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MULTI-SENSOR ODOUR DETECTION AND MEASUREMENT OF POLLUTED FOOD

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This paper describes an experiment into detecting pollution of water and food samples with ammonia. The novelty of the work is the use of an "electronic nose" to measure the smell of the samples, and application of an algorithmic procedure called "decision trees" to these measurements, in order to determine the presence of ammonia in the samples. The results obtained suggest that an appropriate extension of that method should allow not only for qualitative, but also for quantitative analysis of ammonia pollution in food.

INTRODUCTION

Recent years have shown that people are really interested in the volatile components responsible for flavour perceptions. Food sensory attributes are becoming a very important measure of the quality of food, because they reflect the criteria that drive preference and purchasing consumer decision [Grigioni *et al.*, 2000]. For example, unacceptable flavour and odour development is one of the most prevailing reasons for consumer rejection either in raw, processed or packed food [Mottram, 1998]. Gray *et al*. [1996] outlined a classification of undesirable meat flavours that are namely related to oxidative rancidity, processing–induced and feed–derived flavours, among others. Especially in raw meat, variations in flavour and odour arise from animals fed different finishing–diet, *e.g.* pasture or feedlot. Odorant molecules are typically small, partly hydrophobic. They tend to have one polar group which frequently contains an oxygen moiety, although nitrogen and sulfur moieties can also be found. The detection limit for an odorant molecule may be as low as a few parts per million and thousands of distinct odors can be discriminated [Aparicio *et al*., 2000; Burl *et al*., 2001; Clarke, 1986]. Odours can be complex mixtures of many hundreds chemical species and often even subtle changes in their relative amounts can be detected as a change in the odour. Currently, sensory evaluation and headspace direct gas chromatography or mass spectrometry analysis have been carried out to determine flavour quality wherever aroma, smell or the release of volatile components are important and should be taken into account in quality assessment. An electronic nose offers an alternative technology which will, as it is hoped, complement or in some cases replace the currently used approaches. An electronic nose is based on an array of sensors, each of which has a partial specificity and responds to a number of different chemicals or classes of chemicals [Gardner *et al.*, 1994; Albert *et al.*, 2000]. This attempt seems to be similar to biological olfactory system where receptors respond to more than one chemical compound and each chemical compound elicits the responses from more than one detector [Malnic *et al.*, 1999; Pearce, 1997a, b]. Identifi-cation of an unknown molecule cannot in general be achieved by analyzing the response of a single sensor element.

An alternative could be the use of conventional approaches to chemical sensors of "lock – and – key" design, wherein a specific receptor is synthesized in order to strongly and highly selectively bind the analyte of interest [Albert *et al*., 2000; Lonergan *et al.*, 1996]. Such approaches are appropriate when a specific target compound is to be identified in the presence of controlled background and interference. However, this type of approach requires the synthesis of a separate, highly selective sensor for each compound to be detected. It is not particularly useful for analyzing and classifying complex vapour mixtures, *e.g.* cologne, beers, foods, mixtures of solvents, *etc*. Therefore an electronic nose seems to be the right choice for food analysis. It must be complemented by pattern recognition methods necessary to classify, identify and in some cases determine the quantity of chemical compounds in the vapour phase, which interpret the measurements made by that device. They take into account the compound response of the whole array of sensors, and an attempt to identify the flavour by comparing that response to a reference library of previously obtained measurements of known samples [Freund *et al.*, 1995; Lonergan *et al.*, 1996; Li, 2002, 2003].

In this work, used was made of an electronic nose Cyranose 320 (CyranoSciences Inc.) to detect the smell of ammonia, treated as a pollution of the investigated samples. Ammonia appears in different concentrations and in various headspaces generated by food samples. An algorithmic method was proposed to identify ammonia in such headspaces, by analyzing the output of the electronic nose. The algorithm is based on the decision

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trees method [Witten *et al.*, 1999] and is implemented in the form of lazy decision trees [Friedman *et al*., 1996], which guarantees shorter time and memory consumption during the computation.

