

Quantitative analysis of ternary vapor mixtures using a microcantilever-based electronic nose

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The authors report the identification and quantification of the components of a ternary vapor mixture using a microcantilever-based electronic nose. An artificial neural network was used for pattern recognition. Dimethyl methyl phosphonate vapor in ppb concentrations and water and ethanol vapors in ppm concentrations were quantitatively identified either individually or in binary and ternary mixtures at varying concentrations. © 2007 American Institute of Physics.

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After several decades of extensive research that involved the compilation of massive databases, researchers have made significant advances in using mass spectrometry to identify the constituents of complex mixtures of analytes;^{1,2} even then the components of a complex mixture need to be first separated using gas chromatography. Such diagnoses involve large and expensive equipment and are time consuming. The demands of the 21st century (e.g., the war on terrorism, land mine detection, in-office medical diagnostics) dictate a need for miniaturized and inexpensive sensors providing fast detection. After four decades of research on ion mobility mass spectrometry (IMS), somewhat inexpensive and relatively small IMS detectors are being used for chemical and explosive detections.³ However, poor resolution in ion mobility spectra is likely to prevent IMS detectors from becoming significantly smaller. Therefore, a paradigm shift in sensor technology is needed to realize truly miniature and inexpensive sensors.

The biological nose (in particular, the canine nose) is one of the most sensitive detectors in existence today. Its high selectivity originates from the pattern recognition analysis of the output from an entire sensor array. Two decades ago, Persaud and Dodd proposed an “electronic nose” based on this concept.⁴ Just as in the case of olfactory receptors,⁵ the individual sensors in an electronic nose can be only broadly selective since the binding of an analyte needs to be reversible. An advantage of an electronic nose is that all the “trained” components of the mixture are identified and quantified simultaneously. Furthermore, since the sensor response is reversible, the detection can be repeated after a short recovery time.

The biological olfactory system is quite complex and has evolved over millions of years. Recently, exhaustive searches of the almost complete genome sequences of human and mouse have led to the identification of around 900 odorant receptors in humans and around 1500 in mice.⁶ The human olfactory system is able to distinguish thousands of different odors,⁶ and some odors are due to complex mixtures of pure compounds: A particular mixture of odor molecules creates a unique response pattern in the olfactory bulb, which the brain subsequently interprets as a particular odor. At least in the initial stages, the electronic nose does not need to be that complex. In particular, detection of explosive or chemical vapors requires the identification of mostly *one or a few pure compounds*. Furthermore, some of the “interferent” vapors could be removed with the use of a preconcentrator located in front of the electronic nose. Therefore, the ability to detect a few pure compounds in simple mixtures could lead the way to a practical electronic nose for chemical and explosive vapor detections in the near future.

Research on the development of electronic noses based on several sensor platforms has been conducted over the past two decades; see Refs. 7 and 8 and references therein. The holy grail of chemical sensors is the ability to *selectively identify target analytes*. Even though much of the work so far has been devoted to *sensitive detection of individual analytes*, any practical applications cannot be realized until *selective detection* is achieved. Since a single reversible sensor is inherently nonselective, selectivity needs to be achieved via a sensor array. Even with the increased activity in sensor array research recently, successful quantitative identification of component vapors has not been reported for mixtures with more than two components; see, for example, Refs. 9–15 and references therein. The ability to accurately identify different

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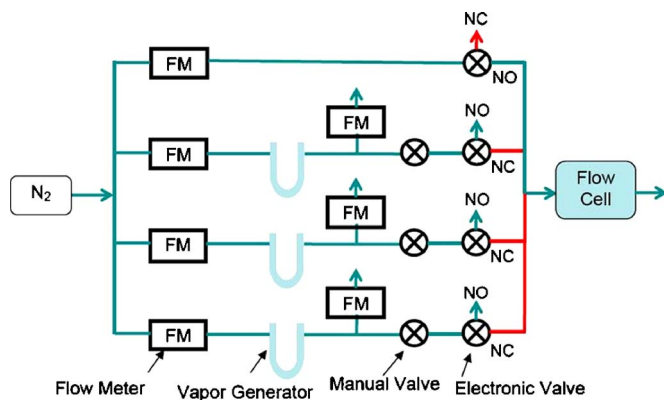


