39.1: Transient Response Chemical Discrimination Module

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Abstract

This paper describes a broad-base portable chemical discrimination module capable of using combinations of homogenous or heterogeneous arrays of chemical sensors for evaluating chemical type. Several types of sensors can be added to or removed from the system in plug and play fashion. Using these sensors, the module supplies the user with real-time chemical discrimination information. Included in the module are signal conditioning circuits designed to process chemical sensor signals in such a way that the output of the conditioning circuits ensures similar dynamic and baseline range, regardless of sensor drift, type or fabrication variation. Baseline compensator circuits use a sensor calibration feedback loop to reduce the sensor dynamic range, and so reduce the number of bits required to process a given concentration resolution, thereby reducing power requirements. Additional signal processing is applied to homogenous sensors arrays to reduce the impact of corrupted sensors. Sensor outputs are displayed in principal component space in real-time enabling the user to evaluate the transient path of the sensors to their final position in principal component space for chemical discrimination purposes.

INTRODUCTION

Many factors contribute to a successful, inexpensive, mobile chemical measurement unit such as signal conditioning to compensate for drift and environmental variation, the ability to flag broken sensors, and streamlined signal processing for pattern recognition. Signal conditioning is used to enhance data acquisition, which involves accurate analog to digital conversion of sensor data. In order to maximize the resolution of a mobile unit, it is useful to fuse sensor signals in such a way that reduces the full response of sensors across all sensor types and manufacturing variations. Baseline compensation is one such way to fuse these sensor signals. Without baseline compensation, analog to digital converters process variations in sensor response as well as in sensor baseline, where as with baseline compensation, the resolution of analog to digital converters is solely allocated to sensor response. Many baseline zeroing methods are limited for chemical sensors. For example, for chemiresistors, standard methods using a wheatstone bridge cannot be applied because the baseline resistance varies significantly across manufacturing, temperature, and lifetime

of the sensor. Likewise, for the ChemFET, the circuit must be capable of accommodating variations in baseline threshold voltage and transistor geometry caused by the chemistry and feature size limitations of microfabrication. Preprocessing compensation modules must transform each type of sensor signal into one that has similar dynamic range and speed limitations for subsequent processing. Signal fusion reduces the total dynamic range required in subsequent analog to digital conversion and thereby increases the system resolution that is allocated to concentration resolution and to discrimination among chemicals.

This variable sensor baseline, whether it be a resistance or FET parameter, is a major issue that affects chemical sensor performance. Specifically, the baseline refers to the response of the sensor when there is no chemical analyte present. For example, in the case of composite film polymer chemiresistors, the baseline is manifested as the (unstimulated) sensor resistance. The resistance of composite film polymer chemiresistors has been measured in our laboratory to vary from $25k\Omega$ to $300k\Omega$. This initial, wide baseline variation is compounded by sensor drift over time and other aging factors. Compensation can eliminate the effects of variable baseline and drift, thereby maximizing resolution in preparation for mobile applications.

A handful of research efforts have demonstrated techniques for improving portable instrument viability by reducing the inherent variation in chemical sensors with baseline compensation techniques. Apsel *et al* uses an adaptive, programmable amplifier to stabilize chemiresistors at a predetermined baseline value using floating gate analog memory and novel filtering techniques. However, these circuits also contribute distortion to the sensor response, generating different response curves for the same analyte, same type of sensor, but different baseline resistances [1]. Using a different circuit design approach, Neaves and Hatfield have constructed an ASIC specifically designed to extract response signals from an array of polymer chemiresistors. This circuit results in fundamental distortion of the sensor signal by creating a non-linear response of the output current in relation to the input concentration. The ASIC is a versatile generic module for sensor resistance preprocessing, but contains bulky amplifiers and multipliers that may limit usefulness for large arrays in portable instruments in terms of space and power consumption [2].

In order to classify chemical analytes of interest, this work uses principal component analysis (PCA). Principal component analysis transforms multiple-dimensional data into a vector space in which each dimension direction is maximized to contain as much variance information as possible. In highly correlated data, higher dimensional principal axes become less significant [3]. PCA has been used in chemical discrimination applications many times [4] [5]. In this work PCA is used to reduce six-dimensional sensor data to two principal component dimensions. These dimensions are then displayed as an interface for the user to make classification decisions.

