What happens at the aroma of coffee beans after roasting?

MOX nanowire technology by Novel Electronic Nose to discover the finger print

Veronica Sberveglieri^{1,2}, Andrea Pulvirenti^{1,2}

Department of Life Sciences University of Modena and Reggio Emilia Via Amendola2, 42014 Reggio Emilia, Italy

2 CNR-IDASC Sensor Lab Via Valotti 9, 25133, Brescia, Italy

veronica.sberveglieri@unimore.it

Abstract— The coffee aroma is one of the most important quality evaluation criteria employed for coffee commercialization and consumption.

The purpose of this study was following the roasting process VOCs creations with the novel Electronic Nose equipped whit 2 of 6 MOX nanowire sensors.

The nanowires exhibit exceptional crystalline quality and a very high length-to-width ratio, resulting in enhanced sensing capability as well as long-term material stability for prolonged operation.

Four different methods of roasting, made by ROSTAMATIC (Table 1) machine, were applied to gain a clearer picture of the differences in roasted coffee aromas by means of a volatile compound analysis. Different methods applied on four different origins of green coffee (India, Indonesia, Honduras, Santos and Nicaragua).

The commercial coffees products are made from a blending from minimum five different kinds of coffee and the consumers have developed an addiction/expectation to a specific flavor and taste.

Different methods of roasting process will provide the coffee different aroma that will add flexibility to those one that already posses the matrix due to different origins.

This work tests and illustrates the broad spectrum of potential uses of the EN technique in food quality control.

Keywords-component; MOX nanowire sensors, electronic nose, coffee beans, GC-MS, colorimeter.

I. INTRUDUCTION

Certification is one of the most challenging matters in food quality control. In the last years, the interest toward the development of novel methods for testing the authenticity of food products has experienced a wide growth, in specific for those brilliant with high market prices[1].

The aim of roasting is to release all the aromatic potential of a specific green coffee origin. Over 1000 volatile compounds are produced, but only about 25–35 are considered as key odorants, responsible for the coffee flavor[2].

Elisabetta Comini^{2,4}, Estefania Nunez Carmona^{1,3}

3 CNR-IBF Via Ugo la Malfa 153, 90146, Palermo Italy

4 University of Brescia, Dep. of Information Engeneering, Via Branze, Brescia, Italy

Green coffee beans are moderately simple to distinguish on the basis of their size, shape and color; in case of roasted beans, a size-based discrimination could be achieved as well. Conversely, the identification and the quantification of Arabica and Robusta in roasted and ground coffee blends results very challenging[3].

Including the highly valuated products, coffee represents the second commodity in the world from the economical point of view, including Africa, Asia and Latin America as the main exporting partners, involving moreover more than 70 coffeeproducing nations, while the export involves more than 150 countries (http://www.faostat.fao.org).

Coffee flavor is enormously complex and ascends from 700 chemicals compounds currently identified, biological and physical characteristics intensely depending on cultivar, coffee cherry maturity, geographical growing location, production, processing, roasting and cup preparation[4][5]. Not shockingly there is a large volume of published research defining the volatile and non-volatile compounds in coffee and that are likely to be playing a role in coffee flavor[6]. Roasting temperature, time, method of roasting and cooling all affect the volatile composition[7]–[9]. The degree of roast effects the formation and degradation of the different volatiles and the final coffee quality[10].

The evolution of bottom-up methods for nanostructure fabrication led to the production of quasi one-dimensional structures in a variety of interesting morphologies spanning from simple nanowires, nanotubes, nano-belts to complex and heterogeneous hierarchical structures[11]-[13]. In particular, metal-oxides (MOX) are attracting an increasing interest for both fundamental and applied research as MOX nanowires feature well-defined crystalline structures, chemical composition and surface termination[2], [14]. In addition, nanowires exhibit physical properties, which are significantly different from their polycrystalline counterpart. The high degree of crystallinity and atomically sharp terminations make nanowires very promising for the development of a new generation of gas sensors; they reduce the problem of instability, typical in polycrystalline materials, which is

associated with grain coalescence and drift of electrical properties [2].

At SENSOR laboratory the studies on chemical sensors started in 1988 with the development of thin films and then of a new technique for the preparation of thin films with a highly porous structure, then the focus was broadened to other oxides and to catalysation and doping processes. Since the reduction of crystallite size produces a significant increase in sensor performance the research is focused on the fabrication of materials with small crystallize size, which maintained their stability over long-term operation at high temperature.

The basic idea of "top-down" approaches is to use existing technology developed by semiconductor industries to micro fabricate nanostructures. This class of techniques uses deposition, etching and ion beam milling on planar substrates in order to reduce the dimensions of the structures to a nanometer size. Using these techniques it is possible to obtain highly ordered nanostructures, but they are very expensive both in terms of costs and preparation times.

The second approach is the "bottom up", which consists of the assembly of molecular building blocks, like vapor phase transport, chemical synthesis, electrochemical deposition, solution-based techniques and template growth. With these techniques it is possible to prepare high purity nano crystalline materials at reduced cost having more control of the growth process, although it is difficult to integrate fabricated nanostructure on planar substrate and have them well arranged and patterned. In this article we will focus on vapor phase growth and liquid phase methods used in our laboratory[14] Fig.1.

The Novel Electronic nose (EN EOS 835) was equipped with two of six sensors made with this advanced techniques (Table 2).

II. MATERIALS AND METHODS

The green coffee beans, from four different origins (India, Indonesia, Santos, Honduras, Nicaragua), was roasted in the ROSTAMATIC machine follow one of the four programmed steps, named, MONO, MIXTURE, ROYAL and AROMATIC.

ROSTAMATIC machine system called "easy roasting", roasting curve setup, exhaust and cooling machines. System roasting equipped with the drum breezy.