FIG. 1. (Color online) Schematic diagram of the experimental apparatus. The three vapor generators are immersed in temperature-controlled baths. For the three-way electronic valves, NO is normally open and NC is normally closed. This arrangement allows the vapor generators to be purged 24 h/day, so that a steady stream of vapor with fixed concentration is available at any time.

odors *presented individually* to the sensor arrays has been demonstrated,^{16–18} and binary mixtures have been successfully analyzed^{11–15} using arrays of different sensors. Partial success on the analysis of ternary mixtures has been described in Ref. 11, and quantitative identification of a single component in a ternary mixture has recently been reported.¹⁴ In all these studies,^{9–18} the concentrations of the component vapors were in the ppm range or higher. In this letter, we report the detection of ppb concentrations of the nerve gas simulant dimethyl methyl phosphonate (DMMP) and ppm concentrations of ethanol and water vapors in ternary mixtures. We recently reported the sensitive detection of DMMP using a miniature sensor unit.¹⁹

The apparatus used in the present study is shown in Fig. 1. A set of computer-controlled flow meters and three-way valves together with manually controlled metering valves were used to direct either the carrier gas nitrogen or any selected combination of the three vapors (in 30 s pulses) to the flow cell containing the microcantilever sensor array. The flow cell accommodating the four Canti-4™ piezoresistive microcantilever chips was $6 \times 5 \times 1.1$ cm³ and had an estimated internal flow volume of 0.5 cm³. Each Canti-4™ chip had two coated levers and two uncoated (reference) levers. We used a combination of self-assembled monolayer coatings and other coatings in these experiments. During the experiments, a flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP) through the microcantilever flow cell was maintained, and thus microcantilever bending due to change in flow was avoided.

We used diffusion vials purchased from VICI Metronics, Inc. to generate the vapors of DMMP, water, and ethanol. These vials have fixed diffusion rates that depend only on the particular diffusion vial and its temperature. Each diffusion vial was located in a “U” shaped holder that was immersed in a heated/refrigerated circulator bath and was maintained at a particular temperature. The estimated concentrations of DMMP, water, and ethanol vapors were 100 ppb, 60 ppm, and 60 ppm, respectively. Flushing of the vapor generators for several days was required to remove water vapor from the system and to achieve a stabilized rate of delivery of the vapors from the generators. Nitrogen gas was used as the carrier and nitrogen flows through all the vapor generators

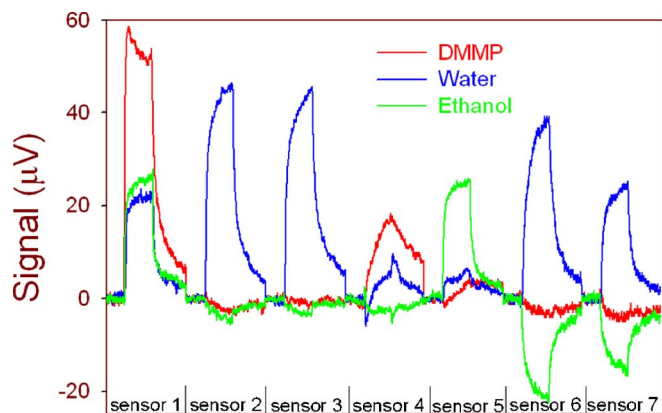


FIG. 2. (Color online) Typical response signatures derived from responses of the set of microcantilever sensors to individual vapor streams of DMMP, water, and ethanol.

were maintained 24 h a day during the 2 week data acquisition period.

Each data run began with the continuous N₂ flow through the flow cell, with a flat cantilever base line response. A 30 s pulse of a vapor (or a vapor mixture) was introduced and the cantilever response was recorded both during the pulse and afterward until the response returned (partially) to the base line level. An example of a set of “signatures” resulting from the response of the seven sensors in the array due to DMMP, water, and ethanol vapors is shown in Fig. 2. Even though most of the sensors responded to all three vapors, the differences in the signal profiles allowed an artificial neural network (ANN) to differentiate among the three vapors. This is similar to the odor discrimination in the biological olfactory system.²⁰ The biologically inspired ANN is a self-adapting system that can modify its response to external forces using previous experience, offering a more flexible and faster method of analysis.²¹ The pattern recognition algorithm we used was a feed-forward back-propagation error-correction neural network written in MATLAB.