MATERIAL AND METHODS

A commercially available electronic nose, Cyranose 320 (Cyrano Sciences Inc.) [Cyranose 320, part number 11 60001], with an array of 32 individual thin-film carbon black-conducting polymer sensors was used (Figure 1). The instrument is very popular in the analysis of volatile compounds and may be regarded as a comparator of chemical vapours. The result of measurements made with this instrument is the measured change of the resistance R of each chemical sensor in the array when the instrument is exposed to a flowing vapour. This is a differential measurement with the sensor response defined as $(R_{max} – R_0)/R_0$ with R_0 being the resistance during a baseline gas flow and R_{max} being the maximum resistance during exposure to the sample vapour. Both values are measured independently by sample paths present in the sampling system. The pump speed at which the pump draws the vapours into the sampling chamber have been determined by the Pc-nose software shipped with the Cyranose 320. Typically low or medium pump speeds (50 and 120 cc/min, respectively) are used for baseline and sample, whereas a high (180 cc/min) pump speed is nearly always used to purge the system. After collection, the raw data is subjected to signal pre-processing, post-processing and statistical analysis. The recognition of unknown samples is usually based on a comparison of measured signals with the learned signals, stored in the memory of Cyranose 320. Because the instrument's response is based on the summation of the chemical and physical properties of the entire sample, the Cyranose 320 is not intended to provide information concerning the composition of complex mixtures. It is designed to perform the classification by comparing the examined vapour to a large number of odours of known characteristics which can be stored in instrument's memory. Standard procedures for pattern recognition: K- nearest neighbours KNN, K means and Canonical Discriminant Analysis CDA are built-in into the device and used for that task.

FIGURE 1. The Cyranose 320, The Cyranose 320 Electronic Nose, User's Manual part number 11 60001, CYRANOSciences, Inc.

Use was also made of another pattern recognition procedure, decision trees, implemented in programming language Java and run on a desktop computer. It was applied to the data gathered by the electronic nose Cyranose 320 that are treated as the input to our program.

Sample preparation. A total of 20 mL of 1 ppm, 10 ppm, 50 ppm, 70 ppm, 100 ppm and 200 ppm experimental solutions of ammonia were made separately, and smelled by Cyranose 320. A pure p.a. ammonia solution 25% was used. All samples were prepared in Lab environment at ambient conditions. In most of the cases, typical variations of temperature in the laboratory had no significant impact on the identification success, both when using the Cyranose 320 built-in software and using decision trees. Time of the exposure of each of sensor and flow rate for the analyte above the detectors was regulated during the experiment. The training protocol for each odorant exposure was 10 sec for flow of clean air, followed by 40 sec for flow of air containing the odorant and followed by another 45 sec for flow of clean air used to purge all remaining samples from the sampling system including the sensors. The detectors were exposed to each sample of odorant at least 5 times, in various orders. The same protocol was applied in the attempt to identify the smell of ammonia in food samples. The high frequency noise in the output data was reduced using digital filtering, namely the Savitsky–Golay procedure.

Decision model. Measurements received from the device were represented as vectors of 32 values. The aim was to create rules that could be used to classify unknown samples. The pattern recognition method used were decision trees (DT). One of the advantages of this approach is that, besides identifying the samples, it also gives the chance to determine which sensors were dominant in the recognition process. PCA was used to increase DT's efficiency by finding statistical correlation between co-ordinates (elements of the vector of the values) and transforming the data in order to make advantage of that knowledge.

In general, the algorithm has two stages: teaching and asking. In the first phase the system is given identified samples which are assumed to be 100% correct (properly identified). On the basis of an analysis of those training samples, the system creates decision trees used in the second phase.

Decision trees. The algorithm to classify an unknown sample, given a set of training samples, is based on the decision trees method [Witten *et al.*, 1999]. Samples, as explained above, are indeed vectors of the responses of 32 sensors.

1. Input: An unknown sample and a set of training samples.

2. Choose a sensor and a threshold value, split the set of training samples into two subsets according to whether the value of that sensor exceeds the threshold or not.

3. Apply the same procedure to the subset in which the unknown sample falls, according to the value of the chosen sensor and threshold.

4. Stop splitting when the set of training samples contains samples of one type, only. Classify the unknown sample to be of the type of the samples in the set.

