Gas sensor array for VOC's monitoring in soils contamination

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ABSTRACT
Aiming to develop low cost devices for in situ volatile organic compounds (VOC) in soils contamination, a gas sensor array has been used to analyze (VOC) in laboratory experiments. Different thin film semiconductor metal oxide gas sensors were arranged in a gas sensor array that was exposed to hundreds of VOC mixtures gas samples fabricated in a full automatized gas line system. Several architectures of backpropagation neural networks were applied to sensor array responses after some preprocessing algorithm and signal normalization for quantification purposes. Partially connected hidden layer networks produced lower network errors than fully connected networks. Typical relative prediction errors about 20% to 40% were obtained. These results has permitted us to go further in the research and in situ soil measurements are being carried out currently using this gas sensor array system.

Keywords: gas sensor, volatile compounds, soils contamination, neural networks

RESUMEN
Este trabajo está dedicado a describir la labor que desarrollamos en nuestros laboratorios, con los dispositivos del bajo costo para detectar los compuestos orgánicos volátiles (VOC) en la contaminación de los suelos. Un sensor del gas se ha utilizado para analizar (VOC) en experimentos del laboratorio. Diversos sensores del gas del óxido de metal del semiconductor de la película fina fueron preparados para trabajar con el sensor del gas que tomó centenares de muestras del gas de las mezclas del VOC fabricadas en un sistema de línea de gas completamente automatizado. Varias arquitecturas de las redes neuronales fueron aplicadas a las respuestas del sensor después de una cierta normalización del algoritmo y de señal del proceso previo para los propósitos de la cuantificación. Las redes ocultas, parcialmente conectadas en una capa, produjeron errores muy bajos a la red de capa superior a la que estaban completamente conectadas. Los errores relativos típicos de la predicción cerca de el 20% a el 40% fueron obtenidos. Estos resultados han permitido que avancemos en la investigación y las medidas in situ del suelo se están realizando actualmente usando este sistema ya probado en laboratorio, del sensor del gas.

Palabras clave: sensor de gas, compuestos volátiles, contaminación de suelos, redes neuronales

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INTRODUCTION

Volatile organic compounds (VOC), are main contributors to soil and subsoil contamination. They can induce health problems and environmental risks depending on their mobility, stability and toxicity. VOC in soils contamination is generally characterized by the presence of complex mixtures of these compounds. In order to estimate specific risks it is necessary to determine the flow characteristics (Eikmann et al., 1995) and transfer models based on experimental data can be used. Hydrocarbons suffer a slow migration toward deeper soil layers until arriving to the phreatic layer where volatile compounds are formed. These compounds ascend to the surface by means of the pressure gradient and there they are introduced in the atmosphere.

Contaminated soil analysis is complicated because of the soil heterogeneity and the difficulties for obtaining representative samples. Most current analytical methods for soils diagnosis are based on chromatography variants: TLC, GC, HPLC and especially high resolution gas chromatography/mass spectrometry (HRGC/MS) (Getino, 1998). These techniques allow compounds identification by means of retention time and by spectral differences. Some mobile methods like GC/MS are also used, but they are high cost and time consumable techniques.

In this work, a new device for VOC in soils analysis is presented. The system is based on a metal oxide semiconductor gas sensor array (Getino, 1998). Different non-selective metal oxide gas sensors arranged in a sensor array and neural networks (NN) algorithms can be used to detect organic compounds in soils. Metal oxide gas sensors change the electrical conductivity when VOC are adsorbed on metal oxide surface, so it is possible to detect the compounds by measuring the electrical resistance of the sensors. This technology presents the advantages of its low cost, small size and microelectronic compatibility, but single sensors are usually low performance devices because of their poor sensibility. However, the use of sensor arrays has been adopted as a feasible method to improve gas sensors performance. The sensors in the sensor array can be all of them working by the same operation principle or not. Moreover, sensor signals can be steady state, differential or modulated signals. But most sensor arrays follow the same schema: once exposed to gas samples, sensor signals are processed to give response vectors and some pattern recognition algorithms are applied to these vectors in order to obtain an estimation of the compound presence and/or concentration.

The gas sensor array integrated in the soil measurement device used is formed by 16 different sputtered thin films of semiconductor metal oxides. Results of two different experiments are presented here, first a laboratory characterization and secondly, in situ analysis

EXPERIMENTAL

2.1 FABRICATION DETAILS

The sensor array was fabricated by growing 16 different metal oxides on a circular alumina (Laser Tech. 99.6% Al_2O_3) substrate of 25.4 mm diameter and 0.38 mm thickness. Each sensing element is 1 mm wide and 8 mm long.

