MICROSYSTEMS FOR IN SITU MEASUREMENT OF VOCS IN GROUNDWATERS AND SOILS

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1. Abstract

There is a growing interest in the substitution of conventional analytical procedures by suitable selective chemical sensors. Devices allowing continuous monitoring of concentrations in field would be of particular significance in environmental analysis. In this work, a tin oxide multisensor with 15 sensor elements has been prepared using the r.f. reactive sputtering technique. Some components of this multisensor have been doped with Pt, Pd and Al by sputtering. Each sensor has been characterized by electrical measurements for various volatile organic compounds (VOCs) in a concentration range from 50 to 500 ppm in synthetic air at 300 °C.

The best responses have been obtained by Pt and Pd doped sensors mainly for the oxygenated compounds, but for all VOCs tested a good detection is found. For the concentration range used it has been possible to detect the threshold limit values (TLV) for airborne contaminants of toluene, octane and methyl-ethyl-ketone. The influence of the oxygen species (O^- and O_2^-), ionosorbed on the sensing surface, on the VOCs detection is also discussed.

On the other hand, the single component classification and the multicomponent analysis of these VOCs have been carried out. The principal component analysis (PCA) classification permitted to distinguish three families of VOCs. The best results from the multicomponent analysis were obtained for the ILS and PCR methods

2. Introduction

At the present time, the diagnosis of waters, when are contaminated with volatil organic compounds, is based on analytical methods. Up to now, the more used technique is the chromatography in its various forms: TLC (Thin Layer Chromatography), GC (Gas Chromatography) or HPLC (High Performance Liquid Chromatography) and specially HRGC/MS (High Resolution Gas Chromatography/Mass Spectrometry) or HPLC/DAD (High Performance Liquid Chromatography/Diode Array Detector). These techniques allow to identify the compounds not only by means of retention time but also by spectral diferences. In situ measuring techniques are also used for the detection of polluted areas, such as GC/MS for analysis of organic compounds, IR-instruments for PAH, PCP, aliphatic and aromatic hydrocarbons. Immuno-assays and laser sonde are also used [1].

Nowadays, the more important problem related to these analytical methods is that they are expensive and need of a lot of time to carry out the analysis.

Besides, they are not fully adecuated for portable measuring systems. As consequence, few samples are analysed and there is a lack of information for a better evaluation. For these reasons, it is very important to develop faster and cheaper mesuring systems for identification and quantification of hazardous pollutants in contaminated sites. Therefore, these systems must allow to perform continuous and in situ mesurements, for offering real-time data and thus a more effective detection of contaminants.

An alternative to conventional detectors consists of the use of resistive gas sensors, based on metal oxide semiconductors, whose operating principle is based upon the initial reversible reaction of atmospheric oxygen with lattice vacancies in the metal oxide and the concurrent reduction in electron concentration [2]. This reaction produces various oxygen species, at different temperatures and oxygen pressures, which can react with certain gaseous species, as VOCs, producing an electrical conductivity modulation on the metal oxide semiconductor. This type of gas sensor tends to be very sensitive to environmental conditions and often they have very poor ageing characteristics, low selectivity and high cross-sensitivity with other gases or humidity. At present, at the laboratory scale, the use of gas sensor arrays including different metal oxide semiconductors with different additives on a substrate, are getting to overcome the problem of poor specificity using pattern recognition methods (PARC) and neural networks [3].

Few devices can be met on the market nowadays, but none of these commercially available sensors are made with microtechnologies. Planar technologies such as are used in microelectronics can be modified for the fabrication of microsensors. In this way the concept of microtechnological mass production of sensors or sensor arrays can be extended to include inexpensive micro-analysers operating "in situ" with integrated data adquisition and evaluation.

In this work, a new field measuring system is presented, formed by the multisensor device on alumina substrate, the electrical heater, the test chamber and the electrical connector (Fig.1). An electrical heater is used to achieve the operating temperature of the sensor. It can be powered up to 12 V dc, for temperatures up to 500 ºC.
The heater is placed within an isolating ceramic material. The test chamber is made in stainless steel and it has an effective volume of 20 cc. At the top of the chamber the gas inlet and outlet are located. At the bottom of the chamber the multisensor device is located.
The electrical connectors are made in platinum ending in a DB25 connector. The data adquisition system consists of a digital multimeter (DMM) with a scanner card up to 16 channels, a personal computer with an IEEE card and software for data storing and treatment.

