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MOS sensors for the recognition of environmental odours: evaluation of sensor sensitivity towards odour concentration and humidity

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The aim of our research activity in the field of electronic noses is the development of a system for the continuous monitoring of odours, suitable for use at receptors and for outdoor use. For this purpose, it is necessary for the sensors employed for gas detection to have specific characteristics, which make the instrument suitable for the use in presence of diluted odours and varying environmental conditions, i.e. high stability and high sensitivity. This paper describes the approach adopted with the aim of selecting a suitable sensor array for the desired application. The work involved a theoretical study for a first selection of a set of sensors to be studied more in depth for a thorough comprehension of their functioning, necessary in order to identify the sensor optimal operational conditions. Moreover, experimental studies were carried out in order to determine the detection limit of the selected sensor set towards some environmentally important gases and to evaluate the sensor capability of discriminating different odours from each other. The information achieved though the theoretical and experimental studies turned out to be very important for the selection and the identification of a set of sensors suitable for the desired application.

1. Introduction

In recent years, the increasing care about topics regarding air quality brought to the development and the refinement of suitable environmental monitoring techniques. Among these techniques, there is a growing interest towards the environmental applications of electronic noses (Negri and Reich, 2001, p.172; Rajamäki et al., 2005, p. 71; Stuetz et al., 1999, p. 442). The aim of our research activity in this field is the development of a system, based on the use of electronic noses, for the continuous monitoring of environmental odours at specific receptors, i.e. directly where the presence of odours is lamented. For this purpose, the instrument should be capable to continuously analyze the ambient air at specific receptors and, in real time, it first should qualitatively classify the analyzed air by attributing it to a specific olfactory class, and secondly it should quantify odour by estimating the odour concentration (EN 13725, 2003) of the analyzed air.

The work required for the development of a similar system is composed of two interconnected fundamental activities, i.e. the instrument design and the definition of its utilization procedures. The instrument design comprises the following aspects: the sensor study and selection (James et al., 2005, p. 1; Chaudry et al., 2000, p. 236); the implementation of a suitable software for the instrument operation and the data acquisition and processing, and finally the study of technical characteristics which are needed in order to make the instrument usable not only in laboratory but also in the field.

As far as the sensor study and selection is concerned, it must be taken into account that the final aim of the research activity is the development of a system for the continuous monitoring of odours, suitable for use at receptors and for outdoor use. For this purpose, it is necessary for the sensors employed for gas detection to have specific characteristics, which make the instrument suitable for the use in presence of diluted odours and varying environmental conditions.

Therefore, the sensors should have the following characteristics:

- High stability: sensors should give stable responses even though working continuously, and in conditions of variable temperature and humidity.
- High sensitivity: electronic noses should be placed at receptors, which may be located at some kilometres from the emission source. For this reason, sensors should be sensitive to highly diluted odours.

This paper describes the approach adopted with the aim of selecting a suitable sensor array for the desired application. The work involved a theoretical study for a first selection of a set of sensors to be studied more in depth for a thorough comprehension of their functioning, necessary in order to identify the sensor optimal operational conditions. Moreover, experimental studies were carried out for the evaluation of some important characteristics of the selected sensor set.

2. Materials and methods

2.1 Studied sensors

Based on a literature study and on the execution of some preliminary experimentations a set of 17 sensors was selected to be studied thoroughly (Table 1).

It was decided to work with metal oxide semiconductor (MOS) sensors, for their documented properties of stability and long term stability (Maekawa et al., 2001, p. 51). Furthermore, it was decided to use thin-film MOS sensors, because of their higher sensitivity with respect to thick-film sensors (Yamazoe et al., 2003, p. 63).

2.2 Evaluation of sensor sensitivity

It is important to study the sensor sensitivity in order to identify an optimal sensor array (Nicolas and Roamin, 2004, p. 384), suitable for the detection of odours at receptors, where the odorous compounds are highly diluted. Ideally, sensors should have a detection limit similar to the detection limit of the human nose. This means that the sensors should be capable to detect the presence of odours at their odour detection threshold concentration, which corresponds by definition to an odour concentration of 1 ou_E/m^3.