Oxide films were grown by radiofrequency (RF) magnetron sputtering using the Alcatel SMC 450 system. Temperature inside the chamber was set to 250 ºC at a total pressure of 0.5 Pa and a RF power of 100 W was selected. Two metal oxide cathodes were used as target materials (99.9% SnO_2 and 99.998% TiO_2 Cerac disks) under a 10% oxygen – 90% argon mixture. Some tin oxide sensors were doped with different amounts of sputtered Pt, changing the deposition time during the sputtering process. Platinum clusters of 200 μm of diameter were introduced over a tin oxide layer, and a second tin oxide layer was grown over the Pt layer, in order to obtain a sandwich structure. Electrical contacts were also deposited by sputtering from a 99.999% Pt cathode in argon atmosphere at 250º and 0.5 Pa. Anode-cathode distance were varied from 50 to 55 mm. (Endres et al., 1995).

Once fabricated, the sensor array was annealed in synthetic air at 520 ºC during 4 hours to obtain polycrystalline thin films formed by nanocrystallites and to stabilize the electrical properties of the sensors. Gas sensor array elements are shown in Table I.

GAS SAMPLING

VOC can be classified by families in a first approach: aliphatic hydrocarbons, monoaromatic hydrocarbons, chlorinated aliphatic hydrocarbons, oxygenated aliphatic hydrocarbons, hidroxylated hydrocarbons, chlorinated monoaromatic hydrocarbons, volatile acids and nitrosamines.

For the experimental testing in laboratory a suitable selection of VOC molecules is needed. According to the importance of their use or disposal, the frequency in contamination cases, the knowledge on their physico-chemical properties and their availability, the following compounds were chosen: octane as aliphatic, chloroform as chlorinated, benzene and toluene as aromatic, propanal and methyl ethyl ketone (MEK) as oxygenated hydrocarbons. All these compounds were supplied in binary mixtures gas bottles (1000 ppm of each compound in nitrogen).

Table I. Gas sensor array details.

#	Layer 1	Layer 2	Layer 3
1	SnO_2 (100 nm)		
2	SnO_2 (150 nm)		
3	SnO_2 (200 nm)		
4	SnO_2 (250 nm)		
5	SnO_2 (100 nm)	Pt (2 s)	SnO_2 (100 nm)
6	SnO_2 (100 nm)	Pt (4 s)	SnO_2 (100 nm)
7	SnO_2 (100 nm)	Pt (6 s)	SnO_2 (100 nm)
8	SnO_2 (100 nm)	Pt (8 s)	SnO_2 (100 nm)
9	SnO_2 (150 nm)	Pt (2 s)	SnO_2 (150 nm)
10	SnO_2 (150 nm)	Pt (4 s)	SnO_2 (150 nm)
11	SnO_2 (150 nm)	Pt (6 s)	SnO_2 (150 nm)
12	SnO_2 (150 nm)	Pt (8 s)	SnO_2 (150 nm)
13	SnO_2 (100 nm)	TiO_2 (120 nm)	
14	SnO_2 (150 nm)	TiO_2 (180 nm)	
15	SnO_2 (200 nm)	TiO_2 (240 nm)	
16	SnO_2 (250 nm)	TiO_2 (300 nm)	

Gas sampling was carried out in a full-automated gas line system (see Figure1). Gas mixing was dinamically performed using mass flow controllers, air-operated valves and electrovalves all controlled by computer. Gas mixture samples are fabricated adding the volumetric contributions of the individual gases to the total gas flow. Using the volumetric concentrations of the binary mixtures gas bottles $C_{b,i}$, the concentration $C_{m,i}$ of each individual component i in the total gas mixture flow, V_{tot} , is calculated by (Endres et al., 1995):

$$C_{m,i} = C_{b,i} \frac{V_{b,i}}{V_{tot}} \qquad (1)$$

where $V_{b,i}$ is the flow of the component i.