The VOCs extraction from soils or groundwaters and their transport to the field measuring system can be performed by permeation cells based on membranes. It is known that elastomeric membranes interact preferencially with organic compounds, therefore they have high selectivities for organics over water. Commercial membranes as: PDMS (Polydimethylsiloxane), PEBA (Polyetherblock-poliamides), SPC (Silicone-polycarbonate copolymer) and PUR (Polyurethane) used in multicomponent pervaporation allow a good separation of VOCs. It has been shown that the solubility of penetrants in the elastomeric membranes determines the membrane permeability and selectivity to a large extent, therefore the hydrophobicity of organics determines the sequence of the permeability and the separation factor [4].

The superposition of membranes onto the sensor, using a appropriate assembly, joined to the heating facilities of the sensor, up to 500Cº, allows to eliminate the distortion in measurement due to the water vapour presence, however in case of direct application on waters, a deeper study about membranes must be carried out.

The results obtained from this work will be used as reference measurements for future "in situ" experiments on gases extracted from groundwaters through permeation cells with specific membranes and transferred to the field measuring system. The vectorial or matricial response is considered as a characteristic "fingerprint" of the contaminants.

3. Experimental

The multisensor is designed with 15 sensor elements distributed on circular sectors on an alumina sheet of one inch diameter as substrate. The base material was tin oxide and different dopants were used, such as: Al, Pt, Pd. The tin oxide thin films (200 nm of total thickness) were grown by reactive sputtering at 250 ºC using a SnO_2 target under 10/90 oxygen/argon mixture at a total pressure of 0.5 Pa. Each doped element was prepared with different amounts of dopant, introduced as an intermediate discontinuous layer between two layers of tin oxide each one with the same thickness (sandwich structure), changing the deposition time during the sputtering process. Table 1 shows the multisensor distribution. It was thermally treated in air at 520 ºC during 4 h for controlling the material morphology (stoichiometry and grain size of the oxide, and dopant distribution) and the semiconductor resistance stability since the parameters of preparation and annealing are fundamental in order to obtain a good detection.

Table 1. Multisensor distribution

Sensor No.	Semiconductor Material	Dopant (time)
1	SnO_2 (1 layer - 180 nm.)	-
2	SnO_2 (1 layer - 180 nm.)	-
3	SnO_2 (1 layer - 180 nm.)	-
4	SnO_2 (1 layer - 180 nm.)	-
5	SnO_2 (2 layers - 90 nm. Each)	Al (16 s)
6	SnO_2 (2 layers - 90 nm. Each)	Al (12 s)
7	SnO_2 (2 layers - 90 nm. Each)	Al (8 s)
8	SnO_2 (2 layers - 90 nm. Each)	Al (4 s)
9	SnO_2 (2 layers - 90 nm. each)	Pt (16 s)
10	SnO_2 (2 layers - 90 nm. each)	Pt (12 s)
11	SnO_2 (2 layers - 90 nm. each)	Pt (8 s)
12	SnO_2 (2 layers - 90 nm. each)	Pd (16 s)
13	SnO_2 (2 layers - 90 nm. each)	Pd (12 s)
14	SnO_2 (2 layers - 90 nm. each)	Pd (8 s)
15	SnO_2 (2 layers - 90 nm. each)	Pd (4 s)

The multisensor was placed in a stainless steel test chamber and the resistance measurements were carried out at 300 ºC with a constant flow rate of 200 ml/min at VOCs concentrations (benzene, toluene, propanal, chloroform, MEK, and octane) varying from 50 to 500 ppm in synthetic air. These mixtures were prepared by means of mass flow controllers. The exposure time to each tested gas concentration was 20 minutes. The measuring (resistence and temperature) and mixing processes were automatically carried out by means of DMMs and PCs.

