

# Detection of chemical warfare agents using nanostructured metal oxide sensors

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## Abstract

The feasibility of thick-film chemical sensors based on various semiconductor metal oxides to reliably detect chemical warfare agents has been studied. Nanocrystalline semiconductor metal oxide (SMO) powders were used as initial materials for the sensors' fabrication. The thick films were prepared using a simple drop-coating technique accompanied with in situ annealing of the deposited films by a heater that is integrated into the sensor's platform. The sensors were exposed to mixtures of hexane, diesel oil vapor, methanol, 1,5-dichloropentane (DCP), or dimethyl methylphosphonate (DMMP) with air. DCP and DMMP were considered as simulants of mustard gas and nerve agents respectively. The performance of the sensors was investigated over a wide range of operating temperatures. They were additionally tested with mustard gas, sarin and soman at a certified live agent facility. The data obtained from the simulant and live agent testing are presented and discussed. In particular, attention is focused on the ability of an array of sensors to detect and identify agents in mixtures of interferents. © 2004 Elsevier B.V. All rights reserved.

*Keywords:* Chemical warfare; Metal oxide gas sensor; Thick film; Sensor array; Principal component analysis; Linear discriminant analysis

## 1. Introduction

The use of chemical weapons against civilians by terrorist groups or fanatic individuals is not just horror fiction anymore, but an absolute real threat. Two sarin gas attacks in Matsumoto and Tokyo, Japan in 1994–1995 confirmed this horrible reality. This demonstrates that there is a critical need for detectors and sensors that are able to warn about imminent CWA danger, to enable people to safely leave a contaminated zone or to protect themselves. Accordingly, highly selective sensitive sensors to CWA have to be the pri-

mary focus, i.e. they have to respond to low concentrations of agents—considerably lower than immediately dangerous to life or health concentrations (IDLH). They also have to discriminate CW agents from the other chemicals in the environment, and they have to identify CW agents on the other chemicals' background.

Modern analytical chemistry has instruments that can detect single molecules [1]. However, in general, these are delicate, stationary, and expensive equipment demanding complex and time-consuming sample preparation. At present, analyses of this kind are possible exclusively within the precincts of sophisticated research laboratories. "Fieldable" detectors of CWA and toxic industrial chemicals (TIC) have to be robust, portable, fast-acting, cheap, simple to operate, and, as discussed above, they have to be very sensitive and selective to the detected gases. There currently exist a wide variety of techniques to detect CW-agents [2,3]. Each, however, has drawbacks and limitations. Infrared spectrometers offer a limited level of standoff detection; they are expensive, complex and bulky. Raman spectroscopy that has success-

*Abbreviations:* SMO, semiconductor metal oxide; DCP, 1,5-dichloropentane; DMMP, dimethyl methylphosphonate; CW, chemical warfare; CWA, chemical warfare agent; IDLH, immediately dangerous for life and health concentration in air; IMS, ion mobility spectroscopy; SAW, surface acoustic wave; P-SAW, polymer coated SAW sensors; TIC, toxic industrial chemicals; PCA, principal component analysis; LDA, linear discriminant analysis

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fully been employed for CWA detection in the laboratory conditions is not applicable for identification of the agents in the real-world environment due to the lack of robustness. Colorimetric indicators, commonly referred to as detector paper, is the fastest, cheapest, lightest, and easiest type of detector to use. However, they detect chemical agents in the liquid form only; they also suffer the high cross-sensitivity to smoke, acetone, gasoline and other interferents. Colorimetric tubes are applicable to both vapors and gases and provide a semi-quantitative indication of the amount of agent presented in the environment. The drawbacks of this technique are the low speed of the responses to agents and the size of instrumentation (a stable air pump is necessary for the operation). Ion mobility spectrometers can detect CWA in real-time, are portable and sensitive. But, this technique requires a radioactive source, has poor selectivity in the presence of interferents, is costly, and the instruments are too large for some applications. Mass spectrometers combined with gas chromatographs (GC–MS) are the most sensitive and most reliable of today's instruments for CWA detection. However, they are bulky, expensive, require sample preparation and need technically trained personnel. Similar limitations are inherent in flame photometers. Polymer coated SAW devices (P-SAW) perform the real-time detection; they are selective and relatively inexpensive. But, previous efforts have reported concerns about their sensitivity and robustness, poisoning with hydrofluoric acid has been observed.