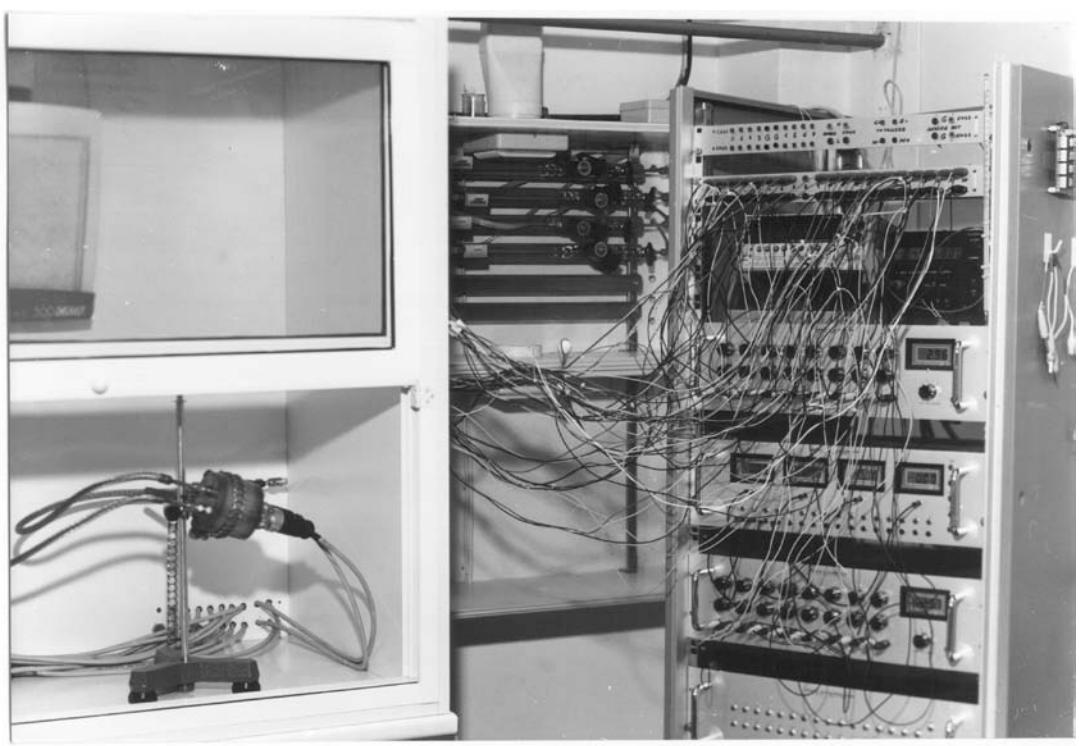

Figure 1. Gas line system and measurement equipment.

Carrier gas is fabricated from pure oxygen and nitrogen gas bottles in order to obtain synthetic air (79:21) in the final mixture. To prepare samples with different test gas concentrations the individual gas flows must satisfy equation (1). This can be achieved using mass flow controllers that can keep constant the desired gas flow.

EXPERIMENTAL SET-UP

A cylindrical measurement device for VOC in soils contamination has been designed. It incorporates the gas sensor array in the bottom of a small stainless steel test chamber (Capital Eq., 2004). Gas inlet and outlet are located in the top of the system. Below the gas sensor array and within a thermal and electrical isolating ceramic body, both an electrical heater and one thermocouple are placed. The heater can be powered up to 12 Vdc to obtain 500 ºC whereas thermocouple is used for temperature control. Gas sensor electrodes are connected mechanically with electrical wires grouped in one cable ending in a standard interface for computer connection.

The measurement device was placed in the test gas line system and fabricated gas samples were dynamically introduced in the test chamber. The electrical resistances of the sensors were measured by means of a Keithley 2700 digital multimeter including a 7706 multiplexer card connected to a personal computer through a GPIB CEC card. A Testpoint (Moore et al., 1993) based runtime application has been designed for automatic control of measuring process and data acquisition. The user interface of this program is shown in Fig.2.