Table 1. Selected sensor set

Sensor set				
#	***Metal Oxide***	***Catalyst***	***Name***	***Type***
1	Tin oxide	Gold	Sn-Au	n
2	Tin oxide	Gold - double layer	Sn-Au-2s	n
3	Tungsten oxide	_	W	n
4	Indium oxide	Silver	In-Ag	n
5	Nickel oxide	_	Ni	p
6	Tungsten oxide	Iron	W-Fe	n
7	Tin oxide	_	Sn	n
8	Tin oxide	Silver	Sn-Ag	n
9	Tin oxide	Molibdenum	Sn-Mo	n
10	Tin oxide	Silica - 20 nm	Sn-Si-20	n
11	Tin oxide	Silica - 80 nm	Sn-Si-80	n
12	Tin oxide	Silica - 160 nm	Sn-Si-160	n
13	Tin oxide - nanowire	_	Sn-nw	n
14	Chromium oxide + titanium oxide	_	Cr-Ti	p
15	Tin oxide	_	Sn-n01	n
16	Tin oxide	_	Sn-n02	n
17	Tin oxide	_	Sn-n03	n

Moreover, for a reliable qualitative classification of the analyzed air, the sensors should not only detect the presence of odours at low concentrations, but they must also be capable to discriminate different odours from each other. For the above mentioned reasons a set of experimental studies were performed in order to:

- determine the detection limit of the selected sensor set towards some environmentally important gases;
- evaluate the sensor capability of discriminating different odours from each other.

2.3 Examined odour typologies

The sensor sensitivity was tested respectively towards:

- pure compounds;
- gaseous mixtures from sites of environmental interest.

As far as the sensor detection limit determination is concerned, the first compound studied was normal-butanol (n-BuOH), because this is the reference odorant for dynamic olfactometry. Next, the study was extended to other odorous compounds that may be present in environmental emissions, i.e. acetaldehyde (CH_3CHO), ammonia (NH_3), ethyl mercaptan (EtSH) and hydrogen sulphide (H_2S). As far as n-BuOH is concerned, its odour detection threshold is known, as it is defined by the reference norm for dynamic olfactometry, EN 13725:2003, and it is equal to 40 ppb. The sensitivity study towards the remaining compounds was preceded by a set of olfactometric analyses, which were carried out in order to determine their odour detection threshold concentration.

Parallely, the sensor detection limit towards some gas samples collected at waste treatment plants was determined. In this specific case, samples representative of the following odours were examined: landfill gas, leachate and fresh waste odours from municipal solid waste (MSW) landfills; and green waste (pruning rests and ligneous-cellulosic material), compost and biofilter outlet odours from composting plants.

As far as the evaluation of the sensor odour discrimination capability is concerned, the experimental study was carried out using samples of neutral air and of different odorants, i.e. ammonia (NH_3), ethyl mercaptan (EtSH) and hydrogen sulphide (H_2S).

2.4 Reference conditions

The tests both for the determination of the detection limit and for the evaluation of the sensor odour discrimination capability were carried out using two different operating conditions, corresponding to two different solutions to the problem of the sensor sensitivity towards humidity, which is known to be one of the most critical aspects associated with the use of electronic noses.

More in detail, the detection limit of each sensor was evaluated analyzing diluted odorous gas samples at two different reference conditions, i.e. with:

Dry reference air, dehumidified with a physical dehydration system, i.e. with relative humidity (RH) equal to zero: $RH_{ref}=0$.

"Wet" reference air, i.e. reference air having the same relative humidity (RH) as the sample air: $RH_{ref}=RH_{sample}$.

The tests with dry reference air were realized using the ambient air internal to the electronic nose installation room, deodorized and dehumidified by filtration through active carbon and silica gel.

The method adopted for generating a reference air with RH equal to the RH of the sample air was based on the proved permeability of the Nalophan™, which is the material used for the sampling bags manufacture, towards humidity (James et al., 2005, p. 1; Welle et al., 2000, p. 372). In this case, the air sampled using apposite Nalophan™ bags at the outlet of the olfactometer sniffing ports was used as reference air. At the time of the sampling, this air is dry, because filtered through silica gel, but, being the Naolphan™ of the sampling bags permeable to humidity, the humidity of the reference air inside the bag tends to increase with time, reaching a RH value equal to the RH of the external ambient air.

