Expanding the Capabilities of the JPL Electronic Nose for an International Space Station Technology Demonstration

M. A. Ryan, A. V. Shevade, C. J. Taylor, M. L. Homer, A. D. Jewell, A. Kisor, K.S. Manatt, and S.P.S. Yen

Jet Propulsion Laboratory, California Institute of Technology, Pasadena CA 91109

M. Blanco and W. A. Goddard, III

Materials Simulation Center, California Institute of Technology, Pasadena CA 91105

ABSTRACT

An array-based sensing system based on polymer/carbon composite conductometric sensors is under development at JPL for use as an environmental monitor in the International Space Station. Sulfur dioxide has been added to the analyte set for this phase of development. Using molecular modeling techniques, the interaction energy between SO_2 and polymer functional groups has been calculated, and polymers selected as potential SO_2 sensors. Experiment has validated the model and two selected polymers have been shown to be promising materials for SO_2 detection.

INTRODUCTION

An electronic nose to be used as an anomalous event detector such as a chemical spill or leak in crew habitat in spacecraft has been under development at JPL for the past several years. This sensing system, the JPL Electronic Nose (ENose), is under development as an array–based sensing system which can run continuously and monitor for the presence of toxic chemicals in the air in real time. The sensing array in earlier versions of the JPL ENose has been made from polymer-carbon composite sensing films [1-5], based on initial sensing film studies done in the Lewis group at Caltech [6, 7]. These conductometric sensing films are made from commercially available insulating polymers which are loaded with carbon black as the conductive medium. In the device designed and built for crew habitat air monitoring, a baseline of clean air is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors is deconvoluted, and chemical species to which the device has been trained are identified and quantified using a set of software analysis routines developed for this purpose.

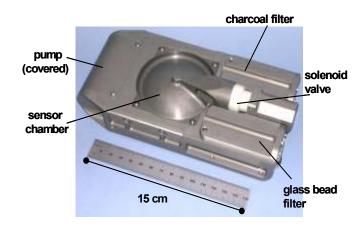When the device is operating, air is pumped from the surroundings into the sensor chamber. The air is

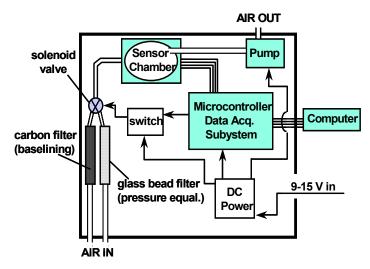**Figure 1:** The Second Generation JPL ENose.

Figure 2: Block diagram of JPL ENose.

directed either through an activated charcoal filter which is put in line to provide clean air for baseline data, or though a dummy-filter of glass beads which is put in line to provide a pressure drop similar to that in the charcoal

filter. A solenoid valve can be programmed to open the path to the charcoal filter and provide clean airflow for a programmable period of time at programmable time intervals; otherwise, the air is directed through the glass beads. Air then enters the sensing chamber, and resistance is measured. The Second Generation JPL ENose is shown in Figure 1 and a block diagram of the device layout is shown in Figure 2.

There have been three phases of development of the JPL Electronic Nose. In the first phase, a device capable of detecting, analyzing and quantifying ten analytes at the 1-hour Spacecraft Maximum Allowable Concentration (SMAC) was developed [1,2]. This device was tested successfully in 1998 on Space Shuttle flight STS-95 [3,4]. In the second phase, the Second Generation ENose shown in Figure 1 was miniaturized and the capabilities were significantly expanded to include 21 analytes and detection at varying humidity and pressure. This device was tested extensively on the ground, and was demonstrated to be able to detect, identify and quantify the 21 analytes at the 24-hour SMACs [5]. The third phase of development, now underway, is focused on two aspects of the ENose. In one aspect, an interface unit is being designed to allow the ENose to be integrated on the International Space Station for a six-month technology demonstration experiment. In the other aspect, the capabilities of the sensing set are being expanded to include the ability to detect two inorganic species, mercury and sulfur dioxide.