On the other hand it has been used a quadrupole mass spectrometer BALZERS QMA 130 with working range from 1 to 300 amu provided with a special device for gas analysis at atmospheric pressure, so that the desorbing products coming from VOCs tested could be analysed. The measurements with the mass spectrometer were performed with the analysis probe placed some milimeters above the multisensor, when the gas mixture (VOCs/air) was interactioning with the multisensor surface, at 300ºC and for 500 ppm of each VOC.

With regard to the single component classification of the sensor array it has been performed to the six VOCs tested. The concentration of each VOC was varied from 50 to 500 ppm/air per experiment. The experiments were repeated between three and ten times for each VOC. The responses were measured after 20 minutes of each gas exposure.

The multicomponent characterization has been performed upon four VOCs (benzene, toluene, octane and propanal) gas mixtures. The selected number of observations was 81, corresponding to the mixtures of four gases and three possible concentrations per gas (0, 50, 100 ppm/air). In this case the responses were measured after 10 minutes of gas mixture exposure.

4. Results and discussion

4. 1. Sensitivity and reactivity

The sensitivity values (S) of the multisensor, defined as the ratio between the semiconductor conductance change and the semiconductor conductance in air, i.e. $S=(G_{gas}-G_{air})/G_{air}$ to 500 ppm for benzene, toluene, chloroform, octane, propanal, and MEK (methyl-ethyl-ketone) at 300 ºC are shown in Fig. 2. The best detection responses (higher sensitivity values) were obtained for the compounds with the carbonil group (aldehydes and ketones) in comparison with those obtained for aromatic hydrocarbons (benzene and toluene) and for chlorinated compounds, as chloroform, which showed the lowest sensitivity values.

A good sensitivity value for octane also appears at this temperature. Since these gases are reducing, the sensor elements doped with Pt and Pd showed the best response, because such dopants activate the oxidation reactions produced on the semiconductor surface.

At 300 ºC, Pd is oxidized, and its catalytic behaviour could be the same as Pt, i.e. by mass transfer (spillover) of the gas from the catalyst nanograins to the semiconductor nanograins where oxygen species are ionosorbed. Furthermore, it was a common feature that the sensitivity increased when the doping level decreased for both dopants for the thicknesses of tin oxide film indicated.

The sensitivity results only were slightly better for Al-doped sensors than for undoped, because this dopant is suitable for oxidant gases. According to the order of better sensitivity values, the sequence of reactivity would be :

propanal > MEK > octane > toluene > benzene > chloroform

At the temperature and concentations tested, it has been possible to measure the TLV for airborne contaminants of toluene, MEK, and octane (100 ppm, 200 ppm and 300 ppm, respectively) as it is seen in Fig. 3a, 3b and 3c. It can also be seen in such figures that the resistance values have a higher decrease when the gas concentration increases and that the reaction equilibrium is reached more quickly for higher concentrations than for the lower ones, which demostrates that the response rate depends on the gas concentration. These facts are more significants for Pt doped sensors.

In order to study the response behaviour of this type of gas sensors, based on the electrical conductivity of gas sensors modulated by the presence of gases, in this case VOCs, and to relate the multisensor outputs to the gas concentrations, it is important to take into account that the reaction processes take place on the semiconductor surface. It is well-known that these sensors work through chemisorption and/or oxidation-reduction reactions. Furthermore, during decomposition and oxidation of carbon-containing molecules, common intermediate compounds are produced on the SnO_2 surface, in such a way, that VOCs molecules exposed on the sensor surface, could produce, mainly as intermediate, oxidized species, radicals, OH groups and adsorbed hydrogen from the reaction steps.

The semiconductor oxide superficial conductivity depends initially on the oxygen vacancies formed in the preparation process, but such conductivity depends later on the adsorbing molecules, it depends on the density of donors (adsorbed hydrogen, oxygen vacancies and reducing molecules) and acceptors (chemisorbed oxygen species and oxidant molecules). The most important aspect to study is the reaction of oxygen species, ionosorbed on the tin oxide surface (O_2^-, O^-), with these volatile organic compounds. Such oxygen species are produced while the thermal treatment is carried out and at the working temperature of the multisensor. It is important to take into account that the reactivity of the oxygen species is as follows : $O^- > O_3^- > O_2^-$, and with regard to oxidation reactions, these oxygen species adsorbed are classified as "electrophylic" reactants which in polycrystalline materials, like tin oxide, preferentially attack the C-C bond [5].

