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A MEMS BASED HYBRID PRECONCENTRATOR/CHEMIRESISTOR CHEMICAL SENSOR

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ABSTRACT

A hybrid of a microfabricated planar preconcentrator and a four element chemiresistor array chip has been fabricated and the performance as a chemical sensor system has been demonstrated. The close proximity of the chemiresistor sensor to the preconcentrator absorbent layer allows for fast transfer of the preconcentrated molecules during the heating and desorption step. The hybrid can be used in a conventional flow sampling system for detection of low concentrations of analyte molecules or in a pumpless/valveless mode with a grooved lid to confine the desorption plume from the preconcentrator during heating.

INTRODUCTION

Chemiresistors are a particularly simple type of chemical sensor whose electrical resistance changes in the presence of certain chemical vapors. There has been a recent upsurge of interest in chemiresistors formed from standard insulating polymers turned into conducting composites by mixing with large (20-40%) volumes of powdered metals, often carbon [1]. These sensors are easy to fabricate, can be made very small, and can be read-out by simple low power circuits measuring DC resistance. By varying the polymer host, these sensors can be selected to sense a very wide variety of volatile organic chemicals, but there has been constant pressure from potential users to improve the lower limit of detectable concentration for many applications. To improve the sensitivity we set out to design a preconcentrator/chemiresistor hybrid.

EXPERIMENTAL

The first experiments with a preconcentrator coupled to a chemiresistor were conducted with a mini-preconcentrator in a brass tube 2 mm in diameter filled with the commercial absorbent resin Tenax TA. The properties of this widely used resin can be found on the webpage: http://www.sisweb.com/index/referenc/tenaxta.htm. The center 1.5 cm of the filled tube was heated by a wrapped coil of insulated wire and a thermocouple was also potted to the tube. Fittings attached to the ends of the tube allowed it to be plumbed in series with our vapor delivery system [1] and to our manifold holding single chemiresistor sensors that had been previously calibrated against many vapors in the system. It takes about 1 watt of power to heat the column to 150°C.

This packed tube requires considerable pressure to flow the vapors and thus a portable system must have a pump for operation. For applications involving very small mobile platforms like micro-robots or badges, present day pumps are too large, power-hungry, and expensive. We report here the first prototype hybrid preconcentrator/chemiresistor array that can operate without pumps or valves. Figure 1 shows a photomicrograph of two silicon chips mounted and wire-bonded into a single 32-pin DIP. The chip on the left is a microfabricated planar preconcentrator. The device

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incorporates a surfactant templated sol gel adsorbent layer deposited on a microhotplate to achieve efficient analyte collection, and rapid, efficient thermal desorption. The preconcentrator microhotplate has been fabricated by through-wafer silicon etching (via the Bosch process), stopping on a low-stress silicon nitride membrane layer. Details of fabrication and performance in a microchemlab application are given in Ref. [2]. The sol gel layer was spray coated on top of the hotplate area before mounting the devices in the DIP.

The chip on the right shows four different chemiresistors on Pt electrodes with a Pt temperature sensor in the middle and two heater strips at the ends. The four different sensors in this particular array were formed from inks as described in Ref. 1 using the following polymers: poly(n-vinyl pyrrolidone) (PNVP), poly(vinyl alcohol) (PVA), poly(ethylene-vinyl acetate) (PEVA), and poly(isobutylene) (PIB). The sensor electrodes were coated at the "wafer-level" with the chemiresistive inks using an Asymtek Century Series C-702 Automated Dispensing Unit. The resulting hybrid is open at the top and experiments were conducted with three different kinds of lids: a cover glass which provides a very small dead volume (< 0.03 cm^3); a manifold head with an "O" ring that allows known concentrations from a flow system to pass over the chips; and a grooved lid with a 1 by 2 mm channel that allows vapors to diffuse in from the outside.

