors for which experimental results are presented. However, since the discrete and integrated thin-film sensors operate on the same basic transduction mechanisms, similar improvements in response time should be achieved in fully integrated systems as well. This system has also been applied to the detection of alcohols for such applications as quick response breath analysis systems.

6.1 The Transient Characteristic of Chemical Sensors

Many chemical sensors that are based on surface reactions exhibit a saturating exponential response similar to the one shown in Figure 6.1. In an array of chemical sensors that vary in operating temperature, catalyst type, or similar parameters, the temporal characteristics of the sensors change from chemical to chemical and from point to point in the array.

Figure 6.1: Typical Transient Response of a Tin-Oxide Sensor

The figure above shows the response of a tin-oxide chemical sensor to isopropanol. The response is approximately a saturating exponential; the drift at the end of the response is caused by stabilization of the chemical within the testing chamber and other second order, longer term effects. Differences in the length of this response and the initial delay to the beginning of a response occur among different chemicals and among different points in a heterogeneous array.

For example, in an array that is made heterogeneous by varying operating temperature, the transient response at elevated temperatures is typically stronger than that at lower temperatures. Within a range of temperatures, subtle changes in reaction rates among sensors and among chemicals are a result of the following factors:

- Variations in the type of oxygen that is reduced at the sensor surface by a chemical
- Differences in the rates at which particular chemicals reduce different types of oxygen

- Variations in the nature of the oxygen bonds at the surface of the sensor:
  - Physiosorbed oxygen (low temperatures)
  - Chemisorbed oxygen (moderate temperatures)
  - Lattice oxygen (high temperatures)
- Variations in the amount of water vapor present on the sensor surface at a particular temperature [64].

The differences outlined above are sufficient to create unique signatures or patterns associated with a particular chemical similar to the signatures produced by steady-state signals in a heterogeneous array (Chapter 5). Unlike steady-state patterns, however, these transient patterns are inherently unstable and must be captured in either an analog or digital form that alone is sufficient for simple discrimination tasks or can provide input to more complex processing centers such as the neural network based systems discussed in Chapter 2.

6.2 System Description

Like the systems described in Chapter 5, a system that uses the temporal qualities of chemical sensor transduction should produce outputs that are reproducible across a range of concentrations and changes in ambient conditions for particular chemicals. The system chosen here to make this conversion normalizes sensor information based on temporal characteristics into a binary output representation that is different for various chemicals. The binary representation is generated by a shift register that stores thresholded values of the chemical sensor outputs over time (Figure 6.2). The system converts a one dimensional, heterogeneous array of chemical sensor outputs into a two-dimensional array by adding time as the new dimension. In this case, the one-dimension of heterogeneity is the operating temperature of each sensor in the array. The dimensions at the output are a thresholded version of the sensor inputs at each operating temperature and at different times. When the outputs of the sensors are digitized and analyzed over time in this manner, a wavefront image is produced that indicates the reaction rates of each sensor relative to the rates of other sensors in the array.

In this wavefront generation system, transient information from the sensory array is first thresholded into a series of digital latches (shift register) using a thresholding scheme that converts an analog sensory input into a binary output based on a suitable reference value. The thresholding scheme may be fixed or variable (Figure 6.3.).