According to the results obtained, from multisensor responses, it would be possible to have intermediate products, as those previously mentioned, and desorbing products, such as: propanoic acid or propanol from propanal, acetaldehyde and ethane from oxidative scission of MEK, since the ketones show more difficulty to be oxidized, and different oxygenated compounds and/or carbon dioxide and water from octane. The lower sensitivity values obtained for benzene, toluene and chloroform could be due to the absence of oxidation reactions between these compounds and the adsorbed oxygen species. With regard to results obtained from the measurements performed with the mass spectrometer [6], it has been possible to observe 2-propanol formed from propanal, CO_2 and H_2O from octane and CO_2, H_2O and acetaldehyde were produced from the scission of MEK (Fig. 4). For the other VOCs, no new compounds were observed in the spectra.

The response has a different behaviour for the different VOCs tested: proportional to the square root of the concentration for aromatic and chlorinated compounds and almost linear, although with change slope on increasing the concentration, for oxygenated and aliphatic compounds [6].

4. 2. Classification

With the data from 94 observations of the single-component characterization, it has been performed PCA to obtain the classification of the six VOCs. The tin oxide sensor signals (resistances), Y_{ij}, for only one gas component j present in air can be approximated by [7]:

$$Y_{ij} = R_{oi}\,(1 + B_j\, X_j\,)^{c_{ij}} \qquad (1)$$

where R_{oi} is the resistance of the sensor element i in air, X_j is the concentration of the test gas j and B_j, c_{ij} are model parameters depending on temperature and tin oxide surface.
To eliminate the gas concentration influence on the sensor signals, these are normalized considering B_j as constant:

$$p_{ij} = \frac{c_{ij}}{\sum_{i=1}^{p} c_{ij}} \qquad (2)$$

The resulting concentration-independent signals, p_{ij}, are mean-centred and variance-scaled and then used as the inputs for PCA [8]. The optimum system rank was 3, since higher rank vectors represented only noise. Considering the loadings of the first two factors, three groups of sensors could be separated: group 1: sensors 1-10, group 2: sensor 11, group 3: sensors 12-15.
The sensors in each group were redundant and indicate collinearity in the response matrix. Considering the loadings of factor 3, two subgroups were found from the previous group 1: Subgroup 1: sensors 1, 2, 4 and subgroup 2: sensors 3, 5-10.

PCA was performed over the response matrix considering three VOCs families as classes: oxygenated (propanal, MEK), chlorinated (chloroform), and aromatic/aliphatic (benzene, toluene/octane). In Fig.5, the results from PCA are shown. The scores of the three families are plotted for factor 2 vs factor 1 (Fig. 5a) and factor 3 vs factor 1 (Fig. 5b).

From only the first two factors, the chlorinated family can be separated quite well, but the other families overlap. Considering factor 3, a more efficient discrimination was found [9].

4. 3. Multicomponent analysis

With the measured data from the multicomponent characterization it has been carried out the multicomponent analysis in order to obtain the quantitative determination of the components of a VOCs mixture. The multicomponent analysis has been accomplished in two steps: the

linearization and the multivariate linear regresion. This has been performed according to the Partial Model Building (PMB) method [7].
With the linearized data set, linear regresion methods, like CLS, ILS, PCR, and PLS, were applied obtaining four regression matrices, one per method. The quality of applied multivariate regression models were not very good. The coefficients of multiple determination were far from one, indicating that the residual sums of squares were high. The means values of the relative prediction errors in percent and the mean values of the width of the 95% prediction intervals in ppm are shown in Table 2. In general, the lowest errors were obtained for PCR and ILS methods and therefore the best analysis of VOCs mixtures. The width of the ILS prediction intervals was narrower than the width of PCR intervals, but the ILS relative prediction errors were higher than PCR relative errors (except octane). With more data, the errors of the analysis would be minimized and a better classification could be obtained [9].