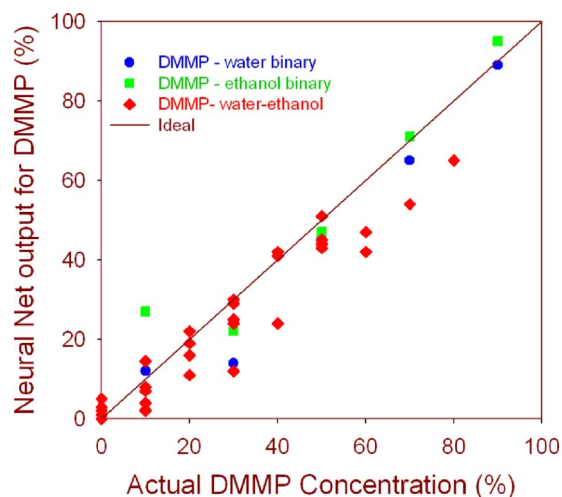


FIG. 3. (Color online) Comparison of the estimated concentrations of DMMP vapor with the actual concentrations that were presented to the sensor array for a single test data set. The data consisted of those for binary mixtures (15 mixtures) and ternary mixtures (30 mixtures), where the mixture compositions were different from the compositions of mixtures used in the training set. Similar results were obtained for water and ethanol vapors.

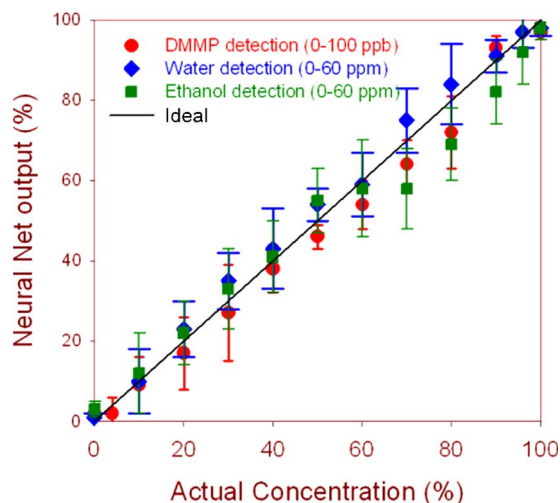


FIG. 4. (Color online) Comparison of the estimated concentration of DMMP, water, and ethanol vapors, with the actual concentrations that were presented to the sensor array. The data shown are from all five test data sets taken over the 2 week period. For concentrations over 70%, each point was the average of four to eight data points; for concentrations in the range of 30%–60%, each point was averaged over 10–20 data points; for concentrations in the 0%–20%, each point was averaged over 24–30 data points. There were nine mixtures for unitary, 72 mixtures for binary, and 92 mixtures for ternary mixtures. So, the bulk of the data taken were for ternary mixtures where all three component vapors had nonzero concentrations.

The neural net was trained using a data set with 25 mixtures corresponding to different combinations (unitary, binary, and ternary) of the three vapors, and then was tested with five other data sets obtained within the following 2 week period. Three of the five test data sets were for the same mixture combinations as the data set used for training (25 mixtures each) and the other two were for different combinations (45 mixtures each). The training of the ANN using the 25 mixture data set took about 1 h with between 1000 and 10 000 epochs on a personal computer. The trained ANN took much less than 1 s to identify and quantify a ternary mixture signature. One of the data sets from the second category (45 mixtures) when presented to the trained ANN yielded the results for DMMP detection shown in Fig. 3.

Figure 4 shows a summary of the results from all five test data sets. This included data for unitary, binary, and ternary mixtures. The bulk of the data taken was for ternary mixtures where all three component vapor had nonzero concentrations (see the caption of Fig. 4). More data were taken at low concentrations as stated in the figure caption, since it is important to evaluate the ability of the sensor array/neural net algorithm to detect low concentrations. For example,

there were 24 data points taken for 0% of DMMP and the neural net outcome was ($2\% \pm 2\%$), with the predicted value below 8% for all the measurements. Thus, there were no “false alarms” for DMMP detection if the threshold of detection was set at 10% DMMP concentration, i.e., about 10 ppb.

In conclusion, this study shows that vapor mixtures can be analyzed by an electronic nose to identify and quantify the presence of up to three components even with one of the components (DMMP) in the ppb concentration range. Further studies are underway to improve the sensor array (by adding more sensors/coatings), and also to incorporate a pre-concentrator so that more complex vapor mixtures could be analyzed.

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