

## 1. INTRODUCTION

ELECTRONIC Noses (EN), in the broadest meaning, are instruments that analyze gaseous mixtures for discriminating between different (but similar) mixtures and, in the case of simple mixtures, quantify the concentration of the constituents. ENs consists of a sampling system (for a reproducible collection of the mixture), an array of chemical sensors, Electronic circuitry and data analysis software. Chemical sensors, which are the heart of the system, can be divided into three categories according to the type of sensitive material used: inorganic crystalline materials (e.g. semiconductors, as in MOSFET structures, and metal oxides); organic materials and polymers; biologically derived materials.

The use of ENs for food quality analysis tasks is twofold. ENs is normally used to discriminate different classes of similar odour-emitting products. In particular ENs already served to distinguish between different coffee blends and between different coffee roasting levels. On the other hand, ENs can also be used to predict sensorial descriptors of food quality as determined by a panel (often one generically speaks of correlating EN and sensory data). ENs can therefore represent a valid help for routine food analysis.

The combination of gas chromatography and mass spectroscopy (GC-MS) is by far the most popular technique for the identification of volatile compounds in foods and beverages. This is because the separation achieved by the gas chromatographic technique is complemented by the high sensitivity of mass spectroscopy and its ability to identify the molecules eluting from the column on the basis of their fragmentation patterns. Detection limits as low as 1 ppb (parts per billion) are frequently reached. The main drawbacks of the approach are, however, the cost and complexity of the instrumentation and the time required to fully analyze each sample (around one hour for a complete chromatogram). Comparatively, ENs are simpler, cheaper devices. They recognize a fingerprint, that is global information, of the samples to be classified. For food products, the sensory characteristics determined by a panel are important for quality assessment. While man still is the most efficient instrument for sensorial evaluation, the formation of a panel of trained judges involves considerable expenses.

Commercial coffees are blends, which, for economic reasons, contain (monovarietal) coffees of various origins. For the producers the availability of analysis and control techniques is of great importance. There exists a rich literature on the characterization of coffee using the chemical profile of one of its fractions, such as the headspace of green or roasted beans or the phenolic fraction. In the literature up to 700 diverse molecules have been

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identified in the headspace. Their relative abundance depends on the type, provenance and manufacturing of the coffee. It is to be noticed that none of these molecules can alone be identified as a marker. On the contrary one has to consider the whole spectrum, as for instance the gas chromatographic profile.

## **2. COMPARISION OF ELECTRONIC NOSE WITH BIOLOGICAL NOSE**

Each and every part of the electronic nose is similar to human nose. The function of inhaling is done by the pump which leads the gas to the sensors. The gas inhaled by the pump is filtered which in the human is the mucus membrane. Next comes the sensing of the filtered gas, which will be done by the sensors i.e., olfactory epithelium in human nose. Now in electronic nose the chemical reaction occurs which in human body is enzymal reaction. After this the cell membrane gets depolarised which is similar to the electric signals in the electronic nose. This gets transferred as nerve impulse through neurons i.e., neural network and electronic circuitries.

### **3.DIFFERENT TYPES OF SENSORS**

There are different types of electronic noses which can be selected according to requirements. Some of the sensors available are calorimetric, conducting, piezoelectric etc. Conducting type sensors can again be sub divided into metal oxide and polymers. In this type of sensors the functioning is according to the change in resistance. The sensor absorbs the gas emitted from the test element and this results in the change of resistance correspondingly. According to the Resistance-Voltage relation  $V=I \cdot R$ . Here 'V' is the voltage drop, 'R' is the resistance of the sensor and 'I' is the current through it. By this relation as resistance changes the voltage drop across the sensor also change. This voltage is measured and is given to the circuit for further processes. The voltage range for using metal oxide sensor is from 200°C to 400°C. The working principle of polymer sensor is same as that of metal oxide sensor. The only change is in the temperature range i.e., the room temperature.

Piezoelectric sensors are sub-divided into quartz crystal microbalances and surface acoustic wave. In quartz crystal the surface absorbs the gas molecules. This results in the change of mass, which causes a change in the resonant frequency of the quartz crystal. This change in frequency is proportional to the concentration of the test material. The change in frequency also results a change in the phase. In surface acoustic wave we measure the change in phase of the resonant frequency.