The same principle was applied for the preparation of the odorous samples of pure compounds from gas bottles, which were diluted using the dry air coming out from the olfactometer sniffing ports as dilution air. At the moment of the dilution, the diluted sample has a RH content that is diminished, with respect to the original sample, by a factor equal to the applied dilution factor. Due to the Nalophan™ permeability to humidity, the RH content of the diluted sample tends to reach the RH of the external ambient air with time. This way, it is possible to obtain reference air and sample air having the same RH value, equal to the RH value of the external ambient air: $RH_{ref}=RH_{sample}=RH_{ext}$.

3. Results

3.1 Pure compounds odour threshold determination

Table 2 reports the results of the different tests conducted in order to determine the odour threshold concentration values (OT) of the examined pure compounds.

It is important to highlight that the threshold values resulting from the above described method represent the so called "odour detection threshold", i.e. the concentration at which the panel starts perceiving an odour, by detecting a difference between sample the reference air. This value is far below the so called "odour recognition threshold", i.e. the concentration at which the panel is able not only to do distinguish the difference between sample and reference air, but also to recognize the odour from a qualitative point of view.

3.2 Detection limit determination

Table 3 and Table 4 show the detection limits, expressed in ou_E/m^3, of the sensor being studied towards pure compounds and towards gas mixtures collected on the odour sources of some waste treatment/disposal plants.

3.3 Evaluation of the odour discrimination capability

Table 5 illustrates the results of this evaluation, reporting for each sensor being studied a qualitative judgement about the capability of discriminating the examined odorants, both in the case of dry an wet reference conditions.

In general, the evaluations about the sensor capability of discriminating the different odours reflect the results of the tests for the detection limit determination. In other words, the sensors (and reference conditions) having a low detection limit towards the odorants being examined also show a good capability of discriminating these odorants from each other.

Table 2. Odour threshold values of pure compounds, determined experimentally by dynamic olfactometry

OT values of pure compounds					
Compound	***OT 1*** ***($ppb/ou_E/m^3$)***	***OT 2*** ***($ppb/ou_E/m^3$)***	***OT 3*** ***($ppb/ou_E/m^3$)***	***OT - geom. mean*** ***($ppb/ou_E/m^3$)***	***Std. Dev.*** ***($ppb/ou_E/m^3$)***
CH_3CHO	7.1	6.2	_	6.6	0.45
EtSH	0.11	0.07	0.05	0.07	0.02
H_2S	_	0.34	0.20	0.26	0.07
NH_3	33	_	104	58.6	35.45

Table 3. Sensor detection limits towards pure compounds in ou_E/m^3 in dry (RH_{ref}=0) and in wet (RH_{ref}=RH_{sample}) reference air

Sensor detection limits towards pure compounds									
#	*Sensor*	*$RH_{ref}=0$*				*$RH_{ref}=RH_{sample}$*			
		CH_3CHO	*NH_3*	*H_2S*	*EtSH*	*CH_3CHO*	*NH_3*	*H_2S*	*EtSH*
1	**Sn-Au**	1	5	>30	1	<1	<1	<1	<1
2	**Sn-Au-2s**	1	<1	>27	<1	<1	<1	<2	<1
3	**W**	>29	>25	>27	>27	<1	<1	n.d.	<1
4	**In-Ag**	1	>25	27	>27	2	>25	27	n.d.
5	**Ni**	>29	<1	<2	2	1	<1	<1	>27
6	**W-Fe**	>29	5	_	6	>29	1	_	<2
7	**Sn**	3	25	<2	>27	1	>25	>27	>27
8	**Sn-Ag**	4	40	>30	1	25	_	30	18
9	**Sn-Mo**	29	40	4	1	29	>25	>27	>27
10	**Sn-Si-20**	3	>25	>27	>27	3	>25	27	>27
11	**Sn-Si-80**	1	5	4	<1	1	_	1	<2
12	**Sn-Si-160**	<1	>25	>27	>27	1	>25	>27	>27
13	**Sn-nw**	>25	_	4	18	_	_	<1	<1
14	**Cr-Ti**	_	25	3	27	_	<1	<2	_
15	**Sn-n01**	_	<1	<2	27	_	<1	<1	>27
16	**Sn-n02**	_	<1	<2	<1	_	<1	<2	<1
17	**Sn-n03**	_	<1	<1	<1	_	<1	<2	<1