This paper focuses on development of polymer-based sensors which are sensitive to sulfur dioxide. SO_2 may be released as a breakdown product of $SOCl_2$ from a leaking or burst lithium-thionyl chloride battery. The detection goal in this development effort is 1 part-per-million (ppm) SO_2 at atmospheric pressure and 25 $^{\circ}$C (2.65 mg/m^3) [9].

One approach to development of sensing materials has been to develop molecular models of the interaction energies of the analyte with functional groups present on polymers [8]. These interaction energies are used to predict which types of polymers are likely to bind to the analyte, and thus may respond to the presence of analyte with a change in resistance in a polymer-carbon composite sensing film [5,7]. Following the prediction of candidate polymers, sensors are made and tested for response to analyte, in this case SO_2.

SENSOR-ANALYTE RESPONSE MODELING

A first principles, quantum mechanical model was used to predict the strength of interactions between SO_2 and organic molecules. This methodology involves calculating interaction energies for organic-SO_2 binary systems. Common classes of organic structures are considered as functionalities which may be found on polymer chains. The calculations undertaken include interaction energies of alkanes, alkenes, aromatics, amines (1°, 2°, 3°), aldehydes, and carboxylic acids with

sulfur dioxide. Interaction energies are calculated using B3LYP and X3LYP flavors of Density Functional Theory (DFT). These QM results are used to develop a first principles force field for use in the calculation of interaction energies (E_{int}) of SO_2 molecules with various polymers. Only interaction energies less than zero (exothermic reactions) will result in binding between analyte and functional group such that there it may result in a change in resistance in a polymer-carbon composite
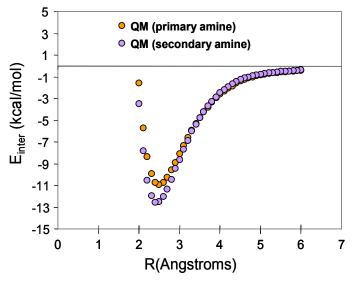

Figure 3: Quantum mechanical interaction energies for SO_2 with amines.

film.

Results of modeled interaction energies of organic-SO_2 systems indicate that a polymer candidate for SO_2 detection would be one containing amine functional groups (primary, secondary or tertiary amine). An example of interaction energy calculations is shown in Figure 3, where the energy is ~ -11 kcal/mole. Other chemical functionalities that have moderate to strong binding with SO_2 are amides, aldehydes, and carboxylic acids. Ethane and benzene showed either no binding ($E_{int} > 0$) or weak binding ($E_{int} > -2$ kcal/mol).

POLYMER SYNTHESIS AND SENSOR FABRICATION

Two polymers were selected and made into polymer-carbon black composite sensors [10]. These two polymers EYN2 and EYN7 are both poly-4-vinyl pyridine derivatives with a quaternary and a primary amine. The polymers were synthesized from poly-4-vinyl pyridine and made into polymer-carbon composite sensing films using protocols which have been previously described [4,5]. These films were loaded with 8-10% carbon by weight and solution deposited onto microhotplate sensors substrates with a sensor area of 200 μm by 200 μm (4x10^{-8} cm^2). The baseline resistance of each sensor was ~ 10 kohms.

Figure 4: Polymers EYN2 and EYN7, selected as sensor material to detect SO_2.

EXPERIMENTAL RESPONSE OF SENSORS

NEW POLYMERS

Sensors were exposed to SO_2 in 22-25 ^{o}C air with water content of 10,000 ppm (~40% relative humidity). SO_2 concentrations ranged from 0.2 to 20 ppm at atmospheric pressure. Sensor surfaces were not temperature controlled during exposure.

Both EYN2 and EYN7 showed good response to SO_2 in air, as predicted by the modeled interaction energy (E_{int}) between SO_2 and primary amines. Figure 5 shows the response of two microsensors made from polymer EYN2 to concentrations from 0.2 to 9 ppm SO_2. The baseline rise in the figure is caused by drift in environmental temperature during the test.

This material responds strongly to sub-ppm levels of SO_2. 0.2 ppm SO_2 results in a resistance change of ~0.15%, which is about one order of magnitude greater than response of most polymer-carbon composite sensors to ppm concentrations of organic analytes.