Similar work in the literature tends to concentrate more on odor localization and relies more on theoretical models for interpreting sensor data [6]. This novel approach to mobile chemical sensing uses intelligent pre-processing to enable effective principal component analysis. Human classification abilities can then be taken full advantage of by displaying PCA data for human interpretation as sensor responses approaches analyte calibration clusters.

SENSOR BACKGROUND

The three types of sensors used in this work are chemFETs, tin-oxide chemiresistors, and composite film polymer chemiresistors. ChemFETs are Chemically Sensitive Field Effect Transistors. They are easy to integrate into support circuitry and are inexpensive. When a chemical is applied to which the chemically-sensitive gate material is sensitive, the fermi level at the gate shifts causing a change in the work function of the metal via bulk and surface modulation thereby causing the threshold voltage of the FET to change in a measurable way [7] [8]. Different types of chemFETs can be integrated onto the chip, including sensors that respond to a primary analyte and its interferents, in order to improve sensor discrimination capabilities. The nature of the input-output relationship between a diode-connected ChemFET's output voltage (in the saturation region of operation) and analyte concentration is logarithmic, providing increased sensitivities to low concentrations of analytes. However, this relationship is only strictly valid for a middle-range of concentrations [8].

The second type of chemical sensor is the tin-oxide chemiresistor. Tin-Oxide is an n-type semiconducting metal oxide whose conductivity properties are highly sensitive to gases present in the environment. Oxygen species in the thin film that make up the sensor build dangling bonds and other lattice vacancies. Reducing gases in the environment combine with oxygen in the thin film to enable the change in sensor conductivity and resistance [9] [10]. A heating element helps to stabilize the thermal environment and improve sensor sensitivity. The nature of the input-output relationship in metal-oxide sensors is an inverse power law. A strong dependence on humidity has further been

observed and characterized [9] [10].

Finally, composite film polymer chemiresistors are made of an insulating polymer matrix implanted with conductive particles of carbon-black [11]. As the sensor is exposed to an analyte to which it is sensitive, the polymer swells. This swelling causes the conductive carbon-black particles to move farther apart, thereby changing the conductivity of the sensor. Large amounts of swelling produce a non-linear relationship with concentration, as determined by percolation theory. For typical small-signal use, these sensors demonstrate a change in resistance from baseline that is directly proportional to concentration. The proportionality constant, k, at least in part depends on the chemical applied and the type of polymer being used [12].

SYSTEM DESCRIPTION

The portable chemical discrimination module combines arrays of homogeneous sensors for improving noise performance and detecting broken sensors with heterogeneous arrays of sensors to discriminate among analytes of interest. Sensors can be modularly added to or removed from the measurement module. Using these sensors, the module supplies the user with real-time chemical discrimination information that tracks the response vector of the sensor as it proceeds from baseline to its steady-state location in multi-dimensional sensor space. The module includes slots for homogeneous arrays of sensors, heterogeneous arrays of sensors, plug-and-play signal conditioning modules, and a microcontroller for converting normalized sensor signals for display in two-dimensional principal component space.

At the single sensor level, the signal conditioning circuits are designed to process chemical sensor signals in such a way that similar dynamic range and baseline states are ensured at the output of the sensor signal conditioning, regardless of sensor drift, type or fabrication variation. Baseline compensator circuits use a sensor calibration feedback loop to normalize sensor baseline states, so that the response of each sensor begins at the same value. Autozeroing baseline compensation ensures that the dynamic range of the sensor output is completely consumed by response to analytes rather than to changes in baseline caused by variations in manufacturing. The details of these compensation circuits are reported elsewhere [13]. Removal of the effects of baseline variation reduces the number of bits required for a given concentration resolution, thereby reducing power and cost requirements for the portable module.

Interchangeable Sensor Interface

As previously noted, the compensation mechanism used here is largely sensor independent. Three factors prevent this compensation technique from complete sensor-independence. These factors are the impact of sensor settling,

the range of values of the initial sensor baseline parameters, and the value to which sensors of different types are to be compensated to.