Table 4. Sensor detection limits towards environmental emissions in ou_E/m^3 in dry (RH_{ref}=0) and in wet (RH_{ref}=RH_{sample}) reference air

Sensor detection limits towards environmental emissions									
#	*Sensor*	*$RH_{ref}=0$*			*$RH_{ref}=RH_{sample}$*				
		Compost	*Green waste*	*Biofilter outlet*	*Compost*	*Green waste*	*Biofilter outlet*	*Fresh waste*	*Leachate*
1	**Sn-Au**	<15	<40	<22	<15	158	<22	4	<3
2	**Sn-Au-2s**	<15	<40	30	<15	158	<22	4	<3
3	**W**	<15	<40	30	<15	<40	<22	4	3
4	**In-Ag**	<15	<40	30	n.d.	<40	<22	4	6
5	**Ni**	<15	<40	40	<15	<40	<22	4	3
6	**W-Fe**	<15	<40	<22	<15	<40	<22	15	12
7	**Sn**	<14	<40	<22	<14	<40	<22	<4	6
8	**Sn-Ag**	<14	<40	<22	<14	<40	<22	60	24
9	**Sn-Mo**	<14	<40	<22	<14	<40	<22	8	12
10	**Sn-Si-20**	<14	<40	<22	<14	<40	<22	30	3
11	**Sn-Si-80**	<14	<40	<22	<14	<40	<22	60	3
12	**Sn-Si-160**	<14	<40	<22	<14	<40	<22	30	6
13	**Sn-nw**	_	_	_	_	_	_	_	_
14	**Cr-Ti**	_	_	_	_	_	_	_	_
15	**Sn-n01**	_	_	_	_	_	_	_	_
16	**Sn-n02**	_	_	_	_	_	_	_	_
17	**Sn-n03**	_	_	_	_	_	_	_	_

Table 5. Qualitative results of the odour discrimination capability evaluation

Evaluation of odour discrimination capability			
#	*Sensor*	$RH_{ref}=0$	$RH_{ref}=RH_{sample}$
1	**Sn-Au**	n.d.	n.d.
2	**Sn-Au-2s**	++	++
3	**W**	--	+
4	**In-Ag**	--	--
5	**Ni**	-	+
6	**W-Fe**	n.d.	n.d.
7	**Sn**	-	-
8	**Sn-Ag**	n.d.	n.d.
9	**Sn-Mo**	-	-
10	**Sn-Si-20**	--	--
11	**Sn-Si-80**	n.d.	n.d.
12	**Sn-Si-160**	-	--
13	**Sn-nw**	n.d.	n.d.
14	**Cr-Ti**	--	++
15	**Sn-n01**	-	+
16	**Sn-n02**	+	++
17	**Sn-n03**	+	+

Discrimination capability:
++ very good; + good; - low; -- very low;
n.d. not determined

4. Conclusions

The research work conducted in the last three years at the Olfactometric Laboratory of the Politecnico di Milano allowed to make important progresses towards the development of a specific system for odour impact determination through the continuous monitoring of odours at specific receptors.

The first important result was obtained by the theoretical and experimental studies on the electronic nose sensors, which allowed to achieve a specific and thorough knowledge of their functioning principles, their response mechanisms, their sensitivity to odorants and to humidity and their stability. The detection limit of a set of MOS sensors, selected based on literature studies and preliminary laboratory tests, towards different environmentally important odorants, i.e. acetaldehyde, ammonia, ethyl mercaptan and hydrogen sulphide, was determined, and their capability of discriminating different odours from each other was investigated. This information turned out to be very important for the selection and the identification of a set of sensors having specific characteristics that make them suitable for the desired application.

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