Table 2. Mean values of relative prediction errors and width of prediction intervals for MVA methods

Method	Relative Prediction Errors (%)				Width of Prediction Intervals(ppm)			
	Benzene	Toluene	Octane	Propanal	Benzene	Toluene	Octane	Propanal
CLS	428.4	43.0	27.9	47.4	817	88	50	235
ILS	60.6	45.8	20.9	43.4	146	70	20	54
PCR	34.6	29.8	25.7	30.2	131	108	33	120
PLS	45.0	34.7	19.4	39.0	124	113	63	119

5. Conclusions

It has been possible to measure low VOCs concentrations (detecting some TLVs) by means of the multisensor system built. The best sensitivity values corresponded to the most reactive compounds, following this order:

oxygenated > aliphatic > aromatic > chlorinated

Pt and Pd were good dopants for VOCs detection. The amount and the good distribution of the dopant on the semiconductor particles are very important to improve the detection.

About the classification of these compounds, considering three principal components it was possible to separate well the chlorinated family from the other ones. Between the oxygenated and aromatic & aliphatic there was overlapping. The best analysis of VOCs mixtures were obtained with ILS and PCR methods.
The width of the ILS prediction intervals was narrower than the PCR intervals, but the ILS relative prediction errors were higher than the PCR relative errors (with the exception of octane).

Departing from the present results after using the semiconductor sensor array, our challenge at the present consists of the integration of these sensors on silicon substrates towards the development of microsensor arrays due to the compatibility between the microfabrication technology (sputtering) and the microelectronic technology. Microsensors integrated present sustancial advantages respect the conventional sensors on ceramic substrates until now developed, such as smaller size, lower heating power, accurate and independent temperature control and eventual lower cost based on batch production. Besides the electronic and the sensor can be fabricated on one single chip.

The development of integrated gas multisensors associated with microelectronic technology and data processing, will allow the realization of analytic microsystems that can operate "in situ". Unfortunately until now, developments concerning integrated gas sensors on silicon are relatively scarce. Our preliminary studies and results of a micromachined solid state integrated sensor can be seen in ref. 10. At present we are working in the development phase.

6. Acknowledgements

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Figure 1 : View of the measuring system.

Figure 2 : Sensitivities to 500 ppm in air for VOCs at 300°C of a doped tin oxide multisensor.