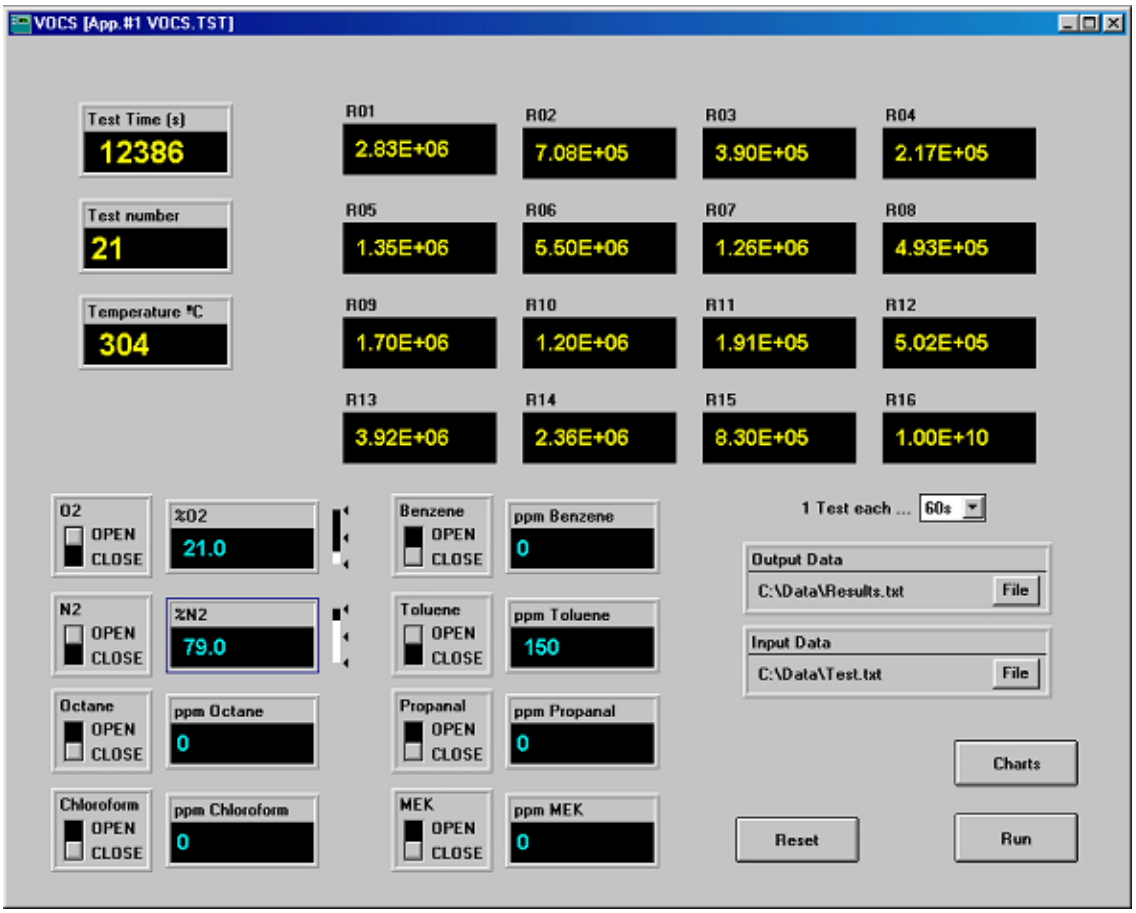

Figure 2. Measurement program user interface.

RESULTS AND DISCUSSION

ELECTRICAL CHARACTERIZATION

Gas sensor array was electrically characterized at 300 ºC with a total flowrate of 200 ml/min exposed to mixtures of single VOC in synthetic air (benzene in air, toluene in air, chloroform in air, octane in air, propanal in air and MEK in air). VOC concentration was varied from 50 to 250 ppm at 50 ppm steps. Experiments were repeated ten times per VOC tested. Sensor resistances were continuously measured at one-minute intervals during 10 minutes of synthetic air exposure and during 10 minutes of VOC exposure.

All tested VOC showed a reducing behavior during the

interaction with the metal oxide surface, producing a resistance decrease in all sensors. Tin and Titanium oxides are both n-type semiconductors and when these are exposed to reducing gases in oxygen containing atmospheres, reducing gases react with the oxygen species adsorbed on the oxide surface. The products of this reaction are desorbed from surface, injecting electrons to the conduction band and increasing then the sensor electrical conductance.

Assuming the value of sensor conductance in air at constant temperature (G_a) as baseline and because the sensor response is positive defined, we can define the dimensionless response of n-type sensors to VOC by the relative conductance G/G_a, i.e., the value of the sensor conductance in VOC divided by the value of the sensor conductance in air.

The average responses obtained to 150 ppm of each VOC are shown in Fig. 3. In the figure it can be shown how responses to oxygenated compounds (MEK and propanal) are much higher than responses to the resting compounds. Among these, the gas sensor array responded better to octane than to chloroform or aromatic compounds (benzene and toluene). Similar patterns were obtained for other VOC concentrations.