Calorimetric sensors are preferable only for combustible species of test materials. Here the sensors measure the concentration of combustibles species by detecting the temperature rise resulting from the oxidation process on a catalytic element.

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## **4. EXPERIMENTAL SET-UP**

### ***4.1 The Pico-1 Electronic nose***

Five semiconductors, SnO<sub>2</sub> based thin films sensors were utilised. Two are pure SnO<sub>2</sub> sensors; one is catalysed with gold, one with palladium and one with platinum. They were grown by sputtering with the RGTO technique. RGTO technique is a technique for growing SnO<sub>2</sub> thin films with high surface area. The surface of the film after thermal oxidation step of the RGTO technique presents porous, nano-sized agglomerates which are known to be well suited for gas absorption. A thin layer of noble metals was deposited as catalyst on three sensors to improve sensitivity and selectivity. Thin film sensor produced by sputtering is comparatively stable and sensitive. Furthermore, since the growing conditions are controllable, they can be tailored towards the particular application. Even if catalysed the sensors are not selective and therefore sensor arrays together with multivariate pattern recognition techniques are used.

The odour sampling system depends on the type of sample and on its preparation. For a simple gas mixtures one uses automated gas mixing stations consisting of certified gas bottles, switches and mass flow controllers. In the case of complex odours like food odours, the volatile fraction (the so-called headspace) is formed inside a vial where a certain amount of odour-emitting sample is put. The vapour can then be collected either by flushing a carrier inside the vial (dynamic headspace scheme) or extracted with a syringe and injected, at constant velocity, in the air flow which is used as carrier (static headspace scheme).

There are two different design considerations of designing the sensors. Those are first design consideration i.e., linear and the second design consideration i.e., parallel design. The first is comparatively less costlier than the second one. At the same time it has

certain disadvantages that the distribution of the sample into each sensor element is uneven, but second consideration have this advantage. The construction of second type is much complex when compared to first.

The basic schematic diagram of an electronic nose is shown in the below figure.