RESULTS AND DISCUSSION

Figure 2 gives a demonstration of the power of a preconcentrator used with a PEVA chemiresistor as the detector. A flow containing 3 ppm of m-xylene in N_2 was passed through the preconcentrator column and then past the chemiresistor. This level of m-xylene produces only a small signal on the PEVA sensor as seen in the inset. After 4 hours of preconcentration, the heater was turned on and the very large signal from a high concentration plug of m-xylene can be seen. The preconcentrator temperature can be seen from the dashed line and the right hand scale. The signal amplification here is about 400x. The level of amplification depends on the total number of analyte molecules absorbed in the column, so a higher flow rate with the same concentration will load the column faster. When the column is hot, no xylene is absorbed on passing through, and this is how the signal displayed in the inset was obtained.

The chemiresistor array shown in Fig. 1 was chosen so that at least one of the four sensors would respond to almost any volatile organic chemical (VOCs). Fig. 3 shows the response to four VOCs with widely different solubility parameters [1,3,4]. Each analyte was presented at 10% of its saturated vapor pressure at 21°C. We have shown that these four chemiresitors can distinguish many individual VOCs from the pattern of responses, independent of the concentration (unless it is so low that no chemiresistor gives a measurable response). One VOC of particular interest to us is methyl salicylate, often called "oil of wintergreen". This VOC has a vapor pressure of only 160 ppm at 21°C and has been shown to be absorbed on the sol-gel material on the microhotplate in earlier experiments.

Fig. 4 shows the calibration curve for methyl salicylate for the PEVA sensor in the array (the responses were much smaller for the other three sensors). Two different kinds of calibration runs were made. One with the flow control lid on the hybrid puts the selected vapor concentration directly on the array at 1 standard liter per minute (SLM) flow rate in a very small dead volume. The other curve was generated with the same flow into a container of about 0.5 liter volume that had the hybrid mounted in a socket with a frame to allow attachment of the grooved lid on the hybrid. The arrangement simulates a

"real world" environment in which the pumpless and valvless sensor system samples the surrounding environment. The two calibration curves are close to the same except that the grooved lid experiments show some delay in achieving steady state due to the filling of the container and diffusion of the analyte molecules into the grooved lid. The lower concentrations are difficult to see in this figure due to the non-linearity of the response with higher concentration, but the response at 1% *p/psat* (1.6 ppm) is 4% $\Delta R/R_0$ and is roughly linear below 3% *p/psat* .

The speed of response of the grooved lid arrangement is important to us for modeling purposes and in Fig. 5 we show the response in the container to two pulses of ethanol vapor, 10% and 5% *p/psat.* The data points are 10 seconds apart and the dashed line shows the flow controller switching of the flow. It takes about 60 seconds to get to 90% of full response, including the filling of the container with the new concentration. The PEVA sensor itself takes less than 10 seconds to respond if presented with the ethanol directly. The diffusion constant of ethanol is about 0.2 cm^2 /sec at 21°C, and using the universal scaling for diffusion of distance ≈ (diffusion constant times time) $^{1/2}$ the distance in 20 seconds is 2 cm. This gives the order of magnitude time scale for the sensor array responding to a background concentration of analyte molecules, and also the rate of loading of the preconcentrator absorbing layer.

The preconcentrator operates by absorbing molecules of volatile organic chemicals that pass over it at ambient temperature. A large number of molecules can be accumulated over time even from low concentrations in the background air, because of the high porosity of the sol gel layer. At a selected time, the preconcentrator heater (seen as the Pt meander line in Fig.1) can heat the hotplate to 150°C in a millisecond with only 300 milliwatts of power. The absorbed molecules are rapidly desorbed creating a plume of much higher concentration of molecules than in the background. Because of the close proximity of the chemiresistor, the plume reaches it very quickly (distance is about 5000 microns).

