Sensors and Actuators B 197 (2014) 280–291

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Analytical capabilities of chemiresistive microsensor arrays in a simulated Martian atmosphere

K.D. Benkstein[a,*], P.H. Rogers[a], C.B. Montgomery[a], C. Jin[b], B. Raman[b], S. Semancik[a]

[a] *National Institute of Standards and Technology, Biomolecular Measurement Division, Gaithersburg, MD 20899-8362, USA*
[b] *Department of Biomedical Engineering, Washington University, St. Louis, MO 63130, USA*

ARTICLE INFO

Article history:
Received 22 July 2013
Received in revised form 10 January 2014
Accepted 26 February 2014
Available online 6 March 2014

Keywords:
Gas-phase sensing
Chemiresistor
Microsensor array
Simulated Martian environment

ABSTRACT

The capabilities of a chemiresistive microsensor array for detecting and identifying trace target analytes were examined under a simulated Martian atmosphere. The simulated environment included low oxygen content (0.15%) balanced by carbon dioxide, low pressure (7.5 hPa) and temperature (199.1 K), and trace levels of up to three target molecules presented simultaneously. The target molecules were selected from four possible analytes (methane, hydrogen, ethane and sulfur dioxide), presented to the sensor array at multiple concentrations of 200 nmol/mol or less. Signals from four elements of a 16-element microsensor array were employed in the data analyses described. Each element used a different sensing film and was operated with a dynamic temperature program tuned to the background environment. The rich data streams collected from the microsensor array as it was exposed to the complex mixtures and carbon dioxide-based background were analyzed using two approaches: Linear Discriminant Analysis (LDA) and Partial Least Squares Discriminant Analysis (PLS-DA). Analysis of the data by LDA was used for initial assessment of the data streams, and indicated that the data from the microsensor array provided sufficient information to identify, and potentially quantify, each of the target analytes. Further analysis showed that it was possible to separate the methane from the other analytes, as demonstrated after analyzing the data by PLS-DA. Furthermore, the models developed using PLS-DA on one day were able to discriminate the analytes on other days. The success rate was qualitatively dependent on the length of time between the day on which the model was trained and the day on which the validation data were acquired. The work demonstrates the potential of this microsensor array approach to be further developed as a low mass, low-power-consumption screening tool for space exploration.

Published by Elsevier B.V.

1. Introduction

Chemical microsensors are used or have the potential to be used in a variety of fields to detect chemical species in complex backgrounds [1–4]. Potential application areas include environmental and process monitoring, medical diagnostics and health, safety, energy and food. Depending upon the operational parameters of a chemical sensor, it may be tuned for a particular application. For example, by tuning materials and temperature operating schemes, the chemical microsensor arrays developed at the National Institute of Standards and Technology (NIST) have shown versatility in applications that include medical diagnostics, homeland security and environmental monitoring [5–7]. The NIST chemical microsensor array depends upon a chemiresistive (conductometric) sensing mechanism [8], generally using semiconducting metal oxide sensing films. Each microsensor in the array employs a low-mass platform (≈250 ng) [9] with an embedded low-power (<25 mW at full power) poly-silicon heater to control the sensor operating temperature below 500 °C. These sensing films may be varied in their chemical composition and/or morphology across an array to provide analytical orthogonality sufficient to detect trace chemicals in complex mixtures when coupled with advanced signal processing approaches [10].

A particularly challenging application area for the detection of trace chemicals is the exploration of planets and other solar system objects. Research has been described for testing electronic noses for use in space-based habitation modules [11,12], and the chemiresistor approach was selected for studying oxidants in the Martian atmosphere [13] and methane in harsh environments [14]. Preliminary results on our array-based, temperature-modulated approach have also been briefly described [15]. For these applications, the testing environment can differ greatly from that typically found

---

* Corresponding author. Tel.: +1 301 975 2847.
E-mail address: kurt.benkstein@nist.gov (K.D. Benkstein).

http://dx.doi.org/10.1016/j.snb.2014.02.088
0925-4005/Published by Elsevier B.V.

on earth, with such factors as the chemical composition of the atmosphere, the pressure and the temperature being particularly relevant in assessments of chemical detection and quantification capabilities. In the test case explored for this work, Mars was selected as the environment of interest. Mars has a background atmosphere that consists largely of carbon dioxide with an atmospheric pressure of 4.0–8.7 hPa and a temperature ranging from 184 K to 242 K [16]. The Martian environment is currently under active exploration with several landers and satellites probing and monitoring the atmosphere and surface. One particularly interesting question relates to confirming the existence of and determining the source for methane in the atmosphere [17–22]. Because of the lifetime expected for methane in the Martian atmosphere, locally high concentrations of methane would suggest an active process (both biogenic and geologic processes are possible) that is currently producing the chemical [17,18]. Identifying these sites of current chemical activity is of particular interest for understanding the atmosphere and geochemistry (and potentially the biochemistry) of an alien world [23]. We have used this scenario as a demonstration study for employing a chemical microsensor array on the Martian surface. The microsensor array could be envisioned as a low-mass, low-powered screening tool, for example on a rover, working to identify methane point-source hot spots (spatially localized, gas-generating sites). After initial detection by the microsensor array, the higher-power analytical instruments could be powered up to confirm and expand upon the initial screening results from the chemical sensor array.

For the studies presented here, the Martian atmosphere has been simulated chemically and with appropriate temperature and pressure. With that as a background, the microsensor array was exposed to trace levels of methane, by itself, and mixed with one or two other trace constituents that could inform on the source of the methane. The capability of the microsensor array to identify, and to some extent, quantify, the components in the complex mixtures was evaluated using Linear Discriminant Analysis (LDA) and Partial Least Squares Discriminant Analysis (PLS-DA).