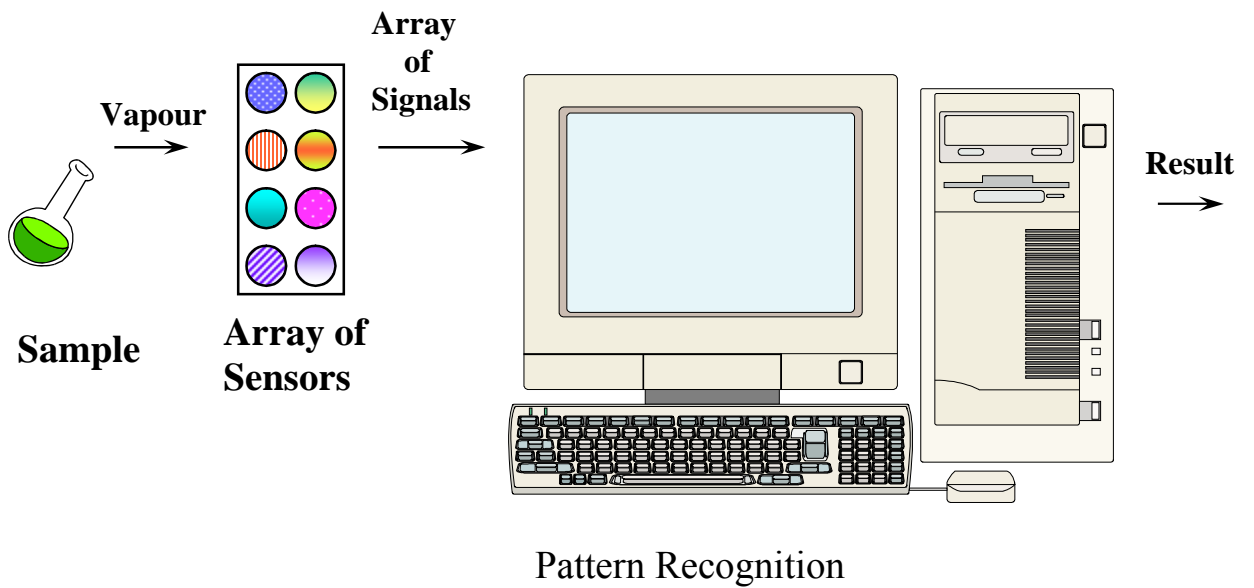


Fig.1 Process in electronic nose

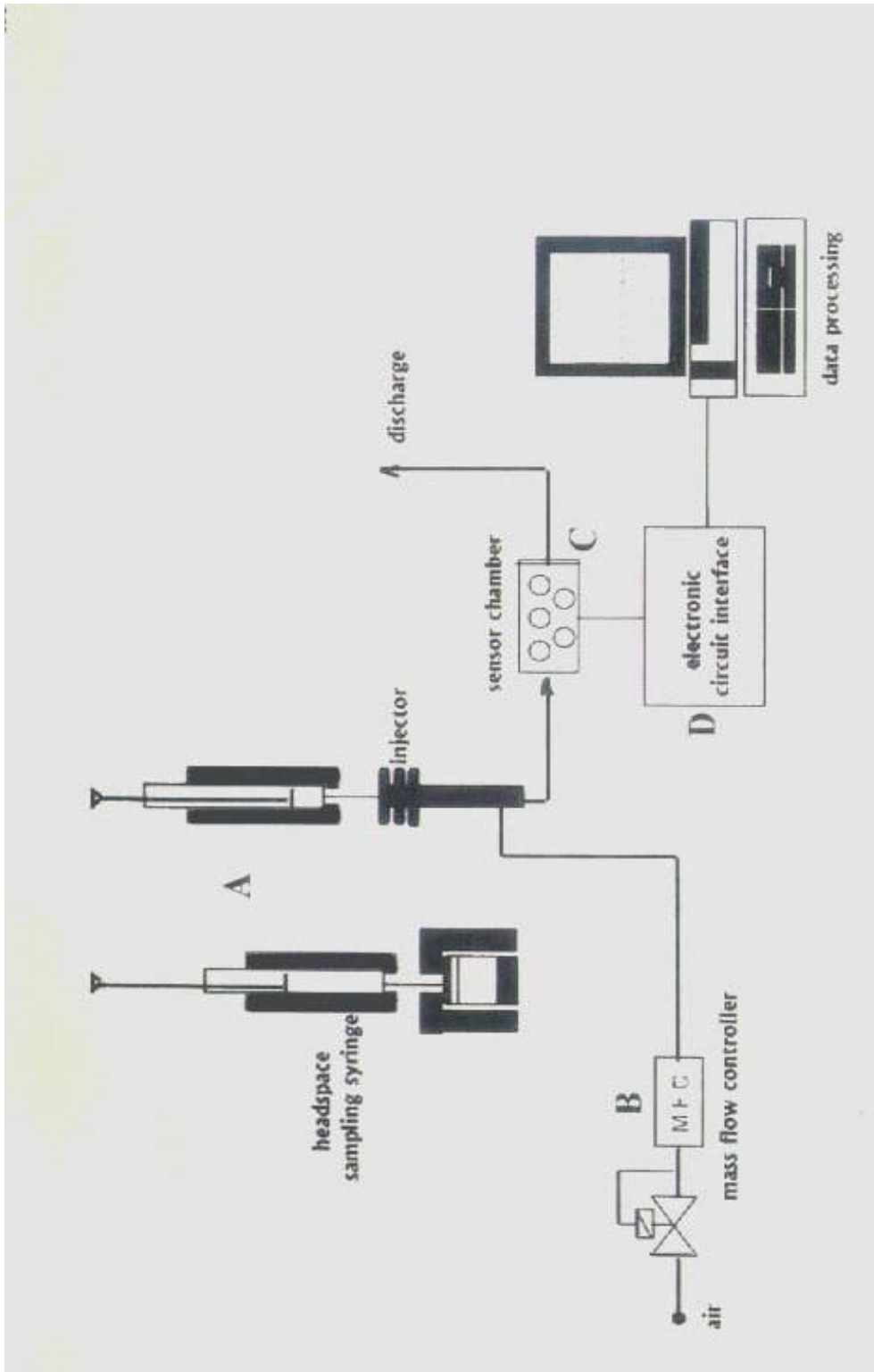


Fig 2. Lab arrangement of electronic nose for coffee analysis

1. An auto sampler (Hs 850 CE Instruments). This device is a standard component of chromatographs; its utility is a high sample throughput and a high reproducibility due to the automation of the measurement process. It consists of a sample carousel, where the vials containing the odour-emitting sample are held; an oven, where the sample is pre-conditioned; a movable mechanic arm with syringe (A).