R_t governs the time that the compensation circuit is enabled. Disabling prevents compensation from occurring when the sensor is legitimately changing in response to an analyte. The time t, in seconds that the compensation circuit will be enabled based on a monostable timer is:

$$t = 1.1 \cdot 10^{-6} R_t \qquad (1)$$

In general it has been observed and can be explained by sensor manufacturing techniques that ChemFETs take longer to settle during compensation and so will require a longer enabling time than the chemiresistors.

As previously discussed, the resistor R_x also affects the range of compensatable sensor parameters and is influenced by sensor technology. For example, minimum baseline resistances for tin-oxide sensors tend to be much less than those for composite film polymer sensors and therefore are better optimized by using a smaller value for R_x.

The final parameter, V_{th}, sets the voltage to which the sensors are compensated. For the chemiresistors, this voltage is a trade-off between power (high values) and noise (low values). A typical value is 2V. However, in the case of the ChemFET, V_{th} must be large enough to ensure that the ChemFET is in the saturation region of operation to ensure proper functionality. This voltage is fairly large because of the large size of chemFETs relative to regular FETs. A typical value is 5V.

In order to make this module capable of plug and play interchangeability, circuit boards were fabricated that contained both the sensors of interest as well as R_t, R_x and V_{th}. Figure 1 shows the compensation process for both the mixed sensor module Figure 1(a) and the tin-oxide module Figure 1(b). The tin-oxide sensor module consists of six tin-oxide sensors, with two each of three different types (TGS sensors doped with different catalysts). The mixed sensor module contains two tin-oxide sensors, two composite film polymer sensors, and two ChemFETs. Multiple compensations occur in both Figure 1(a) and Figure 1(b) due to sensor settling. The module shows no difficulty in compensating for these significantly different combinations of sensors.

Outlier Removal

At the homogeneous array level, additional signal processing reduces noise and removes outlying signals corresponding to corrupted sensor outputs. Software on the module has the capability to be programmed with sensor types present in the array currently being used. For specific types of sensors, drift rates are known a priori, and are typically on the order of days. Therefore, if either a signal is more than one

standard deviation away from the mean of its sensor type or the sensor drifts by more than 80% over a period of time on the order of days, and dependant on the known drift rate, then the sensor will classified as an outlier, and its signal will be removed from subsequent processing. If the drift rate is less than 80% then the sensor can simply be recompensated to eliminate the effects of drift. Sensor removal occurs if the software detects a sensor signal that is over one standard deviation from the mean of that sensor type. The reduction of dynamic range performed by the compensation circuit is an enabling factor of this feature. Figure 2 demonstrates the process of outlier removal. In (a) Sensor 2 and 3 contain real sensor data, while Sensor 1 is a simulated ramp. (b) shows the results of outlier removal on the sensor average as Sensor 1 moves out of the acceptable range defined by one standard deviation from the sensor mean for that type of sensor.

Auto-Zeroing Baseline Compensation

At both the heterogeneous and homogenous array level, signal processing to perform baseline compensation is performed. Baseline compensation establishes the initial output baseline voltage, V_b, at a constant value for all sensors, regardless of the initial baseline parameters. It achieves this result by use of a variable current source, I_{Set}. For example, after baseline compensation, the input-output equation for composite film polymer chemiresistors then changes to:

$$V_o = I_{Set}R = I_{Set}R_o\left(1 + \frac{\Delta R}{R_o}\right) = V_b(1 + k[C \qquad (2)$$

From the above equation, at zero analyte concentration, the output voltage is set to a desired baseline voltage, thereby reducing sensor variation by compensating for the arbitrary baseline resistance. The total range of output voltages seen by all sensors in an array is greatly reduced by baseline
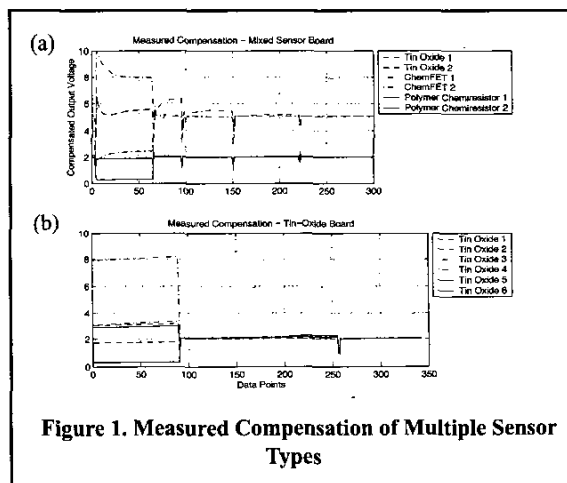