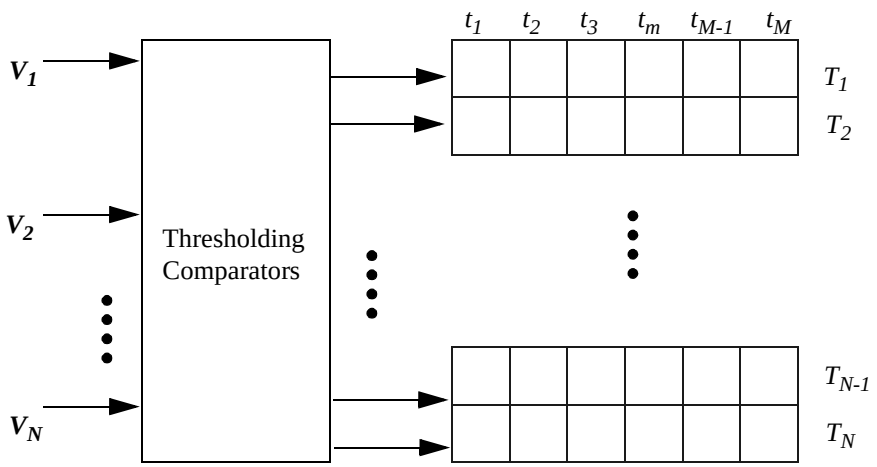
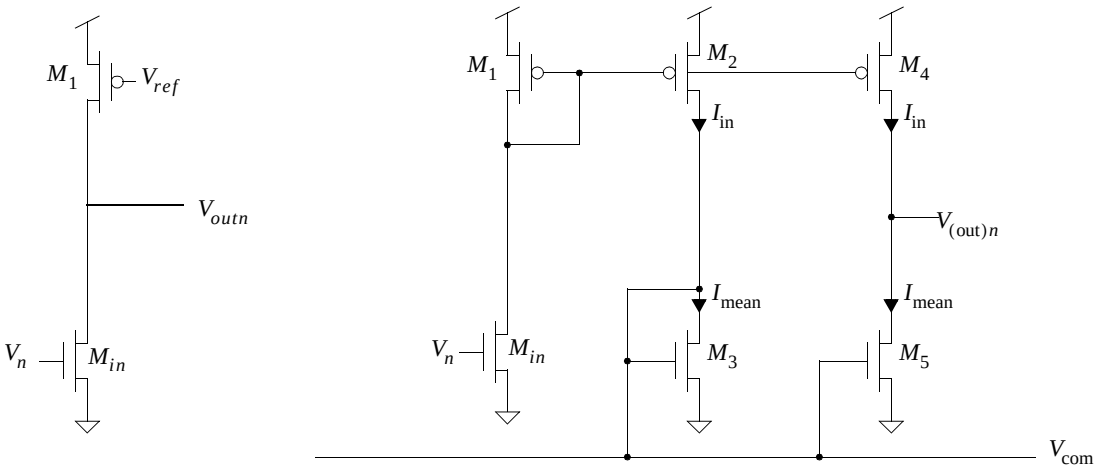


Figure 6.2: Generation of a Digital Wavefront from Temporal Information

In the above system, each of the sensor inputs in the array is first thresholded into a binary signal. The first thresholding step fills the t_1 block in the wavefront. During the next clock cycle, the binary signals in block t_1 are shifted to block t_2 and current temporal information from the thresholding stage is transferred to the block t_1. This process continues until the entire shift register is full, leaving a wavefront that is indicative of the chemical present in the sensing environment.

Fixed thresholding simply compares each chemical sensor output to a reference value and generates a binary high value when the sensor output surpasses the reference. This thresholding technique guarantees that the number of binary outputs in the resulting wavefront will increase monotonically during the transient response of the array. Variable thresholding techniques, such as the mean and median thresholding techniques discussed previously, whose thresholding reference changes in response to input changes, do not necessarily guarantee this monotonic increase; as a result, variable thresholding at the front-end of the wavefront system can produce a more informative, though less intuitive, output wavefront. For simplicity, the feasibility and usefulness of the wavefront system is demonstrated using a fixed thresholding scheme.



(a) Fixed thresholding Element (b) Variable Thresholding Element

Figure 6.3: Thresholding Schemes for Wavefront Generation

The transient response of a heterogeneous array of chemical sensors can be thresholded by (a) simply comparing every array output to some fixed reference value or by (b) comparing each array output to a variable reference value. In the case of fixed thresholding, the number of binary active outputs increases monotonically during the transient response of the sensors to a chemical in the sensing environment. Using a variable thresholding technique, such as the mean and median techniques described in Chapter 5, this monotonic increase in binary outputs is not guaranteed.

The binary output signals generated by the thresholding stage in this system are then shifted into the t_1 block of digital latches. During the next clock cycle during a transient response, the information in the first column of the digital latches is shifted to the second column and a new thresholded version of the temporal sensor response is stored in the first, t_1 column. This process continues until the *M* blocks of the register are full. A typical response for a 8 X 8 array of these latches is shown in Figure 6.4. This particular response is based on a fixed thresholding stage which guarantees that any row in the array will be monotonically increasing. Variations in the thresholding reference and method can be used to expand the flexibility of this system to suit a wide variety of chemical discrimination tasks.