The electro-mechanical part of the EN used in this experiment consists of (see a scheme in fig. 2):

2. A mass flow controller (B) to set the flow of the carrier gas.
3. A stained steel chamber (C) which can contain up to five chemical sensors plus a humidity sensor.
4. Control electronics (D) permitting to steer the system (auto sampler, mass flow controllers and sensors) via PC.

The typical measurement consists of the exposure of the sensors to a concentration step, that is a change of odour concentration from zero to  $c$  (each component of the vector stands for a gas component) and back to zero again, and of the recording of the subsequent change in resistance. The classical feature extracted from the response curve is the relative change in resistance.

A set of Mat lab functions (toolbox) has been developed for analyzing the data. The toolbox permits to perform the following tasks.

- Data cleaning (median filter for spikes removal, possible noise averaging) and plotting (for gaining a first impression of the response curves). Software for drift compensation is currently under study.
- Exploratory analysis (visual). First various plots of the response curves and of the features can be drawn for each sensor separately (univariate analysis). The most important multivariate tool for exploratory analysis is Principal Component Analysis (PCA) (score and loading plots). PCA is implemented with a simple user interface giving the possibility of selecting the sensors and classes to be displayed and of grouping classes together. PCA also serves for feature reduction before the use of Multilayer Perceptrons (MLP).
- Learning with MLP. The inputs to the MLP are the projections of the data on the first  $m$  principal components (the so called PCA scores). The number of inputs  $m$  (PCA dimensions) is then a variable to be optimized. To prevent over fitting early stopping (ES) or weight decay regularization can be used. Both a division in two sets (training and testing) or in three sets for ES (training set is subdivided in training and validation sets) is possible. The error function is minimized with the Levenberg Marquardt algorithm. Ten network initialization are usually performed and the net with the best result on the test set is held.

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- Decomposition of the global learning tasks in successive classification subtasks (hierarchical classification). First the classification between the more distinct clusters is performed, then the finer differences are determined in subsequent steps. This is particularly useful when dealing with a big number of classes and a small number of data. Ensembles of MLPs based on output coding decomposition have also been studied. Work is in progress on the topics of boosting and bagging for increased classification accuracy.