Figure 6 shows an experiment in which the open hybrid was loaded with an (unmeasured) amount of methyl salicylate (MS) from the vapor. The signal from the PEVA sensor during loading indicated that the vapor concentration was on the order of a few % *p/psat* . The a cover glass was used to seal the hybrid with a small dead volume. The small signal from the PEVA indicated that the partial pressure of MS was sub ppm in equilibrium with the MS absorbed on the preconcentrator. The first small pulse in Fig. 6 shows the heating of the array heater to calibrate the temperature coefficient of the PEVA sensor; when the preconcentrator is heated to ≈130°C, heat transferred to the chemiresistor array results in a 3-5°C temperature increase which must be compensated for. The boxes in Fig. 6 show the linear correction of each data point. The second pulse shows the sensor response to heating the preconcentrator, with the boxes the temperature corrected points. The peak resistance change of 26% would correspond to about 4% *p/psat* (6 ppm) as the partial pressure of MS with the preconcentrator hot. This pulse is actually the third cycle of heating and cooling the preconcentrator, with the first pulse giving a 5 megohm signal. In a perfect system with MS molecules only residing in the sol-gel film , the gas phase and the chemiresistor, we would be able to cycle between the higher gas phase concentration when the preconcentrator is hot and the lower when it is cold an indefinite number of times. In reality, it appears the some of the MS molecules are disappearing from the system each time the gas phase concentration is raised.

In Fig. 7, the sensor system with the grooved lid was placed in the ambient laboratory environment and an (unmeasured) concentration of MS vapor was placed near the opening of the groove. The PEVA chemiresistor showed a small response, and a 20

minute relaxation time was allowed for unabsorbed vapors to leave the system, as measured by the PEVA resistance. Fig. 7 shows the PEVA response to a 15 second heating of the preconcentrator. The calibration points in Fig. 4 would indicate that this very large signal results from a plume inside the groove of at least 10% *p/psat* or 16 ppm. The plume eventually dissipates since the groove is open to the ambient.

Experiments are underway to determine the relationship between loading concentrations and the size of the amplified signal on the chemiresistor. The simple grooved lid probably does not optimize the conflicting roles of allowing access to the hybrid by analyte molecules and confining the plume of high concentration when the preconcentrator is heated to give an amplified signal on the chemiresistors.

CONCLUSIONS

Experiments with the grooved lid showed that preconcentration and amplification of signal from background can occur without pumps and valves. Sampling of the vapor is slowed by the diffusion time of analyte molecules in the groove, but the confinement of the plume and the proximity of the chemiresistor allow amplified signals on the one-minute time scale. Many design issues for the optimal configuration and shape of the components are being pursued. There are also materials considerations since many of the desired analyte molecules stick-to and migrate into polymeric construction materials. The loss of control over the flow and volume of air with low concentrations of the desired analyte does result in a loss of information and speed of response. However in many applications, where small size, low power and low cost are very important design issues, this kind of hybrid will deliver useful chemical information.