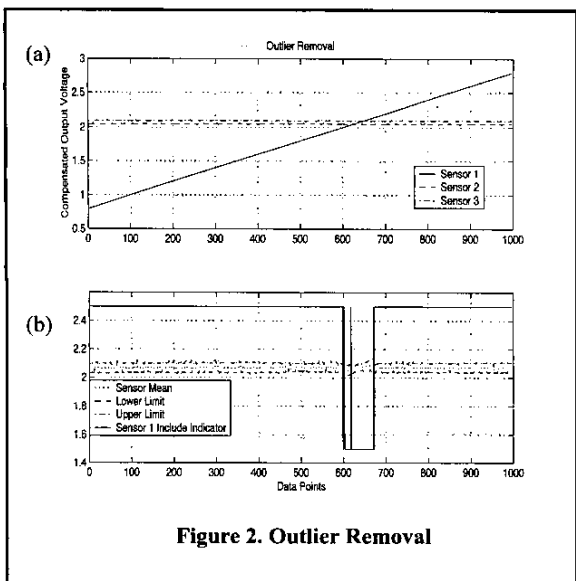Figure 1. Measured Compensation of Multiple Sensor Types

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Figure 2. Outlier Removal

$$V_{Sensor} = \frac{R_{Sensor}V_{DAC}}{R_x} \qquad (3)$$

The equation for the ChemFET is slightly more complicated due to the inherent non-linearities present in FETs:

$$V_{Sensor} = V_t([C]) + \sqrt{\frac{V_{DAC}}{k\left(\frac{W}{L}\right)R_x}} \qquad (4)$$

W, L, and k are device constants; V_t is the threshold voltage of the ChemFET and is a function of analyte concentration, $[C]$.

Principal Component Analysis

The primary objectives of developing the chemical discrimination module in this effort are to demonstrate (a) the modularity of the instrument for different sensor types and technologies (b) the portability of the instrument and (c) the transient path of a sensor array to its steady-state location in principal component space. Providing the transient response as well as steady-state information in principal component space enhances the user's ability to make a decision about the type of chemical present and the possibility of a false alarm. Visual presentation of the data is accomplished via principal component projection of the multi-dimensional sensor data; however, any data reduction system that retains salient discrimination information
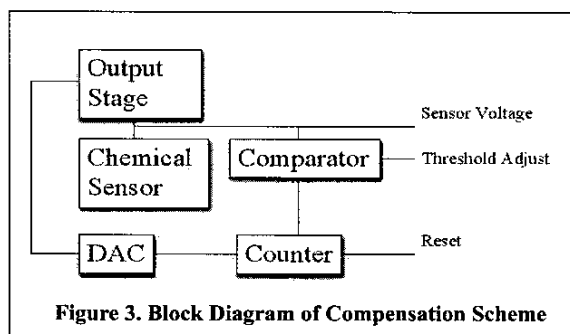
compensation. The linear transformation also preserves the sensor response shape (low distortion). Drift is compensated at appropriate times in the sensor lifetime by re-zeroing each sensor to the predetermined uniform baseline state.

A block diagram of the auto-zeroing baseline compensation scheme is shown in Figure 3. Compensation begins when the system is reset, setting an 8-bit counter output to zero. The counter is then enabled and begins to count up in binary. A voltage ramp is produced at the Digital to Analog Converter (DAC) output. The output stage converts this voltage ramp to a current ramp input to the sensor. The current ramp causes the voltage across the sensor to increase. Once the voltage across the sensor reaches a preset threshold value, the comparator shuts off the counter, thereby freezing the amount of charge flowing into the sensor. Regardless of the initial sensor state, the initial voltage across the sensor will be predetermined by the threshold, and will fluctuate around this value as chemical analytes are introduced. After calibration, the counter is disabled to prevent undesired compensation. Figure 4 demonstrates the compensation process.