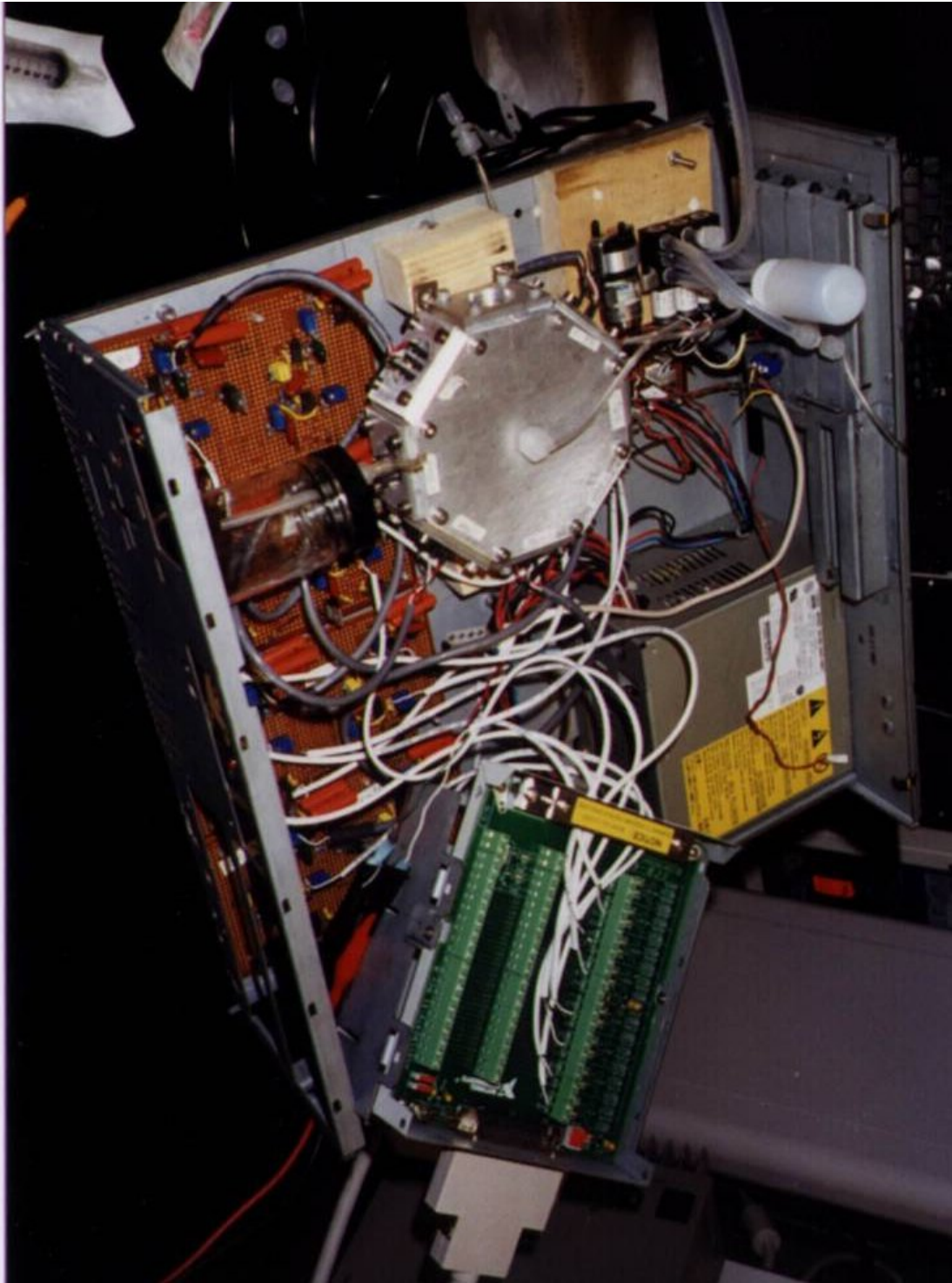


Fig 3. Internal view of electronic nose circuit

#### ***4.2 The measurements***

Measurements were done on ground coffee. Two groups of coffees were analyzed. The first one consists of 6 single varieties (SV) and the blend Italian Certified Espresso (ICE) for reference (this group will be called SV) and the second one of 7 blends, including the ICE, see tables I, II. The fourth row of the tables contains a brief characterization of the coffees, where the commercial value is indicated with + and -. Two grams of ground coffee are introduced into a vial with a volume of 20cm<sup>3</sup> which is crimped with seal and septa. The vial is then left in an incubation oven at 50°C for 30 minutes in order to generate the aroma. Ten vials for every coffee type of the first group and 12 vials for every coffee type of the second group were prepared. Three successive extractions were performed from the same vial. All together there are  $10 \cdot 7 \cdot 3 = 210$  measurements for the first group and  $12 \cdot 7 \cdot 3 = 252$  measurements for the second group. While the data set is not big for machine learning standards, where it is usual to have hundreds of examples for each class, this is a considerable dataset to be collected with an E-Nose, where complete datasets normally don't exceed 100-200 examples (while it is rather common to have less than 10 instances for each class).

Table I. First group of coffee: Single varieties + ICE

# coffee	Name	Type Quality (+/-)
1.	ICE	Blend, +
2.	Brazil	Arabic natural, +
3.	Ethiopia	Arabic washed, +
4.	Rio Minas	Arabic natural with defects, -
5.	Guatemala	Arabic washed, +
6.	Peru	Arabic natural,-
7.	Cameron	Arabic,-

TABLE II. The second group of coffees: blends.