ACKNOWLEDGMENTS

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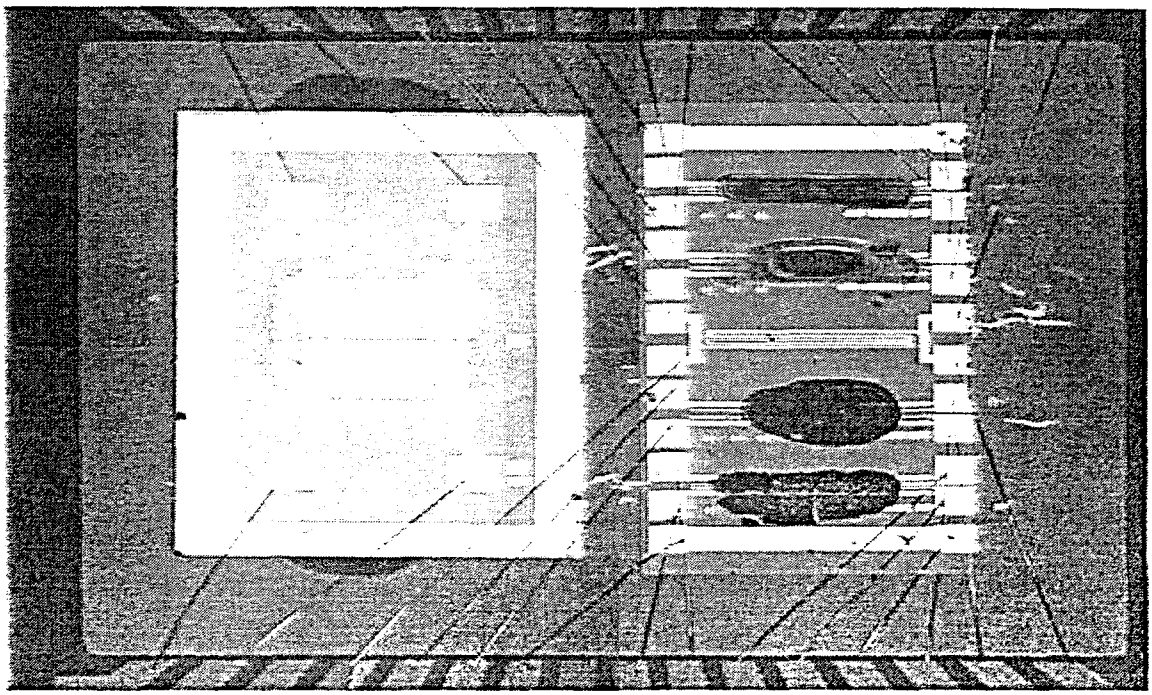

Figure 1. Hybrid preconcentrator/chemiresistor array in a 32-pin DIP package. The well is 1.3 cm by 0.9 cm, and the overall DIP package is 1.5 cm by 4 cm. The microfabricated planar preconcentrator is the chip on the left with two Pt meander line resistors for heater/temperature sensors. The chemiresistor array chip on the right has four different polymeric chemiresisters, with a Pt temperture sensor in the middle and heaters on the ends.