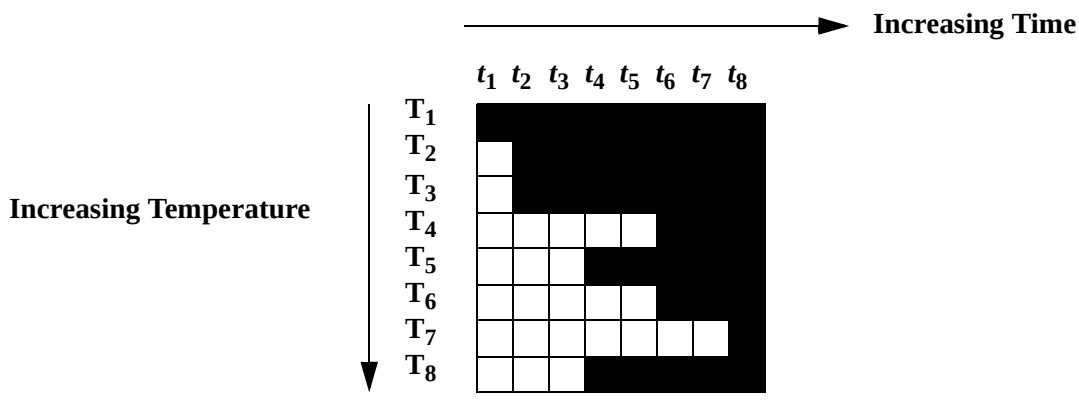


Figure 6.4: Typical Response of the Wavefront Analysis System

Shown above is a typical wavefront representation of the response of a tin-oxide sensor array responding to a reducing chemical in the sensing environment. Each column of the array corresponds to a different time in transient response. Each row in the array corresponds to a different sensor in the array. In this case, each sensor is different in operating temperature.

6.3 System Testing

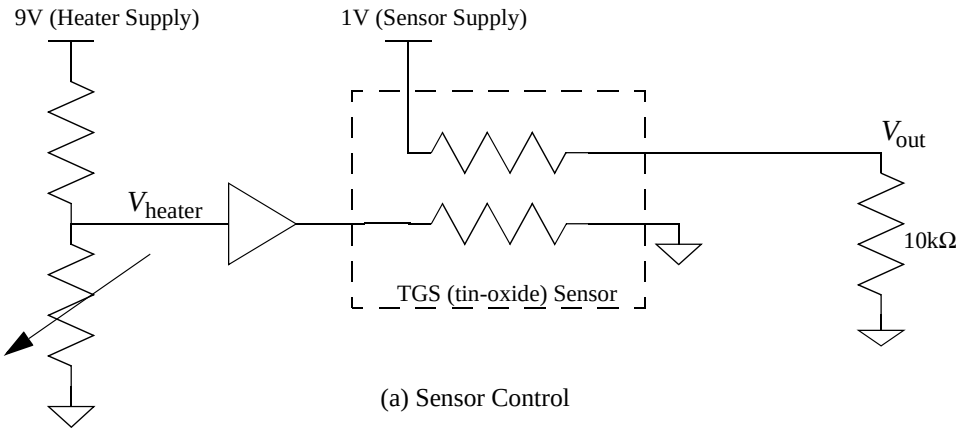
A wavefront system has been fabricated in a standard 2.0μm, *n*-well CMOS process using the MOSIS fabrication service in order to analyze the transient response of a 10-element array of chemical sensors. This system uses a basic, fixed thresholding scheme to convert the sensory input into a binary array. The system has been tested across a wide temperature range (125° C to 485° C) and a narrow temperature range (300° C to 390° C) to evaluate its potential for discriminating among a variety of reducing chemicals. Below, the results for each of these tests are discussed as well as their usefulness to particular discrimination applications.