All circuit components of the compensation scheme shown in Figure 3 are straight forward except for the output stage. The circuit is a modified instrumentation amplifier acting as a voltage-controlled current source. An op-amp is bootstrapped to require that the voltage across a resistor, R_x be equal to the applied voltage from the DAC. Ideally no charge flows into the op-amp input so the voltage across R_x will be directly injected into the sensor, producing the uniform baseline compensation results in sensor output voltage [13]. For the chemiresistor,

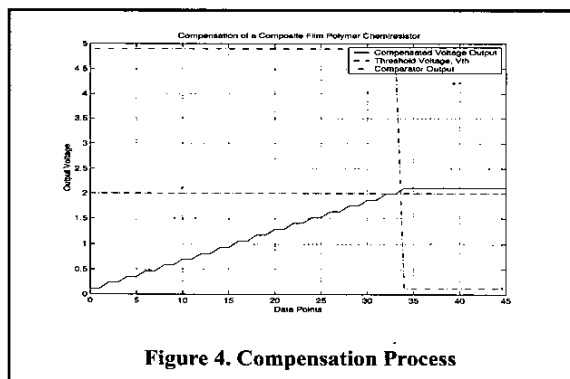**Figure 3. Block Diagram of Compensation Scheme**

Figure 4. Compensation Process

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would a be appropriate for this type of system.

Sensor signals from similar sensor types (homogeneous arrays) are first baseline compensated and averaged, allowing outliers to be removed, and chronically misbehaving sensors to be flagged. The averaged aggregate outputs of the heterogeneous array are then transferred to a microcontroller and a principal component transformation is applied to the multi-dimensional sensor data for projection onto a portable display.

Principal component analysis allows the subsequent extraction of analyte information from data in an efficient and compact manner. Using this type of analysis to convert the data into principal component space, the data can be displayed on a two-dimensional LCD screen. Pre-calibrated points for air and the analytes of interest are displayed on the screen as well. Users are then able to watch in real-time as the point on the screen moves in response to an applied chemical. In using a graphical display, this work takes advantage of the built-in pattern recognition abilities in the human brain to estimate that a certain analyte may be present if the data point on the screen is closer to one calibration point than others. The use of this built-in pattern recognition ability drastically reduces circuit complexity and power requirements while still supplying needed information for chemical discrimination.

EXPERIMENTAL RESULTS

The portable chemical discrimination system has been calibrated on multiple concentrations, up to sensor saturation, of methanol, formaldehyde, and ammonia and tested on multiple concentrations of methanol. Both tin-oxide sensor modules and mixed sensor modules have been used to demonstrate the performance of the system for these analytes.

Figure 5 demonstrates the results of principal component analysis, used here for analyte classification purposes. Data was taken using each of the two sensor boards described above. Calibration data is shown for each of the three analytes, formaldehyde, ammonia, and methanol. Figure 5(a) and (b) show the subsequent response to and recovery from methanol for the tin-oxide sensor and the mixed sensor modules respectively. The path of the sensor response clearly travels from the initial baseline area to the methanol calibration point, thereby revealing the analyte to which the module is responding. In Figure 5(a), the separation between analyte clusters is well-defined. Upon recovery, the signal approaches but does not fully return to baseline conditions. Reasons for this incomplete recovery include the need for a longer recovery time than what is provided in these experiments, or sensor drift, which can be directly compensated on a periodic basis (compensation period dependent on sensor technology type) using the autozeroing baseline compensation circuits described previously in this paper. In Figure 5(b) the analyte clusters are not very well defined, making it difficulty to differentiate analytes. This result is unfortunate but expected as the chosen chemiresistors demonstrate low sensitivity to the tested analytes. The contrast in results between Figure 5(a) and Figure 5(b) show the obvious result that the signal processing cannot compensate for insufficient sensitivity in the sensor technology itself. The tin-oxide sensor module, used at the tested concentrations, demonstrates a consistent and reproducible transient response vector to the steady-state location of the 3 analytes in principal component space. This transient response vector in combination with the steady-state destination of the sensor array are shown for a typical exposure to methanol in the display screen of Figure 6. In this typical response, the sensor response travels from initial baseline conditions to the methanol calibration cluster, which is well separated the ammonia calibration cluster. There are also three voltages at the bottom of the screen which represent average response voltages for the three different homogeneous arrays of tin-oxide sensor types. The original baseline voltage is 2V.

