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Chemical Microsensor and Micro-instrument Technology at Sandia National Laboratories

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ABSTRACT

Important factors in the application of chemical sensing technology to space applications are low mass, small size, and low power. All of these attributes are enabled by the application of MEMS and micro-fabrication technology to chemical sensing. Several Sandia projects that apply these technologies to the development of new chemical sensing capabilities with the potential for space applications will be described. The Polychromator project is a joint project with Honeywell and MIT to develop an electrically programmable diffraction grating that can be programmed to synthesize the spectra of molecules. This grating will be used as the reference cell in a gas correlation radiometer to enable remote chemical detection of most chemical species. Another area of research where micro-fabrication is having a large impact is the development of a "lab on a chip." Sandia's efforts to develop the μChemLab™ will be described including the development of microfabricated pre-concentrators, chromatographic columns, and detectors. Chemical sensors are evolving in the direction of sensor arrays with pattern recognition methods applied to interpret the pattern of response. Sandia's development of micro-fabricated chemiresistor arrays and the VERI pattern recognition technology to interpret the sensor response will be described.

INTRODUCTION

Utilization of chemical sensing technology in space related applications, imposes additional constraints on the technology in terms of size, weight, and power requirements. These requirements to minimize space utilization and power consumption are met nicely by the application of MEMS and micro-fabrication methods to the fabrication of chemical sensing devices. Two kinds of chemical sensing applications can be envisioned in space, remote sensing from the spacecraft of a planetary, asteroid or comet surface and point chemical sensing inside or outside of the spacecraft. Here we will present several technologies being developed at Sandia National Laboratories that can impact chemical sensing applications in space.

POLYCHROMATOR

An algorithm has been developed that calculates diffraction grating profiles that diffract multiple wavelengths at the same angle [1]. <u>This development extends the application of diffractive optics from spatial domain optical processing into the spectral domain.</u> This algorithm can be used to define novel diffraction gratings that are complex spectral filters with any spectral content desired. In fact, they can even be used to synthesize the absorption spectra of specific molecules [2]! Gratings have been successfully fabricated in silicon using conventional lithographic methods for HF, toluene, methyl isobutyl ketone, and kerosene and the diffracted beam successfully reproduces the spectra of these molecules. One space related application of this technology would be to replace the reference cell in a

correlation radiometer for remote optical sensing. These gratings offer the ability to use correlation radiometry with transient or dangerous chemical species, and to greatly reduce the size of the reference cell for weak absorption lines. The gratings can also reproduce the complement of the transmission spectrum for a specific molecule in the reference cell rather than the transmission spectrum. This greatly reduces the unmodulated light background and thus the noise level in the detector. A joint project is underway with Honeywell and MIT as partners to develop a programmable grating structure [3] that will allow real-time reconfiguration of the grating elements to produce any spectral band-pass filter one desires. This capability allows spectral modulation of the diffracted beam in such a way as to enhance the ability of the radiometer to distinguish between chemical species with similar spectral features.

μChemLab™

A miniature, integrated chemical laboratory (μChemLab™) is being developed that utilizes microfabrication to provide faster response, smaller size, and an ability to utilize multiple analysis channels for enhanced versatility and chemical discrimination [4]. Our μChemLab™ program goal is to develop a small (palm-top computer sized), lightweight, and autonomous systems that provide rapid (1 min), sensitive (1-10 ppb), and selective detection of target analytes. Improved sensitivity and selectivity are achieved by using a cascaded approach where each channel includes a sample collector/concentrator, a gas chromatographic (GC) separator, and a chemically selective surface acoustic wave (SAW) array detector. Prototypes of all three components have been developed and demonstrated and current work is focused on integrating these into a complete analysis system.

The sample collector/pre-concentrator requires a medium to absorb the vapor sample to be analyzed and a method to desorb the accumulated sample in a short pulse. Microfabrication methodology has been used to fabricate "micro-hotplates" [5] that provide the means of rapidly heating a surface with limited expenditure of energy. Thus, the micro-hotplate structure can be utilized as a sample collector with the addition of a coating to absorb and concentrate the sample. This is the structure chosen for the μChemLab™.

Gas chromatographic (GC) separation, used to separate compounds in time, is a powerful tool for enhancing chemical discrimination. While conventional GC systems utilize micro-capillary columns, miniature on-chip GC columns can provide improved ruggedness, smaller size, lower power, and an ability to integrate other components such as pre-concentrators and detectors. We have developed a novel fabrication technique for making columns up to one meter long on a one-cm^2 chip. These columns are fabricated using high aspect ratio silicon etching (HARSE) [5,6] to form a high aspect ratio column that is narrow and deep (typical columns 40-80 μm wide by >350 μm deep). This reactive ion etching process results in parallel sidewalls providing a constant column width, a critical feature to achieve effective separations. With only 5 psi of pressure (miniature diaphragm pumps can provide this quite easily), we have demonstrated separation of up to five components in less than 30 seconds.