6.3.1 Experimental Set-Up

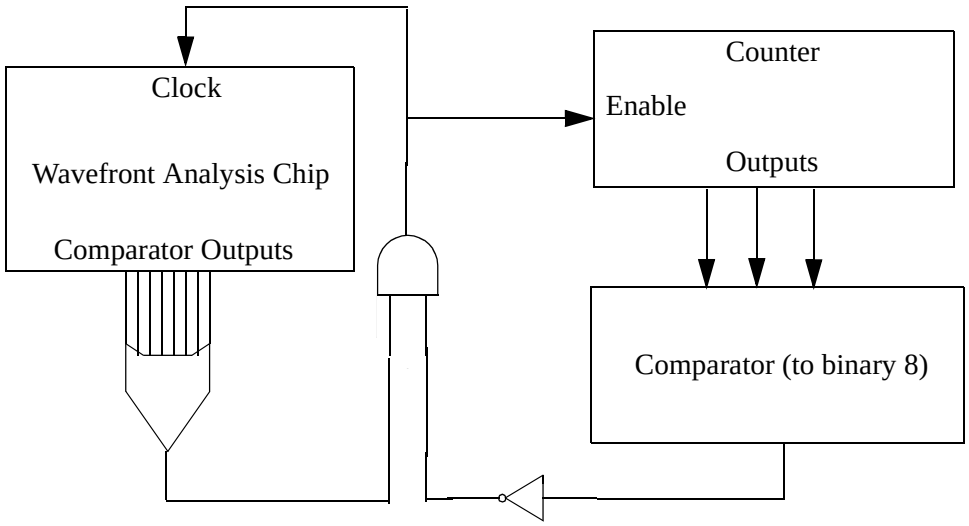
System testing of the wavefront analysis system is performed using a set-up that is similar to the testing of the homogeneous and heterogeneous arrays described in Chapters 4 and 5 respectively.

The basic experimental set-up for these experiments is shown in Figure 6.5 and Figure 6.6. Each tin-oxide sensor (Figure 6.5a) contains its own on-board heater. The heater temperature is maintained by a buffer operating at a constant voltage which is consistent with the desired temperature according to specifications provided by the manufacturer. The buffer input is controlled by a variable resistance voltage divider. The inputs to the wavefront analysis system are generated from eight TGS822 (alcohols sensitive) tin-oxide sensors connected in this manner. The heaters are maintained between 1.9 and 6.3V across the array, corresponding to sensor surface temperatures from 125°C to 485°C, according to manufacturer's specifications.

The output of each sensor is connected to a corresponding input in the wavefront analysis chip. These outputs are then thresholded on the chip itself; after a chemical is introduced into the sensing environment, the first sensor to cross the threshold of the wavefront system enables the clock for the wavefront latches and for the external counter (Figure 6.5b). Both the wavefront latches and the counter remain enabled until the counter reaches a binary 8; at this point, the counter and wavefront latches are disabled so that the wavefront does not continue to fill with binary high values. At this point, the binary pattern in the wavefront latches can be scanned off-chip using a Unix Workstation via an IEEE-488 interface. As in previous experiments, all of the sensors are allowed to stabilize for a week at the desired operating temperature before testing is performed.



(a) Sensor Control



(b) Clock Control of wavefront analysis

Figure 6.5: Experimental Set-Up for Testing the Wavefront Analysis Circuits

Shown above is the testing set-up for evaluating the performance of the wavefront analysis system on an array of tin-oxide sensors (TGS822) Each sensor (a) consists of a resistive heater and a chemically sensitive resistor. The sensor output voltage is then taken across a 10kΩ load resistor. The latches in the (b) wavefront analysis chip begin receiving information when at least one of the sensors has crossed the comparator threshold. Eight clock cycles after that initial crossing, the comparator output goes high, disabling the wavefront latches and the counter itself. At this time, the binary values in the wavefront latches are scanned off the chip for analysis.

Various reducing chemicals are introduced into a large chamber (Figure 6.6) and allowed to evaporate into the chamber. A valve between this chamber and a smaller testing chamber is then opened, allowing the gas to diffuse into the environment of the sensor arrays. A fan inside the testing chamber keeps the gas well mixed and evenly distributed. The gas remains in the chamber until the wavefront analysis system stores a wavefront for the gas and is disabled by the control circuitry used for these experiments. Both the testing and evaporation chambers are then aired for at least 30 minutes before another experiment is performed.