# coffee	Name	Note, Quality
1.	ICE	Reference, +
2.	ICE, more toasted	Strong, +
3.	ICE, without natural	Study, +
4.	Robusta	Bad,
5.	ICE def#1	Unripe, -
6.	ICE def#2	Rancid, -
7.	Commercial	Arabic + Robusta +/-

Experimental parameters like samples' conditioning temperature and fluxes were optimised to reduce the sensor stress and to increase the measurement rate while still reaching sensor's steady state conditions (which are believed to be more reproducible). The time interval between the extractions sufficient for the headspace to reach equilibrium conditions was found to be 40 min.



Fig. 4

An external view of an Electronic Nose interfaced with PC is shown in the above figure.

As for the sensorial analysis, the panels (formed respectively by 18 and 14 judges) judged the final product (cups of espresso coffee) according to 10 quantitative descriptors (colour intensity, cream texture, olfactory intensity, roasted, body, acidity, bitterness, astringency, global positive odour and global negative odour) and 4 qualitative descriptors (attractiveness, finesse, balance and richness). Each descriptor is given a mark from one to nine. One sample for every coffee type (plus a random repetition per group) is tasted. In the quantitative analysis the panel is given a reference for adjusting its judgements, while this is not the case for the qualitative analysis which should provide a personal, "hedonic" impression. Since the qualitative values are not calibrated, their spread is

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considerable. Therefore, for every coffee type, the mean over the 4 qualitative descriptors and over the panellists is considered as a reliable global parameter characterizing the sensorial appeal of a coffee. This quantity is pictorially termed Hedonic Index (HI). The two averages help to reduce the uncertainty (standard deviation) by a factor  $\sqrt{N}$ , where  $N$  is the number of sensorial measurements, i.e.  $N = \text{judges} \cdot \text{qualitative descriptors}$ . For the SV group the standard deviation of the HI is  $\sigma_{\text{mean}} = 0.2$ ). The detailed procedures adopted for testing the Espresso in this study are described in.

## **5.ADVANTAGES OVER HUMAN SNIFFERS**

The human sniffers are costly when compared to electronic nose. It is because these people have to be trained. This is a time consuming that a construction of an electronic nose. Now for the confirmation of the values obtained from a sniffer the result obtained from the sniffer has to be compared with some other sniffer's value. And here there are great chances of difference in the values got by each individual. Detection of hazardous or poisonous gas is not possible with a human sniffer. Thus taking into consideration all these cases we can say that electronic nose is highly efficient than human sniffer.

## **6. OTHER APPLICATIONS OF ELECTRONIC NOSES**

There are various applications in which an electronic nose may be used. For example, to monitor the characteristic odour generated by a manufactured product (e.g. drink, food, tobacco, soaps). The electronic nose research group has considerable experience in the analysis of coffee odours (e.g. roasting level and bean type), lager beer odours (lager type and malodours) as well as having analysed tobaccos, spirits, wines, transformer oils, plastics and drinking water. More recent work is on the use of e-noses for medical diagnostics and biotechnology. It is also used in automotives. The use of this over here is to analyse quantity of smoke that is given out and the quantity of the desired gas. One another application is for environmental monitoring especially to test the presence of poisonous material in the environment. It is also used for military application for the very same purpose. It is also used in medical field.

## **7. CONCLUSIONS**

In this contribution I presented a description of E-Nose the advantage of which consists in the sensor type and in the data analysis software. Thin film semiconductor sensors are stable and sensitive, while the Mat lab toolbox permits to reliably analyze small datasets. Two groups of measurements on coffee samples were analyzed. Classification figures of over 90% for both groups have been obtained with PCA and multilayer perceptrons. More importantly, EN data have been correlated with panel test judgments. As far as we know, the prediction of a global sensorial parameter, as the coffee's hedonic index, using just EN data has been never reported. These results show that it is possible to use the Electronic Nose for routine work in food quality analysis.

Researches are still going on to make electronic nose much more compact than the present one to make it more compact and to make electronic nose I.C.s. In future we might be able to manufacture olfactory nerves.

## **8. REFERENCE**

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