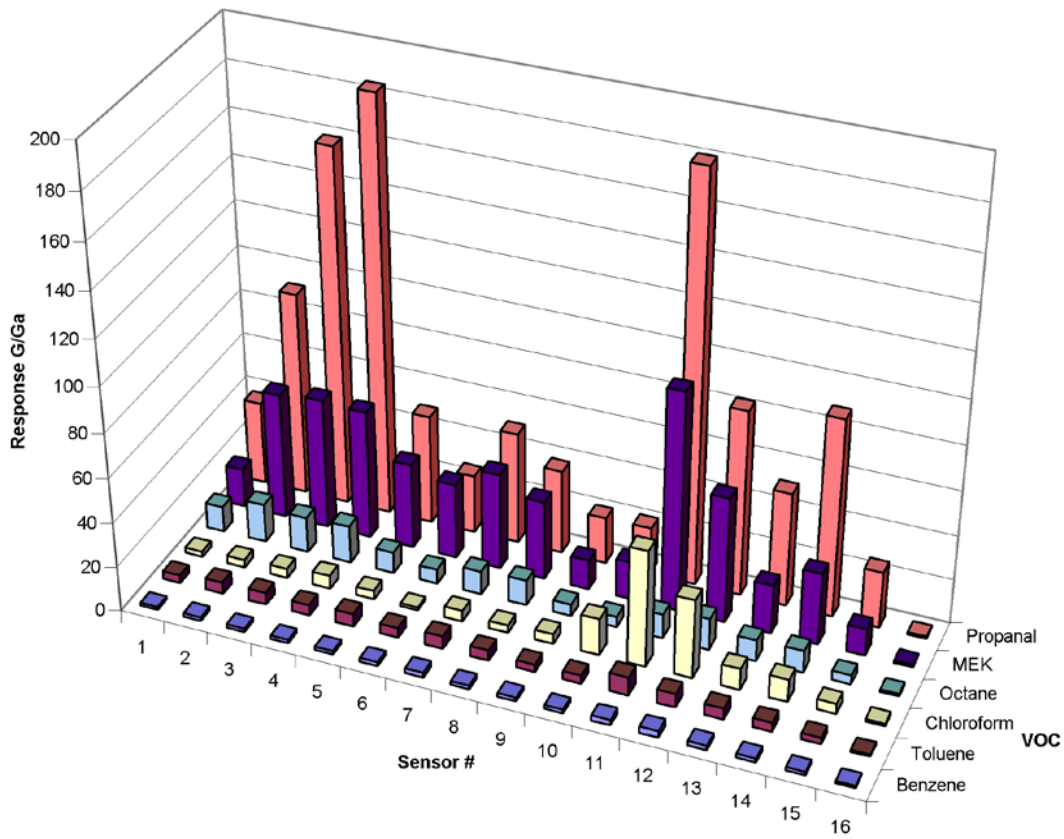

Figure 3. Response of gas sensor array to 150 ppm of VOC in synthetic air measured at 300 ºC.

Undoped tin oxide films (sensors 1 to 4) were more sensible to oxygenated VOC than Pt-doped sensors (sensors 8 to 12) or the two layer SnO_2-TiO_2 films (sensors 13 to 16), with the exception of sensors 11 and 12. Sensor 16 manifested some problems with the electrical contacts and some times its response could not be obtained from the resistance measurements. The sensor array behavior when exposed to chloroform is very similar than when exposed to oxygenated compounds, especially for sensors 11 and 12. For octane and aromatic compounds, most sensors responses are very close, as it was expected for this type of gas sensors.

Once characterized for single test VOC detection, the sensor array was exposed to different mixtures of several VOC in synthetic air. It is possible to fabricate 57 different mixtures with six different compounds at a

fixed concentration. This is the result of two concentrations (compound presence and absence) and six compounds combinatory (2^6=64). The single binary mixtures (6) carried out previously and the absence of all VOC in the mixture (just air) have to be removed from this quantity, giving the above-mentioned 57 possible mixtures. Rising the number of concentrations in one unit, the possible number of experiments goes to 672. Considering that it should be very important to repeat the experiments we found a high cost and time consuming situation. So, instead of characterizing all possible mixtures in a wide concentration range, just a hundred of different VOC mixtures were selected and each experiment was repeated once. Concentrations for each compound were varied between 50 and 150 ppm when such compound was present in the mixture. Experiments were carried out at 300 ºC, monitoring the gas sensor resistance in air and in VOC cycles of 10 minutes. Again, responses to mixtures containing oxygenated compounds were much higher than responses to non-containing oxygenated VOC mixtures, and the gas sensor response pattern was very similar to the obtained during single VOC in air characterization.

LABORATORY ANALYSIS

All experiments were analyzed by means of neural networks. Backpropagation was chosen as learning rule for all NN, using both momentum and an adaptative learning rule to speed this process. Different network architectures were tested: both fully and partially neuron connection (Moore et al., 1993), between hidden layer and output layer neurons were used in two-layer network architectures using logarithm sigmoid function as transfer function. NN were trained removing each one of the samples before normalizing. After training, the removed sample was used to validate the network (Holmberg et al., 1995).

The normalized fractional conductance change was chosen as preprocessing algorithm for network input:

$$\frac{(G-G_a)/G_a}{\sqrt{\sum (G-G_a)^2/G_a^2}} \qquad (2)$$

where G is the conductance of the sensors when exposed to gas sample and G_a is the conductance of the sensors in air at the same fixed temperature. This function has been successfully used in backpropagation NN for classifying purposes (Gardner et al., 1992).

Network inputs were normalized in a way that all values were comprised in the range (-1, +1) according to:

$$x_{ij}^{norm} = \frac{2\left(x_{ij} - min(x_{ij})\right)}{max(x_{ij}) - min(x_{ij})} - 1 \qquad (3)$$

where x_{ij} is the network input for sensor i and gas sample j.

The network output function is defined as a normalized concentration, so all output values are comprised in the range (0,+1):

$$\frac{c}{c_{max}} \qquad (4)$$

where c_{max} is the maximum concentration for each compound present in the gas sample.

NN were simulated using Matlab's Neural Network Toolbox (Demut, 1994). First network architecture tested was 15:*h*:6, eliminating responses from malfunctioning sensor 16, so network input was reduced to 15 sensors and network output aims to determine the 6 VOC tested. The number of neurons in the hidden layer was varied from 0 to 36 training the networks up to a maximum number of 10000 iterations. In Fig. 4 the influence of neurons number in the hidden layer after 2000 iterations is shown. The lowest sum squared network error was found for 12 neurons in the hidden layer. For this 15:12:6 network we can see in the figure how increasing the iterations no further error decrease can be found.

Partially connected 15:6x*h*:6 networks in which the hidden layer was split in six different groups of *h* neurons were also tested. Output for each compound is calculated exclusively using its corresponding group in the hidden layer and there is no connection with resting groups.