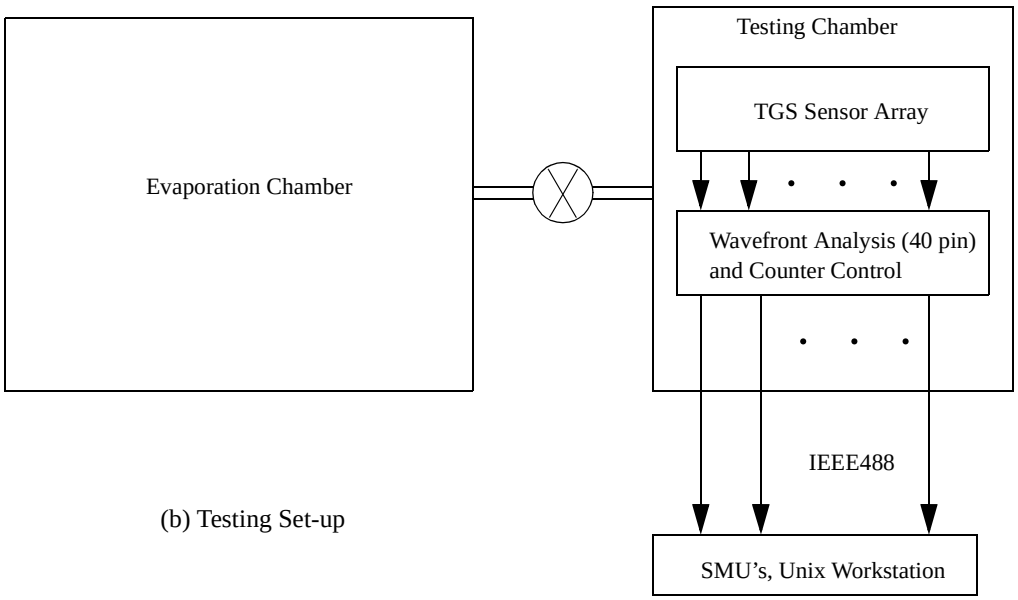


Figure 6.6: Introduction of Gases to the Wavefront Analysis System

A chemical, in liquid form, is introduced into the evaporation chamber and allowed to evaporate and diffuse throughout the chamber. A valve between the evaporation chamber and the testing chamber is opened to allow the gas into the testing chamber where it is diffused by a fan. The fan ensures that the gas reaches all of the sensors at approximately the same time. The wavefront analysis system does not begin counting until at least one sensor crosses the threshold and stops counting 8 clock cycles after the first sensor has crossed the threshold. After the wavefront is filled (8 cycles after the first sensor has crossed the threshold, the values in the wavefront latches are read out by a Unix Workstation using several source measurement units and an IEEE488 Interface.

6.3.2 Wavefront Analysis over a Wide Temperature Range

Given a fixed number of heterogeneous sensors in an array, it can be necessary to vary the spacing of dimensions in the array to improve the flexibility of the overall system in discriminating among a wide variety of chemicals. For example, if in a particular application, it is desired to detect two very different chemicals such as isopropanol and carbon monoxide, the array operating temperatures in can be spaced uniformly across a large range, on the order of 350° C, to detect a significant response from both chemicals. Experimental results for performing such broad discrimination tasks using the wavefront analysis system are shown in Figure 6.7.