Arrays of chemically sensitive micro resistors produced from semiconductor metal oxides (SMO) are considered as one of the most promising basic technologies for CWA-detection [4]. SMO sensors offer a wide variety of advantages over other analytical instruments such as low cost, short response time, easy manufacturing, and small size. SMO chemoresistors also can be successfully used in combination with other types of CWA detectors (with IMS or P-SAW detectors for example), and as demonstrated lately, the combinatorial approach makes it possible to produce more sensitive and reliable CWA-detection equipment [5,6].

A common concern about the SMO sensor technology is the lack of selectivity. The current state-of-the-art has identified four general approaches to improve this parameter. They are: (a) use of catalysts and promoters, (b) optimization of sensors' operating temperature, (c) use of surface additives promoting the specific adsorption, and (d) use of molecular filters [7,8]. The implementation of SMO sensor arrays combined with appropriate pattern recognition tools is also considered as a promising approach to compensate for this lack of selectivity and to provide coverage for multiple types of agents [9]. The authors of this paper have recently demonstrated the feasibility of a SMO sensor array to discriminate and recognize various constituents of a combustion gas [10]. Principal component analysis along with several classification methods was successfully used to identify nitrogen oxides, ammonia, sulfur dioxide, and hydrogen sulfide. It has also been demonstrated the viability of SMO thick-film gas sensors prepared using cheap commercial sensor platforms

and a very simple drop-coating technique accompanied with in situ annealing of the deposited films by integrated heaters.

We continue the investigation of the SMO sensors prepared using the drop-coating method. In this paper we present comprehensive data for the porous SMO thick films considered as potential sensitive elements for the detection of CWA. Various thick-film compositions have been studied at different operating temperatures in gas flows containing CWA simulants, interferents, or chemical warfare agents. The tests using the CW agents, which were sarin, soman, or mustard gas, were carried out at a certified live agent facility at the Southern Research Institute (Birmingham, AL, USA). We present and discuss the performance of the SMO sensors in respect of sensitivity and selectivity towards CWA. A subset of the SMO sensors was selected for inclusion in the sensor array for chemical warfare detection. A primary objective of this study is to analyze the ability of the array consisting of five selected metal oxide sensors to identify the gases under tests by means of pattern recognition techniques.

## 2. Experimental

### 2.1. Fabrication of thick-film sensors

Porous metal oxide thick films approximately 50  $\mu\text{m}$  thick were fabricated using a drop-coating technique and an in situ annealing method. The films were deposited onto commercial UST sensor platforms (UST Umweltsensortechnik GmbH) which are 3 mm  $\times$  3 mm alumina substrates suspended by platinum leads in a TO-8 housing [10,11]. The substrates were equipped with integrated platinum heater and two platinum electrodes. To form the film, a drop of metal oxide paste was applied onto electrodes. Metal oxide pastes were prepared by mixing nanocrystalline oxide powder precursors with glass frit and an organic binder. The SMO powders (Table 1) were acquired from the NanoProducts Corporation (Longmont, CO, USA) [12] and the Nanophase Technologies Corporation (Romeoville, IL, USA) [13]. After the thick-film deposition the samples (sensors) were put into a test gas chamber and in situ annealed using the integrated heaters in airflow of 200  $\text{cm}^3 \text{min}^{-1}$ . A trapezoid temperature profile with heating and cooling ramps of 5  $^\circ\text{C} \text{min}^{-1}$  and a 10 min exposure at a peak temperature was used for annealing. Prior to the start of each test the sensors were pre-heated for 60 min at the test temperature to allow the SMO films to thermally stabilize.

### 2.2. Gas delivery system and electrical sensing testing

The experimental setup used for testing the thick-film sensors is shown in Fig. 1. It consists of the SMO test chamber in parallel with the SAW test chamber containing reference DMMP-selective SAW sensors, SRD gas delivery system, mass flow controller units, 10-channel heater unit and 10-channel resistance measurement unit for the SMO sensors,

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