The crux of the method is the principle how to choose the sensor and how to set the threshold in point 2 of the algorithm above. We used the number of pairs with different answers that are differentiated by that split to choose the sensor and threshold. At each stage of the computation, the optimal choice of sensor and threshold is made, *i.e*. the one which guarantees the maximal number of pairs correctly differentiated.

In the simplest case, we have samples of two types in our set (Figure 2). One is the set of samples with specific odour and the other is the set of samples without it. Of course, the first few sensors used to split the set of training samples in the procedure above are the most important ones when deciding about the presence/absence of that odour. The information about those sensors is an additional outcome of the identification procedure.

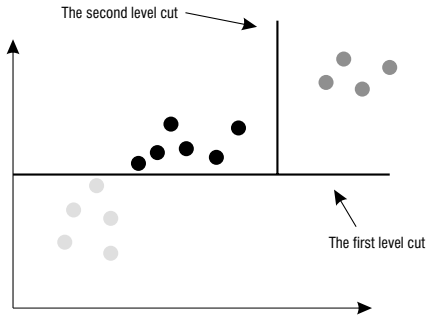

FIGURE 2. Decisive trees example.

In our implementation, the above algorithm is modified in order to reduce its running time and memory consumption, by using the lazy decision tree technique [Witten *et al*., 1999]. It is achieved by memorizing the chosen sensors and thresholds after each unknown sample. The algorithm used guarantees that always the same sensors and thresholds are chosen, independently of the unknown sample, as long as it falls in the same subset after the split as one of the previous unknown samples. Therefore in such cases it is enough to use the sensors and thresholds chosen for previous samples, without the need to search for the optimal choice in each time. Only when the unknown sample falls into a subset into which no previous unknown sample has fallen, the search for the optimal choices must be conducted.

Principal Components Analysis. PCA can be used to find correlation in the data sets. Afterwards the data is rotated so that the principal components become the axes – a change of the co-ordinate system is performed. As a result, the decision tree algorithm is working more efficiently – it can create more efficient trees. On the other hand, the side-effect is the loss of knowledge which sensors are the most important ones.

RESULTS AND DISCUSSION

The experiment focused primarily on the qualitative analysis. Samples were divided into three basic groups: pure water, ammonia water with various concentrations of ammonia and natural food samples: canned meat and smoked pork sirloin, and the same samples polluted with ammonia. The presence of the smell of ammonia in the headspace of all three groups was detected. Because the pump speeds were the same in all experiments, the effects of pressure change or other flow effects had no impact on the calculation of sensor responses. The examinations of the decision trees used by our algorithm show that sensors 23, 5, 6 in that order are relevant for recognition of water vapour in the headspace (Figure 3).

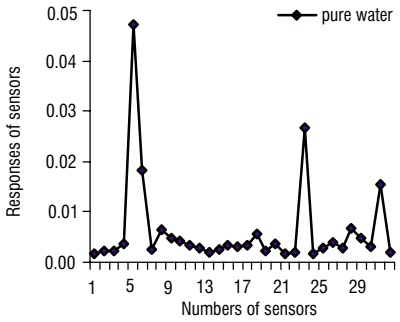

FIGURE 3. Changes in the electric resistance of each chemical sensor in the 32-sensor array of the Cyranose 320 during the investigation of the headspace of pure water.

The shapes of the curves describing the behaviour of all sensors active during the investigation of the headspace for samples from the second group were shown in Figure 4. The detailed analysis indicated that the same sensors as in the case of pure water have had meaning. Especially sensors 6 and 23 seem to be useful in detecting the smell of ammonia independently of its concentration, in the range of the investigated concentrations. The changes in the sensors response for these sensors compared to the changes that appeared for samples of pure water, are distinctively different.

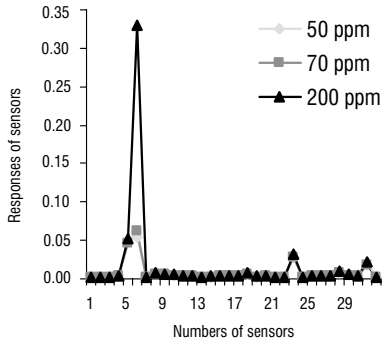

FIGURE 4. Mean of the response of the sensor from 1 to 32 to headspace of ammonia water with various percentages.