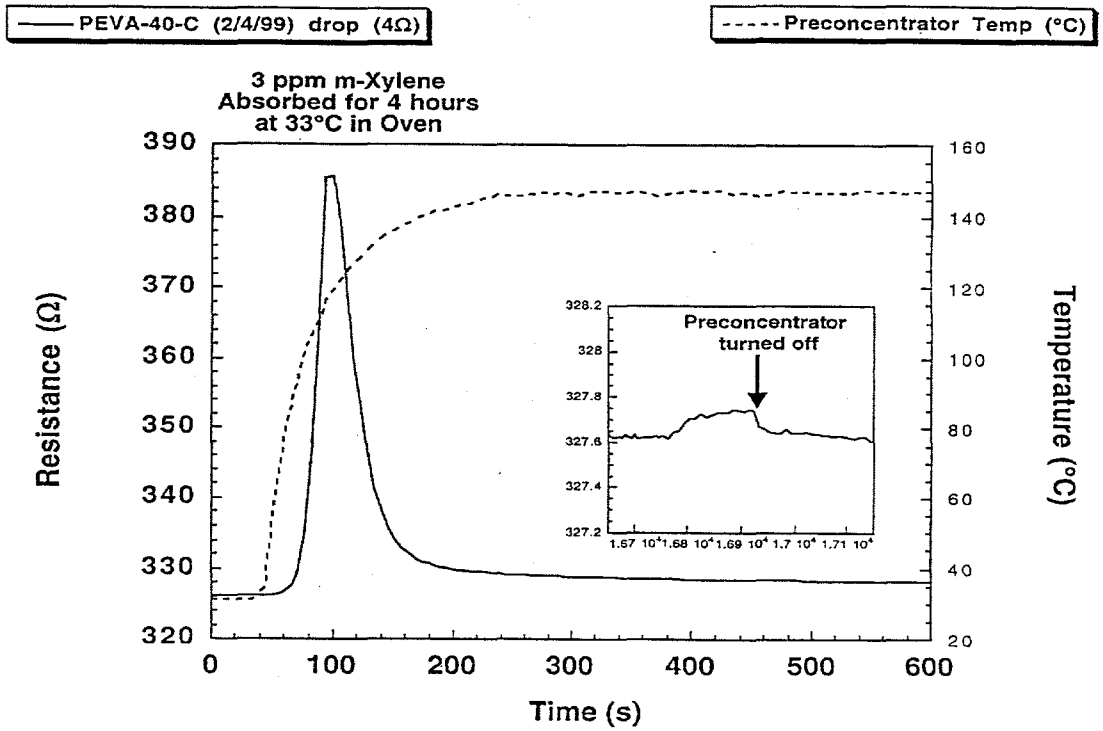

Figure 2. The signal from a PEVA chemiresistor resulting from desorption from a mini-preconcentrator using Tenax as the absorbant resin. A low flow with a concentration of 3 ppm m-xylene was used to load the preconcentrator at 33°C, and the temperature of desorption is shown by the dashed line and right-hand scale. The inset shows the size of the chemiresistor signal with the 3 ppm flow on, but the preconcentrator hot so that no absorption takes place until the heat is turned off, indicated by the arrow in the inset.

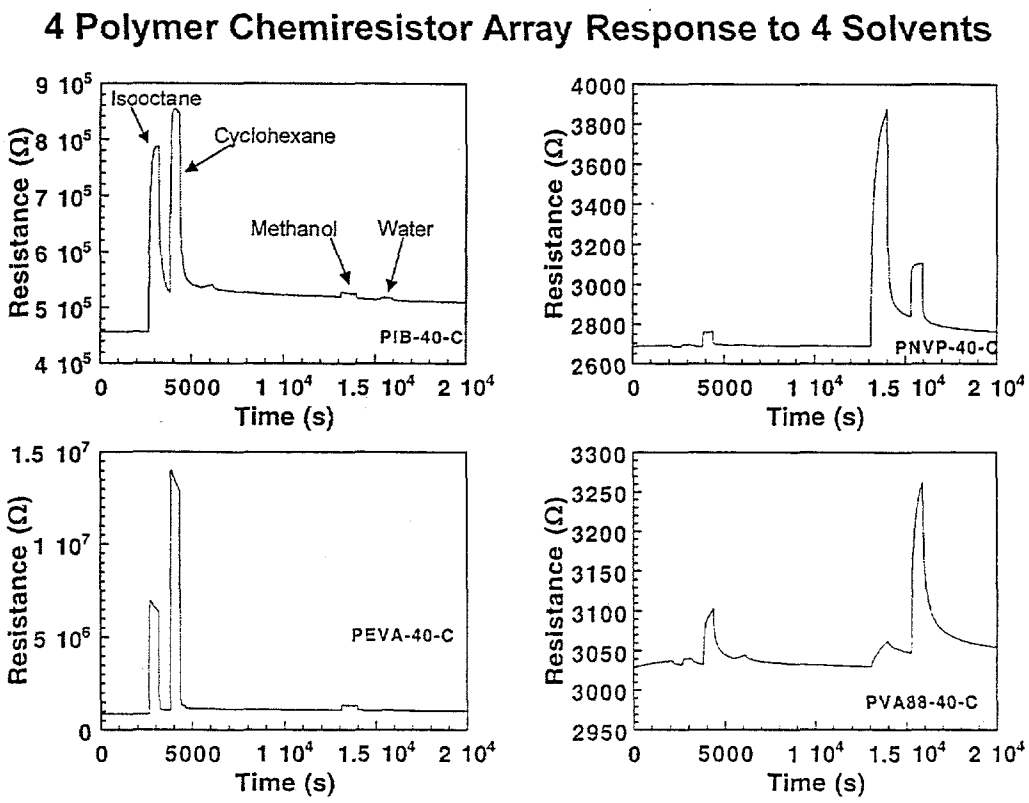

Figure 3. The resistance response signals from the four sensors in the array shown in Fig. 1 to four different VOCs. The polymer hosts for each sensor is given in the lower right hand corner of each plot, and the "-40-C" designation indicates that it is loaded with 40% carbon particles. The vapors in each pulse are from 10% of the saturated vapor pressure of the liquid at 21°C. The pulses of VOC are preceeded and followed by a flow of dry N_2. The pattern of responses is a clear signature of the identity of each VOC.