To enable selective detection, miniature SAW sensor arrays containing four 380 MHz SAWs with an active coated area of less than one mm^2 have been developed [7]. In addition, an integrated sensor measuring about 0.2 cm^2 containing the SAW array and all high frequency electronics has been designed. This device is being fabricated using GaAs, a unique substrate since it is piezoelectric and is an excellent semiconductor for fabricating high frequency electronics. This design incorporates amplifiers to provide the gain and phase comparators to provide a DC output proportional to SAW phase. All components have been demonstrated in discrete versions and the integrated design should provide DC in/DC out operation.

The μChemLab™ can provide chemical analysis capability in a small package for use on a planetary surface or inside a manned spacecraft for analysis of the cabin atmosphere or biomedical evaluation of the cabin occupants. The micro-components developed for this device can also be combined in more complex structures in order to solve other chemical and biochemical monitoring problems.

SENSOR ARRAYS

An alternative approach to micro-instruments for chemical analysis is an array of chemical sensors with different sensing chemistries. While it is difficult to develop sensing chemistries that are completely orthogonal and specific to particular target species, a partially selective sensing array with pattern recognition can be effectively used instead. The pattern recognition algorithm relieves the requirement of complete orthogonality of the sensing chemistries and can even help identify the best sensing chemistries for a particular application. Perhaps the simplest method of producing an array of small, inexpensive chemical sensors is to fabricate a series of chemi-resistors [8]. The simple, low temperature fabrication of chemiresistors by computer-controlled liquid dispensing will allow easy integration with sensing electronics. The dimensions of the entire sensor array and electronics will be < 1 cm^2. In this technology, a series of electrical resistors are fabricated out of materials that change their conductivity with exposure to chemical vapors. Such materials may be conductive polymers, carbon-loaded polymers or even metal films. The choice of materials depends on the chemical species one wishes to detect. These devices are the basis for the "electronic noses" that have received such publicity recently [9]. The mechanism for influencing the conductivity is different for the different materials. Conductive polymers bind molecules that either donate or accept electrons from the polymer and thus act just like dopants in semiconductors. Carbon-loaded polymers swell with exposure to solvents and this increased separation of the carbon particles decreases the conductivity of the materials. Thin metal films can react with some materials such as oxygen and decrease the effective thickness of the metal and thus its conductivity. In other films, the bulk conductivity can be changed by electron scattering processes, e.g. hydrogen in palladium. Some of these processes are reversible and others are not. Generally speaking, the stronger the chemical interaction, the greater the sensitivity and the less reversible the process. For an irreversible process, the sensors may still be used in a dosimetric mode where the conductivity change is proportional to total fluence of vapor. Here the rate of change in conductivity is proportional to the concentration of the chemical vapor being sensed. Interpretation of the chemical, sensor array response is handled very successfully by a new pattern recognition methodology described in the next section.

VERI PATTERN RECOGNITION METHODOLOGY

A new, non-parametric pattern recognition (PR) method based on the visual empirical region of influence (VERI) clustering technique [10] is being developed at Sandia. This method is based on an evaluation and modeling of cluster analysis performed visually by human beings in two dimensions. The resulting algorithm has been generalized to n dimensions and can be applied to the evaluation of data sets ranging from sensor arrays to visual images. The VERI PR algorithm provides a powerful, general-purpose alternative both to statistical analysis methods and popular non-parametric methods (e.g. neural nets and k-nearest neighbors). VERI evidently provides the first effective pattern recognition technique that is completely automated, i.e. problem-dependent training optimization and outlier thresholds are not provided by the user. The VERI method implicitly contains multivariate "goodness-of-matching" thresholds, derived from human clustering threshold judgments, which are functions of the arbitrarily complex multivariate shape of each class in the data. This provides fully automated performance on arbitrarily complex data distributions, without risk of "over-learning", that can exceed the best results achievable with even careful optimization of neural net or k-nearest-neighbor approaches. The method automatically recognizes atypical outliers and automatically detects data for which multiple class matches are acceptable. This is accomplished in a truly multivariate fashion, rather than with the simple univariate reject thresholds that are commonly adjusted in other approaches. These properties are especially useful for pattern recognition in uncontrolled/ unpredictable environments and for suppressing false alarms. VERI also provides an efficient, automated approach for directly searching for optimal feature sets for pattern recognition and data mining applications. The automated VERI approach allows an inexperienced user to correctly apply PR to problems in which unknown classes or incompletely distinguishable classes may be encountered, without the need to supply any additional information. Further information about application of the VERI method to sensor arrays is available at Sandia's web site [11].

SUMMARY

As illustrated by the above examples, the general trend in micro-sensor and micro-instrument research and development is to small size and lower power devices. Both of these trends increase the potential for utilization of these new technologies to applications in space. The miniaturization trend will impact both remote sensing and point sensing applications since the key issue is launch mass of the spacecraft.

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