2. Materials and methods

A testing system (shown schematically in Fig. 1) was assembled to simulate the Martian atmosphere, including chemical composition, temperature and pressure. The background gas was 0.15% oxygen with the balance carbon dioxide, and was delivered from certified gas cylinders. Four target analytes were used: methane, ethane, hydrogen and sulfur dioxide. The targets were premixed with the background gas in certified cylinders with concentrations of 4 μmol/mol, 4 μmol/mol, 2 μmol/mol and 1 μmol/mol, respectively. The sensor array, in a 40-pin dual in-line package, was loaded into a sample chamber that allowed computer-controlled flow and mixing of background gas and the analytes. A reduced-pressure atmosphere was produced with a scroll pump at the exhaust and throttling controlled using manual valves. The sample-cell pressure was monitored using a convection gauge tube, and maintained at ≈7.5 hPa. Temperature was maintained at ≈199 K by immersing the sample cell in a dry ice/methanol cooling bath. The temperature of the sample cell was monitored using three calibrated platinum-resistance thermometers (PRTs): one located near the gas inlet, one located near the gas exhaust and one located at the sensor array. Temperature was recorded for all three PRTs throughout experimental runs. An experimental run typically consisted of presentations of trace levels (20–200 nmol/mol) of analytes singly or in binary or ternary mixtures. Three binary mixtures and three ternary mixtures were studied overall. Each mixture contained methane plus one or two additional analytes. Prior to starting the gas exposure cycle, the simulated Martian background was flowed over the microhotplate sensor array located in the environmental simulation cell as the entire assembly came to thermal equilibrium in the methanol/dry ice bath. Temperature operations for the microhotplates in the array, which included calibration and initiation of the temperature-modulation program, commenced once the temperature was below ≈205 K. Each ternary experiment was run multiple times (See Table S1 for the timing of experiments).

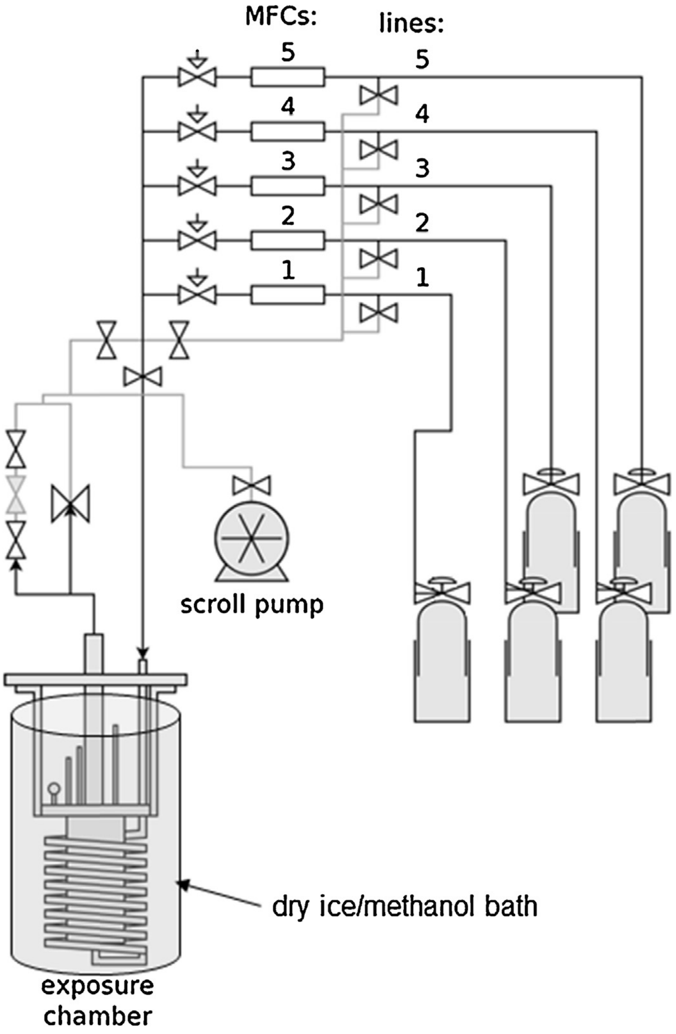

Fig. 1. A schematic of the sensor testing system. Mass flow controllers (MFC) were used to control gas delivery and mixing ratios. The lines in gray are bypass lines, used for pumping ambient air out of the testing system before introducing the simulated Martian background. The dry ice/methanol bath is used to maintain a low temperature (≈199 K), and the scroll pump is used to effect low pressure (≈7.5 hPa).

For the experiments reported here, four sensing films from a single microsensor array were primarily used: tin oxide, tungsten oxide, indium oxide and microshells composed of antimony-doped tin oxide nanoparticles (Fig. 2). The tin oxide, tungsten oxide and indium oxide were all deposited from solution [24], and the microshells from an aqueous dispersion [25]. All materials were deposited from polycarbonate microcapillary tubes using a Pneumatic PicoPump (World Precision Instruments) [26] with a pulse pressure of ≈550 kPa. The microsensor heaters were used to process the films in air (annealed at 500 °C for 5 h) before they were used in the simulated Martian chemical environment. For sensor operations, different temperature programs were assigned to the various sensing films, tuned for their resistance ranges in the simulated Martian environment (Fig. 3). The uncertainties in sensor operating temperatures for the programs were estimated by comparing the daily calibrations of sensors running the selected