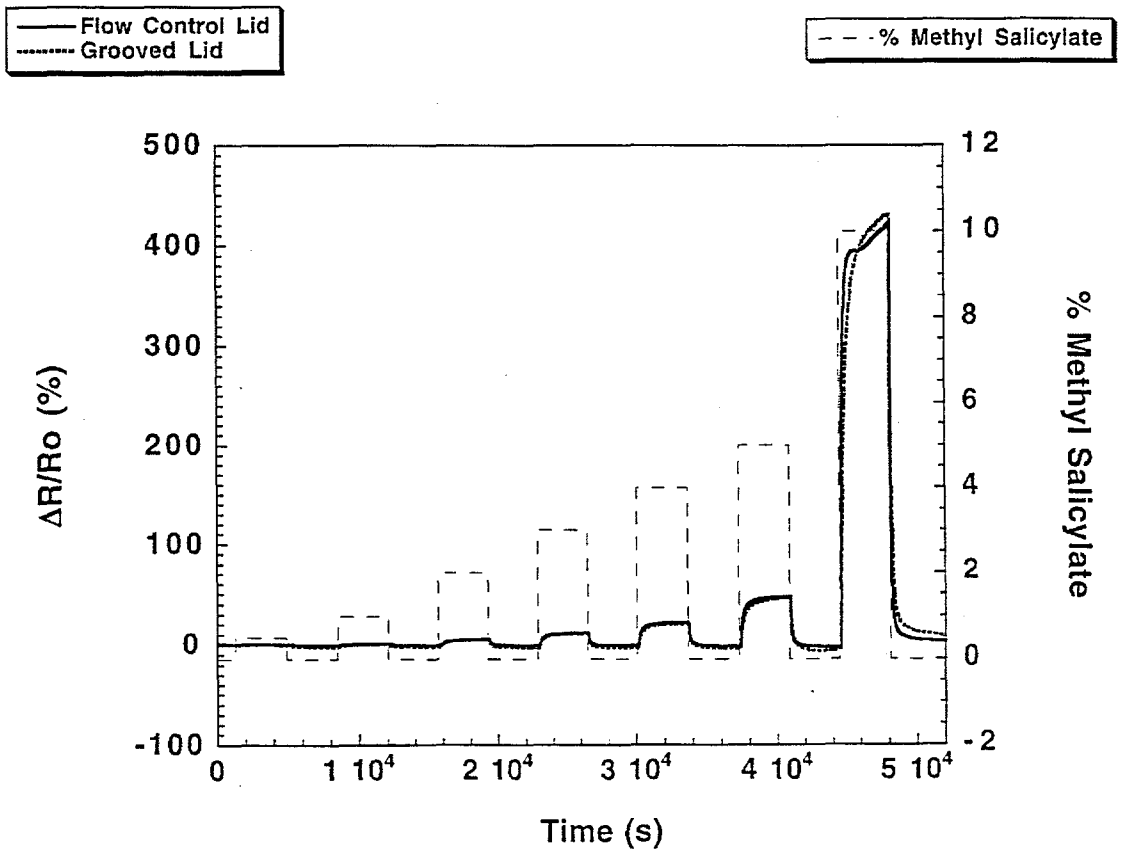

Figure 4. Calibration of the PEVA sensor in the array to pulses of different concentrations of methyl salicylate. The dashed line shows the flow controller settings and the concentration on the right-hand scale. The two sensor response lines are for two different configurations of the hybrid chip: the solid line for a flow control lid with a "O" ring seal to the DIP package and positive flow across the chips, and the short dashed curve for a grooved lid on the DIP package where the analyte only reaches the chips by diffusion from the vapor in the container in which the sensor is mounted. The vapor pulses were one hour each. The response at 1% *p/psat* (1.6 ppm) is 4% $\Delta R/R_0$ and is roughly linear below 3% *p/psat* .