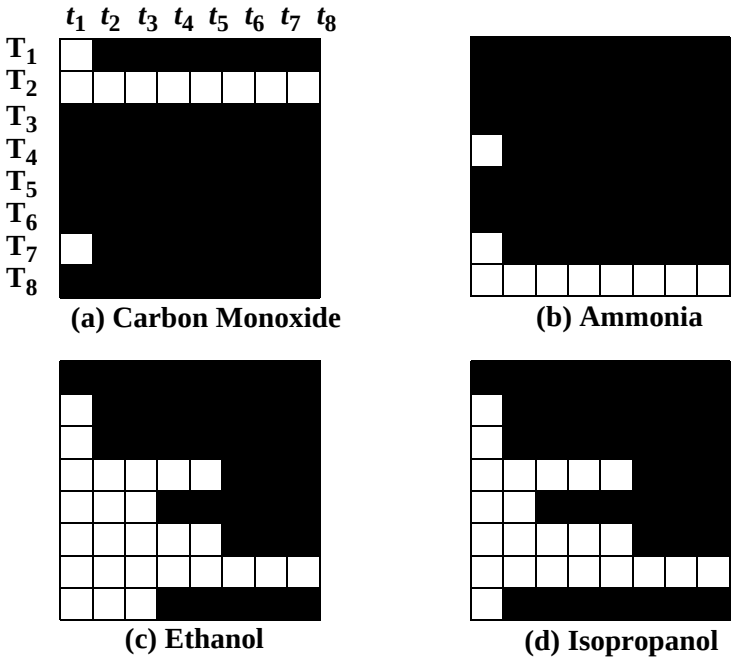


Figure 6.7: Wavefronts for four chemicals across a wide temperature range

Shown above are experimental wavefronts for (a) carbon monoxide, (b) ammonia, (c) methanol, and (d) isopropanol across a wide temperature range from 125° C to 485° C. Note that carbon monoxide, ammonia, and alcohols (isopropanol, methanol) are easily distinguished because the array exhibits sensitivity to these three groups of chemicals in this temperature range. Isopropanol and methanol, however, are not distinguishable since the dimensions of the array are spaced closely fine enough to allow the subsequent wavefront images to reflect the subtle differences between these two alcohols. These tests were reproducible over approximately 80% of the concentrations and chemicals tested.

The circuits used to generate these results employ a fixed thresholding reference of 2.5V and a fixed clock speed of 2 Hz. The temperatures in this eight-element array of tin-oxide sensors vary evenly from 125° C to 485° C. In this operating range, widely different chemicals such as carbon monoxide, isopropanol, and ammonia are easily distinguished whereas the more closely related chemicals, methanol and isopropanol are not. These wavefront results are 70% reproducible over a range of concentrations (500 to 4000 ppm of alcohol).

6.3.3 Wavefront Analysis across a Narrow Temperature Range

In an application where two closely related chemicals such as the alcohols methanol and isopropanol are to be discriminated, it is preferable to set up the operating temperatures in an array across a much smaller range to capture the subtle differences in sensor response that make finer chemical discrimination possible. Experimental results for a more narrow range in operating temperature for a 8X8 wavefront array that uses a fixed thresholding reference of 2.5V and a fixed clock speed of 2 Hz are shown in Figure 6.8. Operating temperatures in the sensor array are spaced evenly between 300° C and 390° C in these experiments. Using the narrow temperature range, it is now possible to distinguish between isopropanol and ethanol. Carbon Monoxide, however, generates a trivial, uniformly low output; this result can be directly attributed to the reduced sensitivity of the tin-oxide sensors to carbon monoxide at elevated temperatures. The thresholding reference for this array is set above the sensitivity of the sensors to carbon monoxide within this narrow, elevated temperature range, hence making the array ineffective for detecting carbon monoxide. As in the previous wavefront experiment, these wavefront results are approximately 70% reproducible over a range of concentrations (500 to 4000 ppm of alcohol); problems with reproducibility are assumed to be caused mostly by interference from previously tested chemicals in the testing chamber. Although the chambers are completely aired after testing, some chemical residue does stick to the testing chamber and can cause potential interference in subsequent experiments.

The wavefront analysis system has proven useful for distinguishing among closely related alcohols on arrays of chemical sensors operating within an elevated but narrow temperature range. Since acetone and isopropanol are two of the most common nuisance chemicals experienced in breath alcohol (ethanol) analysis, this technique can be useful for developing low-cost, quick-response breath alcohol analyzers.