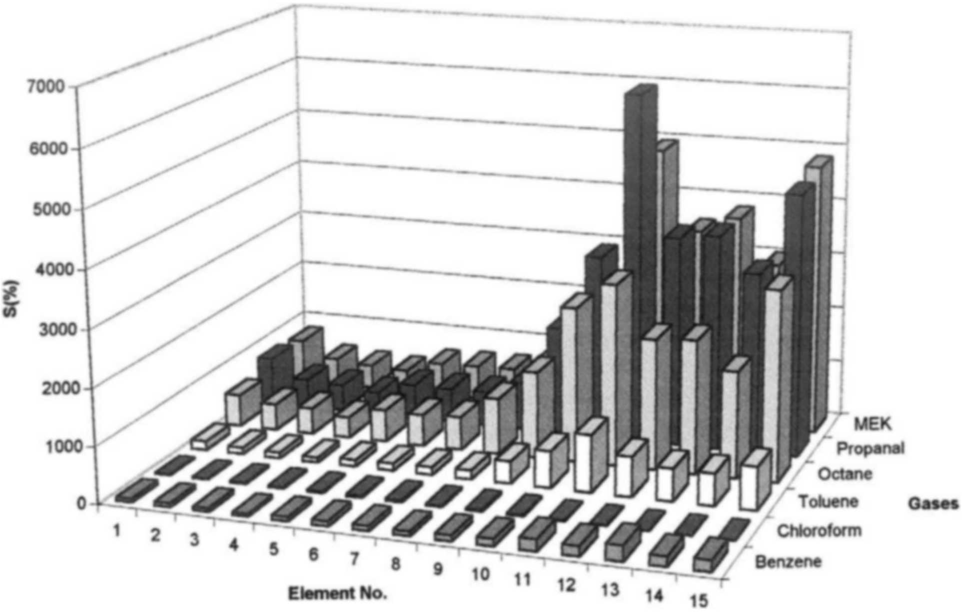
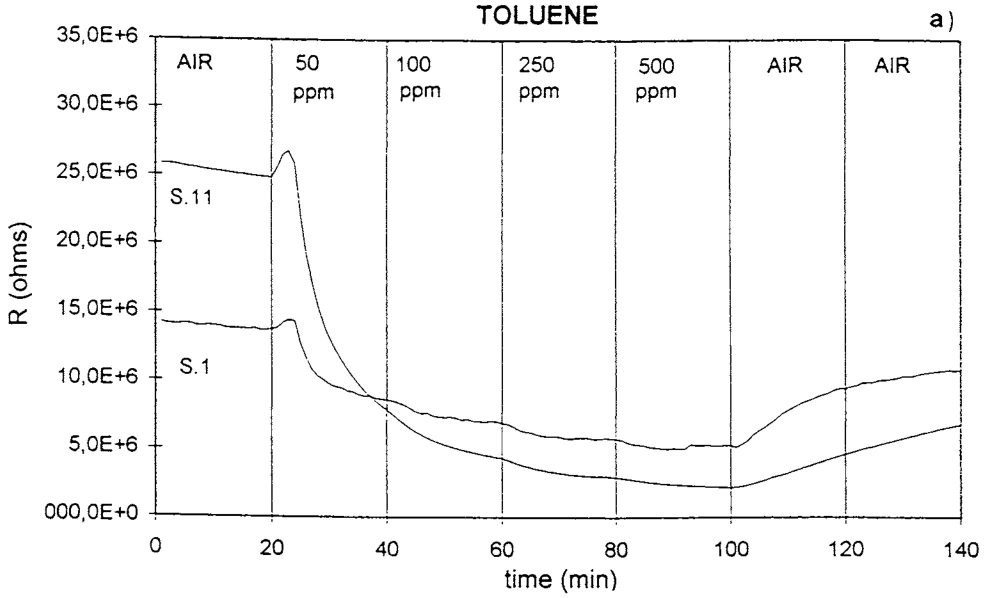


Figure 3 : Responses to a) toluene and b) MEK for an undoped sensor (S1) and Pt doped sensor (S11).



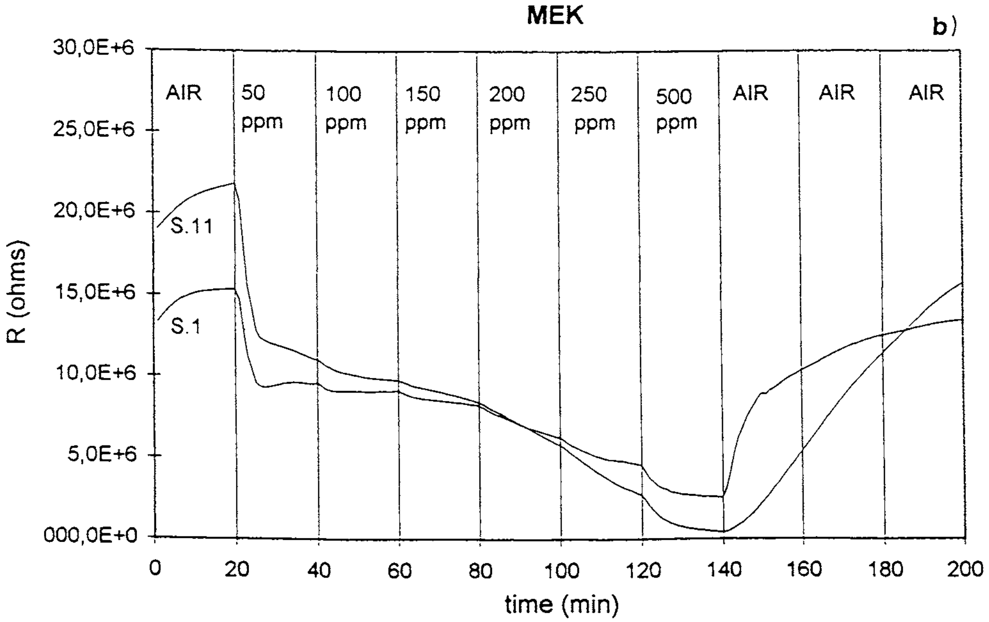


Figure 3 : Responses to octane for an undoped sensor (S1) and Pt doped sensor (S11).