Fig. 5 shows errors for 15:6x*h*:6 networks after 2000 iterations varying neurons number in each group in the split-hidden layer. Errors decrease with neurons number up to a value of h = 3. Similar network errors are found using more than three neurons in hidden layer groups.
Figures 6, 7 and 8 represent predicted VOC concentrations by 15:6x5:6 network versus real concentrations of all these compounds. At high concentrations predicted values are far from the ideal straight line of slope unity. Using this network the following mean values of relative prediction errors for each compound in the (50-250) ppm concentration range were obtained: 26% for benzene, 36% for toluene, 22% for chloroform, 39% for octane, 27% for MEK and18% for propanal.

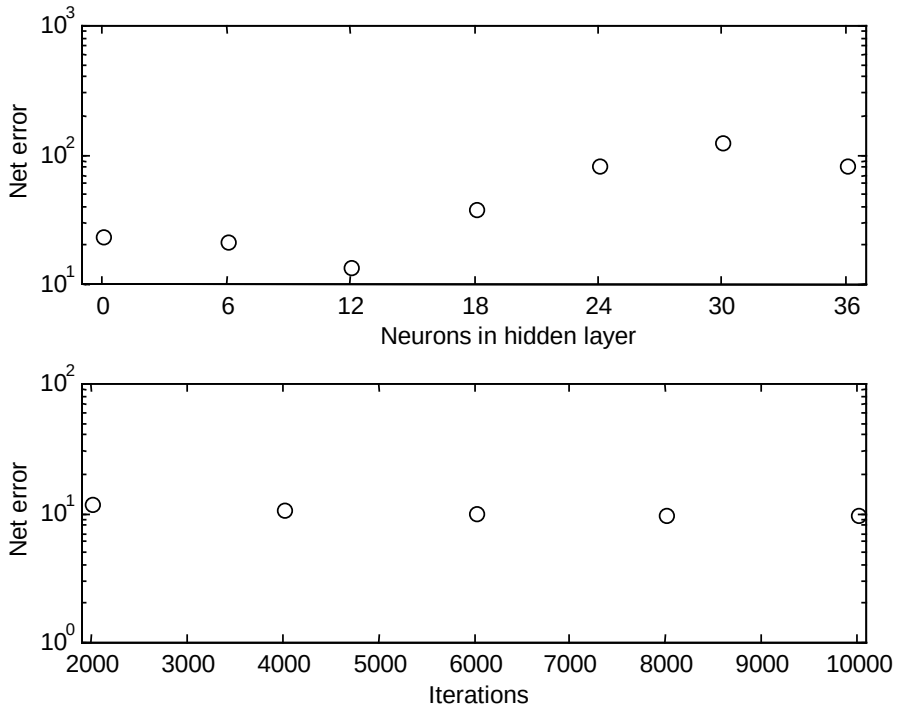

Figure 4. Influence of neurons number in the hidden layer on 15:*h*:6 network error and influence of iterations number on 15:12:6 network error.

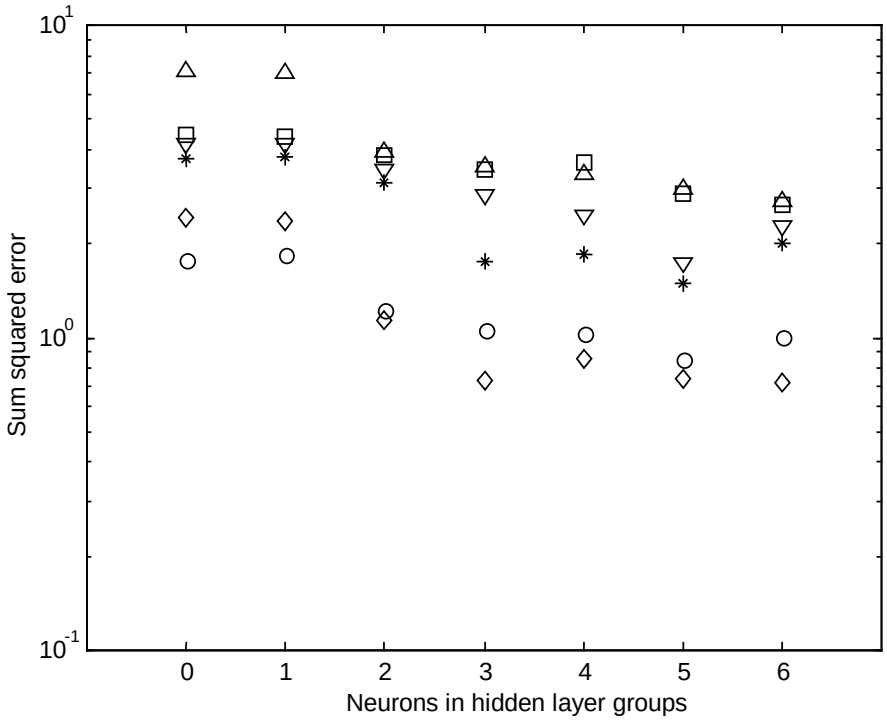

Figure 5. Influence of neurons number in hidden layer groups on 15:6x*h*:6 network error for benzene (o), toluene (△), chloroform (*), octane (□), MEK(▽) and propanal (◊) after 2000 iterations.