Because of the fairly strong E_{int} between SO_2 and a primary amine (see Figure 4), it was not expected that a polymer-carbon black composite sensor with this functionality would release the analyte easily in room temperature air. As discussed in a previous paper, microhotplate sensors were adopted in order to make it possible to regenerate sensors by heating them in flowing clean air [9]. EYN2, however shows good, if somewhat slow, recovery after exposure to target concentrations of SO_2. This recovery indicates that it is

likely that only gentle heating (30-40 ^{o}C) will be necessary to regenerate these sensors.

GENERATION 1 AND GENERATION 2 POLYMERS

Polymers used in the first and second generation JPL ENose were also tested for response to SO_2 in air with 10,000 ppm H_2O. As can be seen in Figure 6, some polymers responded to 10-15 ppm SO_2 in air, and some did not. Traces in Figure 6 are numbered 1 through 7, corresponding to polymers:

    1 - polyimide
    2 - polyamide resin
    3 - polycaprolactone
    4 - ethylene-propylene
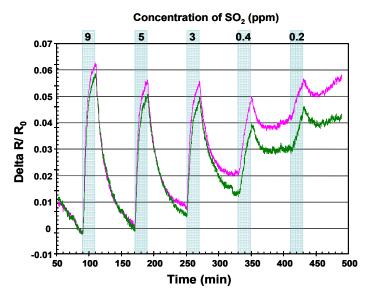   5 - poly 4-vinylphenol
    6 - polyvinyl acetate

Figure 5: Response of sensors made from polymer EYN2 to 0.2 to 9 ppm SO_2 in air.

The response of the polymer-carbon composite films shown in Figure 6 is consistent with the results of quantum mechanical modeling of interaction energies. The two polymers which responded relatively strongly to the presence of SO_2 are a polyimide and a polyamide; both functionalities are predicted to respond to SO_2. One polymer, polycaprolactone, responded moderately well to SO_2; polycaprolactone contains an ester functionality, which may be expected to respond to SO_2 based on carboxylic acid response. Polymer #6, polyvinylacetate, also contains an ester functionality, and it responds very weakly (but measurably) to SO_2. The two other polymers contain ethane and ethene (#4), or benzene (#5) functionalities, both predicted to bind weakly or not at all, and the response is either very weak or it does not respond.

Note that the responses for the composite films made of 1st and 2nd generation polymers are significantly smaller than responses for the amines selected from the

modeling work. The responses are about one order of magnitude smaller for one order of magnitude larger SO_2 concentration. This response size is also consistent with the predicted interaction energies for these functionalities; primary and secondary amines were predicted to have the largest interaction energy (absolute value) and ethane was predicted to have the smallest (absolute value).

Those polymers which respond to the presence of SO_2 do not recover fully in room temperature air. Experiments showed that they will recover by heating to ~32 - 36 $^{\circ}C$ in flowing clean air.
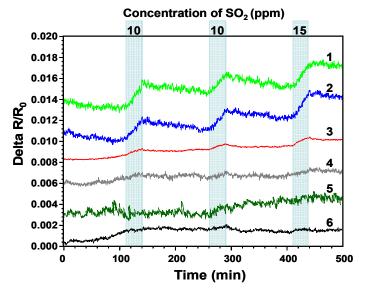

Figure 6: Response of six ENose polymers to SO_2 in air. Traces have been shifted along the y-axis to separate them.

CONCLUSION

Quantum mechanical modeling of the interaction energy of functionalities which may be found on polymer chains with SO_2 predicted that polymers containing primary or secondary amines would respond strongly to SO_2. Experiments with two such polymers confirmed that strong response to sub-ppm concentrations is possible. Experiments with other polymers to check the use of interaction energy models has validated the model.

Further work will use similar calculations to select polymers which will respond to mercury and to other analytes.

ACKNOWLEDGMENTS

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CONTACT

Dr. M. A. Ryan
MS 198-235
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena CA 91109
tel: (818) 354-8028
fax: (818) 393-5007
email: mryan@jpl.nasa.gov