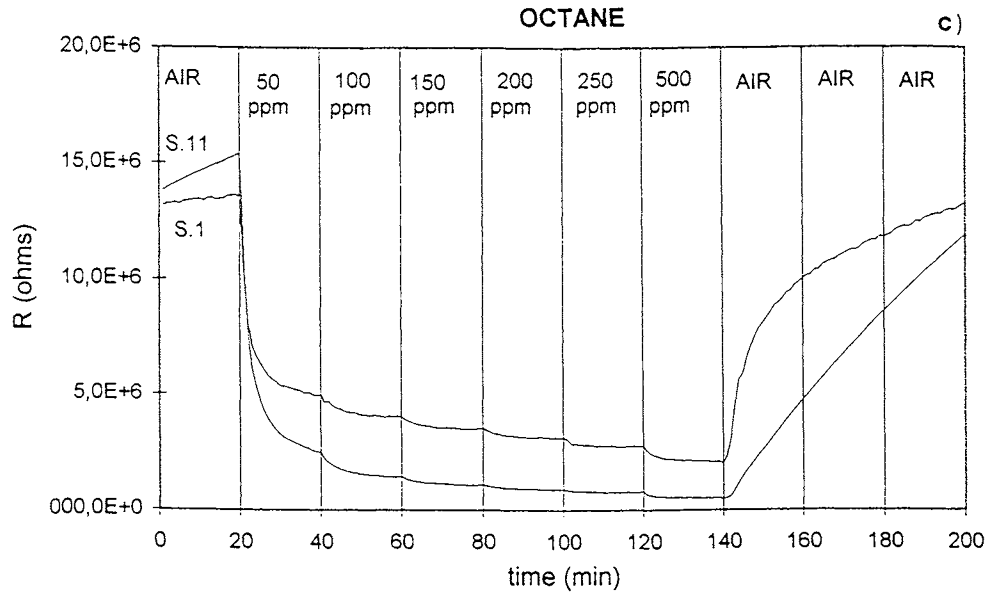


Figure 4 : Mass spectrum of 500 ppm of MEK interactioning with the multisensor.

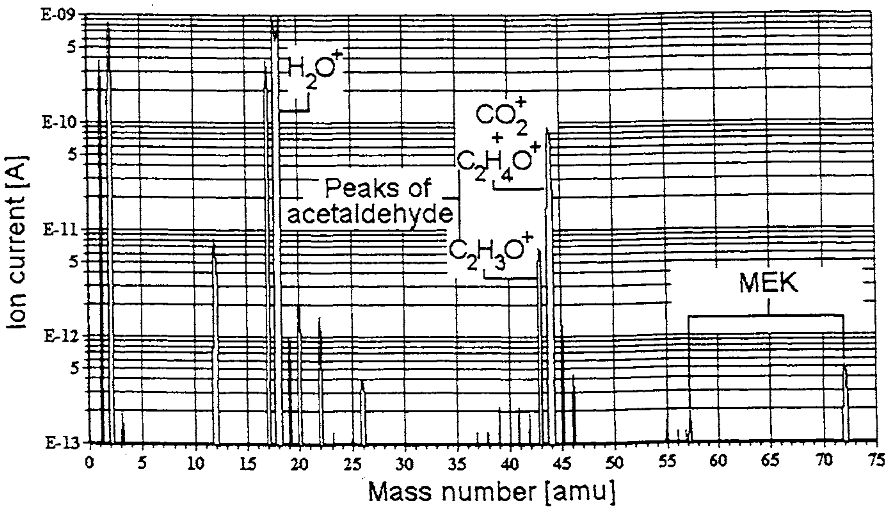


Figure 5 : Results of PCA for the 15 element sensor array showing the scores of three VOCs families for principal components a) 1 and 2, and b) 1 and 3.