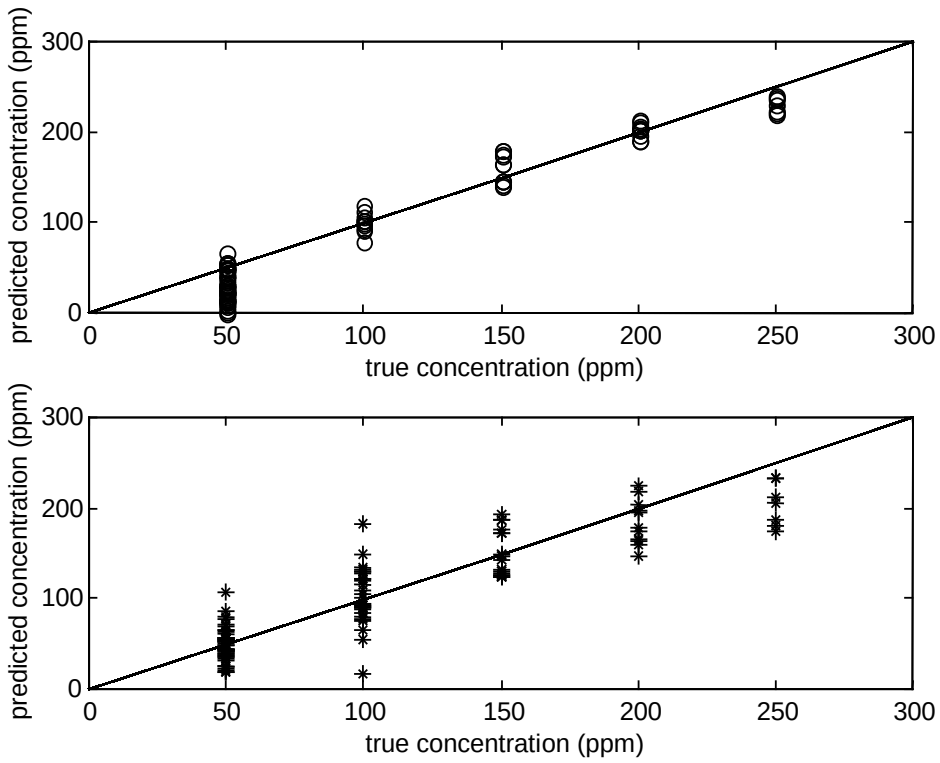

Figure 6. Predicted benzene (o) and chloroform (*) concentrations by 15:6x5:6 network versus true concentrations.

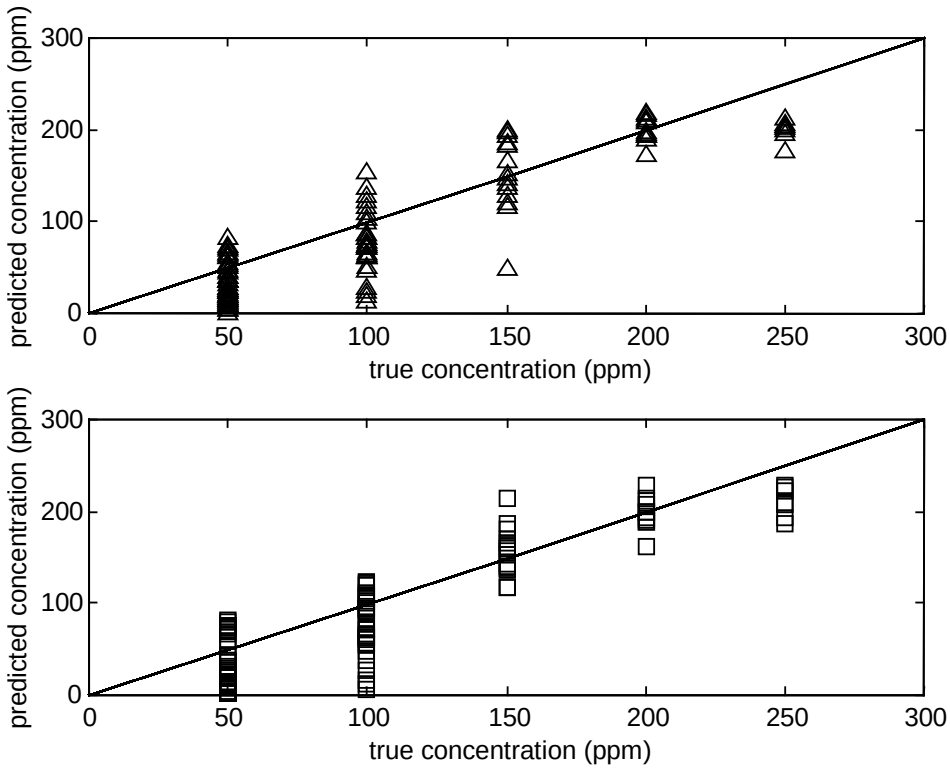

Figure 7. toluene (△) and octane (□) concentrations by 15:6x5:6 network versus true concentrations.