In the case of ammonia treated as chemical pollution of food, it was possible to distinct natural, unpolluted samples from the polluted ones for canned meat as well as for smoked pork sirloin. Similar results were obtained for slices of dry, smoked sausage.

CONCLUSIONS

Cyranose 320 was successfully applied to detect the presence of smell of ammonia in several headspaces. In all cases of the experiment, the background was the water vapour of different levels of saturation, that was acting on

the same sensors as ammonia but with other responses. In the case of water solutions, it was possible to distinguish several levels of concentration of ammonia. For more complex headspace, as is produced by food samples, we have been able to distinguish between clean samples and polluted samples. The quantitative analysis of food samples depends on the presence of other odours in the investigated headspace and should be possible only in the case of canned meat.

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REFERENCES

1. Albert K.J., Lewis N.S., Schauer C.L., Sotzing G.A., Stizel S.E., Vaid T.P., Walt D.R., Cross-reactive chemical sensor arrays. Chem. Rev., 2000, 100, 2595–2626.
2. Aparicio R, Rocha S.M., Delgadillo I., Morales M.T., Detection of rancid defect in virgin olive oil by the electronic nose. J. Agric. Food Chem., 2000, 48, 853–850.
3. Burl M.C., Doleman B.J., Schaffer A., Lewis N.C., Assessing the ability to predict human percepts of odor quality from the detector responses of a conducting polymer composite-based electronic nose. Sensors and Actuators B, 2001, 72, 149–159.
4. Clarke R.J., The flavour of coffee. 1986, *In:* Food Flavours. Part B. The Flavour of Beverages. (eds. I.D. Morton, A.J. Maclead), Elsevier, Amsterdam-Oxford--New York-Tokyo, pp. 1–47.
5. The Cyranose 320 Electronic Nose, User's Manual part number 11 60001, CYRANOSciences, Inc.
6. Freund M.S., Lewis N.S., A chemically diverse conducting polymer-based "electronic nose". Proc. Natl. Acad. Sci., USA, Chemistry 1995, 92, 2652–2656.
7. Friedman J.H., Kohari R., Yun Y., Lazy Decision Trees. 1996, *In*: Proceedings of the Thirteenth National Conference on Artificial Intelligence and the Eighth Innovative Applications of Artificial Intelligence Conference. (eds. H. Shrobe, T. Senator). AAAI Press, Menlo Park, California, pp. 717–724.
8. Gardner J.W., Bartlett P.N., A brief history of electronic noses. Sens. Actuators B, 1994, 18, 211–220.
9. Gray J.I., Gomaa E.A., Buckkley D.J., Oxidative quality and shelf life of meats. Meat Sci., 1996, 430, S111–S123.
10. Grigioni G.M., Margaria C.A., Pensel N.A., Aroma of fresh and processed meat assessed by an electronic nose. 46th ICoMST 2000, 591.
11. Li J., On board signal processing the brains of the Cyranose 320. http://cyranosciences.com/technology /onboard.html, 2002, 1–4.
12. Li J., The Cyranose chemical vapor analyzer. http://www. .sensormag.com/articles/0800/56/main.shtml, 2003, 1–9.
13. Lonergan M.C., Severin E.J., Doleman B.J., Beaber S.A., Grubbs R.H., Lewis N.S., Array-based vapor sensing using chemically sensitive, carbon black-polymer resistors. Chem. Mater., 1996, 8, 2298–2312.
14. Malnic B., Hirono J., Sato T., Buck L.B., Combinatorial receptor codes for odors. Cell 96, 1999, 713–723.
15. Mottram D.S., Chemical tainting of foods. Int. J. Food Sci. Techn., 1998, 33, 19–29.
16. Pearce T.C., Computational parallels between the biological olfactory pathway and its analogue "The Electronic Nose": Part II. Sensor-based machine olfaction. BioSystems, 1997a, 41, 69–90.
17. Pearce T.C., Computational parallels between the biological olfactory pathway and its analogue "The Electronic Nose": Part I. Biological olfaction. BioSystems, 1997b, 41, 43–67.
18. Witten I.H., Frank E., 1999, Data Mining: Practical Machine Learning Tools and Techniques with Java Implementation, Morgan Kaufmann.