Figure 6 also shows the entire transient response chemical discrimination module. A small fan on the side of the box helps to deliver analyte to the sensors in a controlled manner. The entire box weighs under five pounds. Battery power enables the box to be on continuously for over two hours in the field. Future implementations of the baseline compensation circuits onto custom integrated circuits are predicted to increase the time required between battery recharges by a factor of 10. Software will also be expanded to enable analyte calibration points to be added in the field rather than in the laboratory. Calibration points taken in the field are more accurate because they take into account variable field conditions such as humidity and temperature.

CONCLUSION

We have successfully demonstrated the operation of a modular and portable chemical discrimination system to track and display response paths of multidimensional sensor arrays in principal component space. The modules are designed to be low power to achieve low-power objectives and principal component analysis does not overload the low-power microcontroller (PIC 16F877) in this low-overhead system. Response paths have been shown on the module in calibration and tested to be easily identified with the human eye for three different analytes. The ability to inter-

change sensors of the same or different types and to compensate for unknown baseline conditions has been demonstrated. Simple noise removal techniques and outlier removal have also been used to improve the classification ability of the module. The end result is a portable box that a user can take with them into the field to search for pre-calibrated analytes using intuitive human-oriented classification methods.

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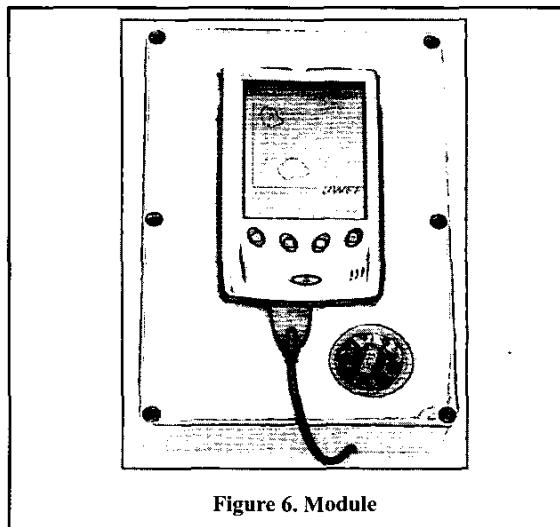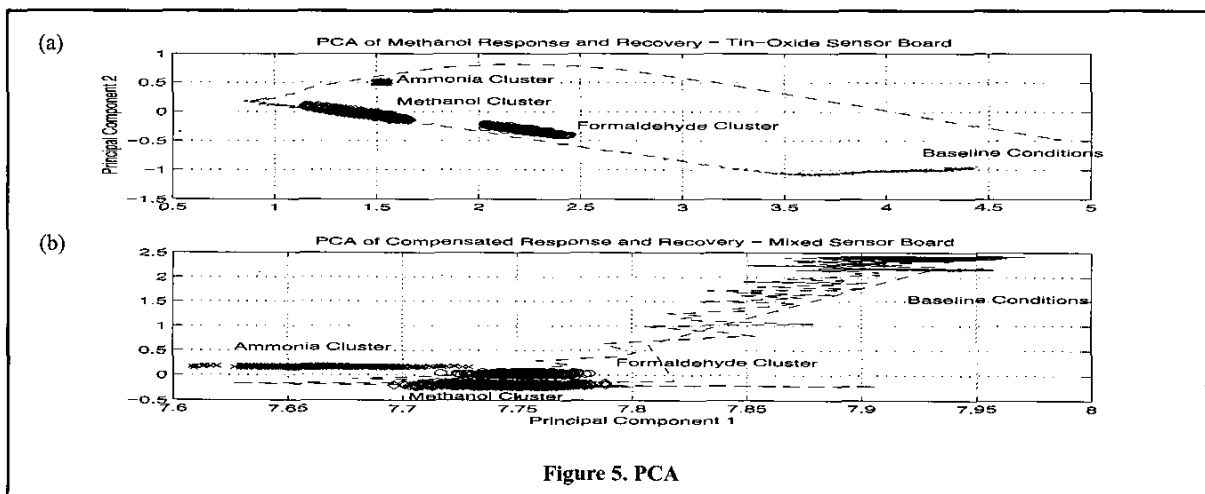
Figure 6. Module

Figure 5. PCA