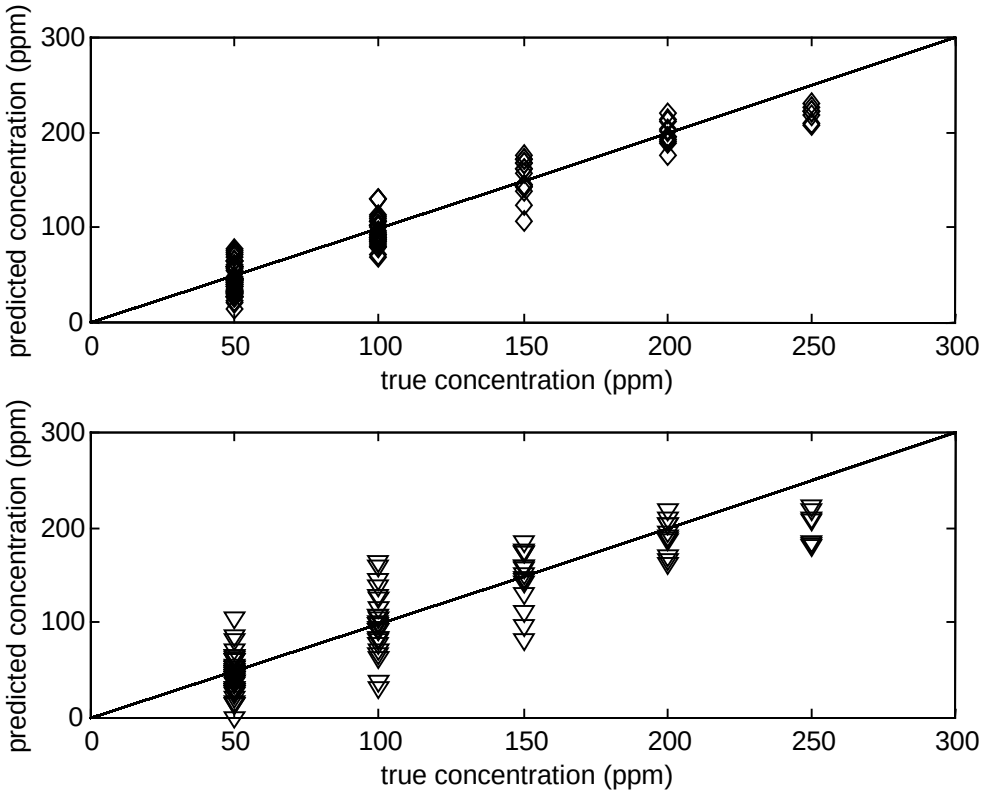

Figure 8. Predicted propanal (◊) and MEK(▽) concentrations by 15:6x5:6 network versus true concentrations.

CONCLUSIONS

Gas semiconductor sensor arrays can be used to develop new measuring techniques for VOC in soils contamination monitoring. Sputtered thin films metal oxide gas sensors respond highly to oxygenated compounds (MEK and propanal) and aliphatic compounds like octane. Lower responses were found to chloroform and aromatic compounds (benzene and toluene) but generally speaking, responses from the fabricated sensor array were important and suitable for analysis tasks.

Artificial neural networks, in special two-layer networks, result valid methods to process the sensor array output. The preprocessing algorithm of normalized fractional conductance change is required to obtain good results. Conductance change techniques were first proposed to compensate the temperature dependence of chemical sensors (Heiland, et al., 1982), while normalization over the sensor array results very useful for discrimination processes (Gardner et al., 1991). Main problem of sensor arrays in which all the sensors operate by the same sensing principle is the sensors redundancy and the consequent diminution of the discrimination capability. Different metal oxides (tin oxide and titanium oxide) were used aiming to reduce collinearity problems in the response matrix.

Although predicted concentration errors are high enough to consider the system as an analytical instrument, we have proved the validity of this device to detect the presence of VOC concentrations at ppm levels in air. This is the basis for future measuring systems capable to give a precise on-site estimation of soil contamination in real time.

Currently, in situ measurements are being carried out using the fabricated sensor array. For future works, the sensor array can be miniaturized using sputtered thin films over thermically isolated silicon micromachined structures in order to obtain an integrated array device with low power requirements and small size.

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