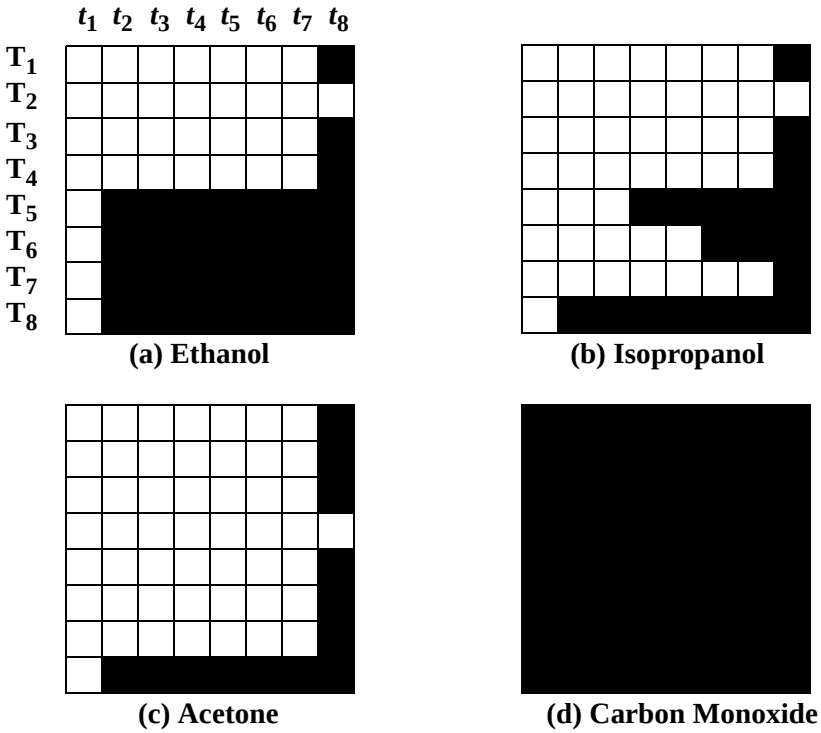


Figure 6.8: Wavefronts for three chemicals across a narrow temperature range

Shown above are experimental wavefronts for various concentrations of (a) ethanol, (b) isopropanol, (c) acetone and (d) carbon monoxide across a narrow temperature range from 300° C to 390° C. Note that isopropanol and ethanol are now easily distinguished because the dimensions in the array are fine enough to detect subtle differences between the two chemicals. The chemical acetone (a reduced alcohol) is also easily discriminated from its two related neighbors, ethanol and isopropanol. Notice that carbon monoxide, because of its reduced reaction with tin-oxide at elevated temperatures, does not cross the threshold at all during this experiment. These wavefronts were reproducible across approximately 75% of the concentrations and conditions tested. Interference from previously testing chemicals in the testing chamber are suspected to be part of this reproducibility problem.

In integrated systems, wavefront analysis has an added benefit because of the quick thermal response time inherent in miniaturized chemical sensors whose size can approach tens of square microns. These quick thermal response times enable the temperature range of a chemical sensor array to be changed quickly and efficiently to suit several chemical discrimination tasks. Such fast

thermal response time constants are attained when the chemical sensor heaters are small and close to the chemical sensors themselves, as would be the case in an integrated microsystem.

6.4 Comparison of Wavefront Analysis to Existing Systems

The most obvious advantage of the wavefront analysis systems described in this chapter over other chemical discrimination systems is the improved response time required to discriminate among chemicals. Since the wavefront system is able to distinguish among chemicals before the actual sensors in the array have reached steady state, the response time is significantly lower than the response of systems which analyze the steady-state characteristics for discrimination information. Listed in Table 5.1 are response times of various tests described in this chapter as compared to the response times of tests conducted in other research on discrete chemical sensors. For example, using the same or similar array of chemical sensors to distinguish between isopropanol and methanol, the wavefront system requires approximately 2 seconds while a system using statistical analysis of a steady-state chemical image requires almost 2 minutes. This substantial improvement should be further enhanced in future systems as sensors and signal processing are integrated onto the same substrate. In these systems, the response time will not only be improved by analyzing the temporal response of the system but also by performing the signal processing on the same substrate as the sensor array. In software-based systems, the analog array of inputs must first be scanned off a large array before further pattern detection can occur; in the wavefront systems, the array of outputs to be scanned off for further analysis will be already digitized. This reduction of incoming sensory data is expected to further improve the overall response time of the sensing system.

TABLE 6.1: Comparison of Response Times among Chemical Discrimination Systems

System and Application	Response Time	Comments
Wavefront Analysis of discrete tin-oxide sensor arrays	2 sec	Discriminate carbon monoxide, ethanol, acetone, isopropanol, and ammonia (Chapter 6)
Discrete tin-oxide sensor arrays (Figaro Eng)	20 sec	Discriminate carbon monoxide, ethanol, acetone, isopropanol, and ammonia (Chapter 5)
Discrete Palladium ChemFET	50 sec	Detect carbon monoxide with no additional processing for chemical discrimination [19]
Discrete Palladium doped, tin-oxide SGFETS	2 min	Detect ammonia with AC techniques [61]
Discrete Polypyrrole film sensors	24 sec	Detect alcohols with no additional processing for chemical discrimination; short lifetime [10]
Arrays of tin-oxide sensors	2 min	Discriminate basic perfume scents and alcohols using software-based statistical analysis [44]
Arrays of Palladium and Platinum ChemFETs	1.5 min	Discriminate ammonia and hydrogen using software-based, artificial neural network [37].