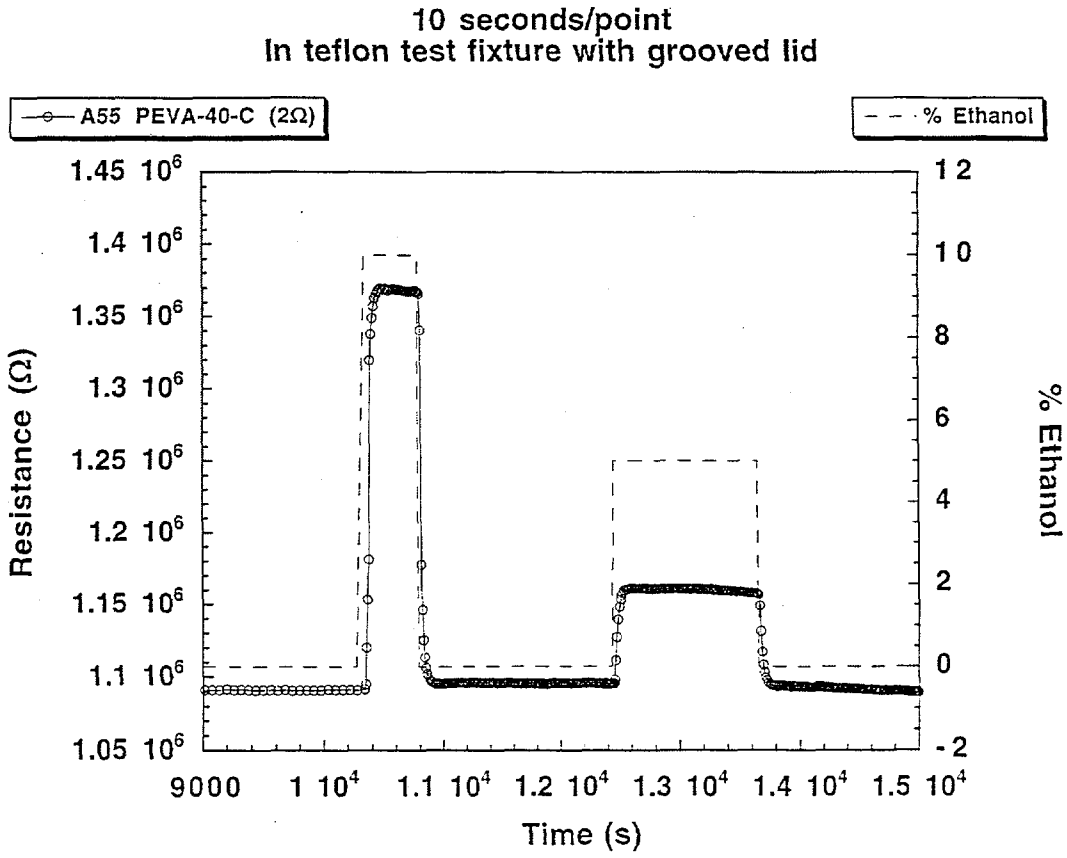

Figure 5. The response of the PEVA sensor in the array on the hybrid to two different concentrations of ethanol at 21°C. The hybrid was coverd with the grooved lid and each data point was 10 seconds apart. The time response includes the time required to fill the container with the ethanol vapor and the diffusion down the groove to the sensors; on the purge side it includes the time to diffuse out of the sensor material and out the groove.

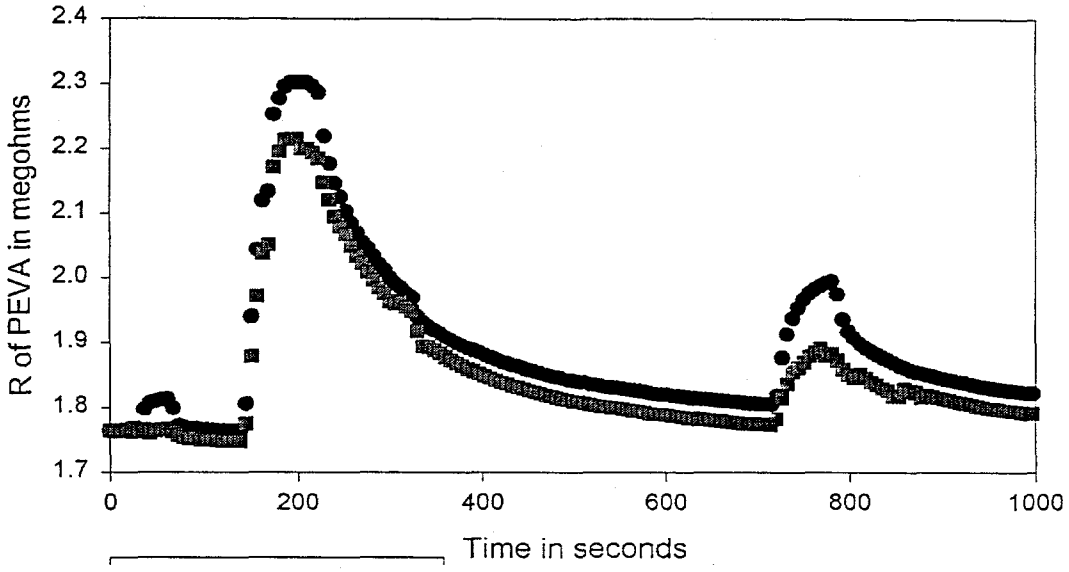

Figure 6. The response of the PEVA sensor in the array to desorption of MS from micro-hot plate preconcentrator. The hybrid is sealed with a cover glass after loading of the preconcentrator with MS vapor. This shows the result of an array chip heating (for calibration) in the first small signal followed by desorption heating of the preconcentrator. This shows the third and fourth heating and cooling cycles; the first two gave even bigger signals from the PEVA.

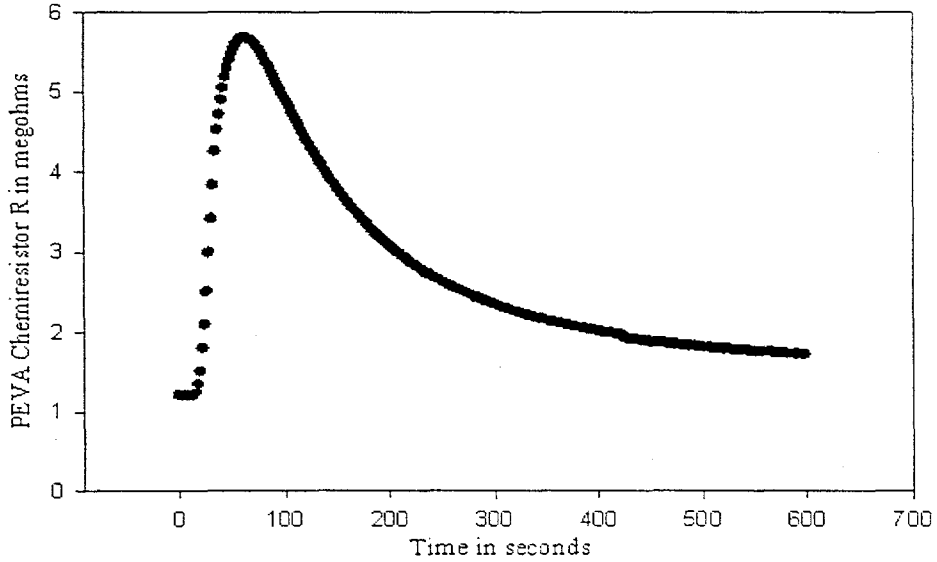

Figure 7. The response of the PEVA sensor in the array to 15 second desorption of MS from micro-hot plate preconcentrator. The hybrid was fitted the grooved lid, and loading of MS was done with vapor outside the groove. No active pumping or flow was used.