All the origins have been roasted using the different process.

At the end of the roasting processes we have obtained 16 different types of roasted coffee.

The roasted coffee obtained was grinded with IKA A11 basic Analytical mill, for a few minutes to obtain a uniform mesh of coffee powder.

The powder was used to fill the vials for the novel EN.

The novel EN is equipped with a carousel of 40 positions, fundamental device to have the possibility to follow the analysis also during the night and to remove the humans errors linked to the injections[15], [16].

Cycle of Roasting			
Name	Time (minute)	Temperature (°C)	
MONO	212	10	
MIXTURE	214	12	
AROMATIC	216	18	
ROYAL	218	14	

Table 1 ROSTAMATIC Parameter.

Four different methods of roasting, made by ROSTAMATIC machine, were applied to gain a clearer picture of the differences in roasted coffee aromas by means of a volatile compound analysis.

The effect of roasting variation was also captured using colorimetric measurement.

The colorimeter is able to provide information regarding the homogeneity of the sample analyzed.

This kind of measure was done on all the origin of coffee beans.

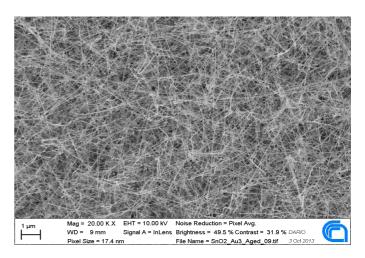


Fig.1: SEM image of SnO2 nanowires synthetized by evaporationcondensation technique.

III. RESULTS AND DISCUSSIONS

In general, volatile chemicals compounds (VOCs) always play an important function in the palatability and preferences for heat-treated of foodstuff and beverages[10].

Also, the specific conditions of heat treatment significantly influence the final flavor of foods and beverages. The present study found that the Novel Electronic nose is able to recognize the roasting conditions significantly changed the concentrations of certain volatile chemicals in coffee beans.

The PCA score PLOT Fig. 2 was obtained using the feature extraction algorithm, FFT, Fast Fourier transform of signal.

If P1=0 then the FFT is normalized at the max point of BEFORE step otherwise it isn't normalized. If P2=1 the FFT

is made only with the DURING step otherwise it's made with the DURING and AFTER step. P3 and P4 represent the FFT components used as features. Min=1, Max=500[16].

The results obtained with the colorimeter were able to give to us an answer about the homogeneity of the samples.

The results achieved show that the significative difference relapse between the origins more than between roasting methods Fig. 3.

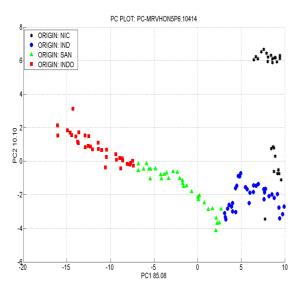


Fig. 2 PCA score PLOT of 4 different kinds of roasted coffee beans.

IV. CONCLUSIONS

All the described case studies showed promising results, thus confirming that our novel EN could represent a rapid device for monitoring and improving the microbiological quality of foodstuff. This work attests that the electronic nose, once trained, is a potential and useful (rapid and economic) tool. A kind of sensor technology like a novel EN provides a faster and stabile response of finger print in food matrix than the conventional and classical techniques (also compared with the commercial EN equipped only with traditional MOX sensors). The new sensors technology is able to improve the capacity of the threshold of the EN. Really important parameter if this technique is applied on food that not always gives a big quantity of aroma. Aroma sometime produced also by microrganism or chemicals in a random way during the food chain[17].

The obtained results show that different roasting methods give completely different effects on the origins. The electronic nose is able to distinguish the different features and to find also the similarities[18]. The differences like the similarities, are useful tools for the coffee-chain to obtain the desired blend. The other techniques applied in this study are in good agreement with the EN[19].

Table of Sensors			
Sensors	Nanowire	Temperature (°C)	
Sn-NW1	Х	350	
Sn-NW2	Х	400	
SnO2_bs1		450	
ZH0504		380	
SnO2 Au_bs2		480	
SU0303		450	

Table 2. Array of sensors used for the novel electronic nose, with 2 of six nanowire.

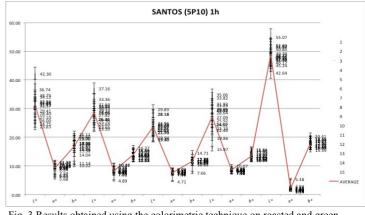


Fig. 3 Results obtained using the colorimetric technique on roasted and green coffee beans from Santos (Brazil).

ACKNOWLEDGMENT

This work was partially supported by CAFIS "Utilizzo di tecniche analitiche per la determinazione di indici di qualità nel caffè verde, tostato e macinato", ProgettoOperativo FESR 2007-2013–CUP G73F12000120004.

REFERENCES

- P. D. C. Mancha Agresti, A. S. Franca, L. S. Oliveira, and R. Augusti, "Discrimination between defective and non-defective Brazilian coffee beans by their volatile profile," *Food Chem.*, vol. 106, no. 2, pp. 787–796, Jan. 2008.
- [2] G. Sberveglieri, I. Concina, E. Comini, M. Falasconi, M. Ferroni, and V. Sberveglieri, "Synthesis and integration of tin oxide nanowires into an electronic nose," *Vacuum*, vol. 86, no. 5, pp. 532– 535, Jan. 2012.

- [3] J. W. Gardner, H. V. Shurmer, and T. T. Tan, "Application of an electronic nose to the discrimination of coffees," *Sensors Actuators B Chem.*, vol. 6, no. 1–3, pp. 71–75, Jan. 1992.
- [4] D. D. Roberts, P. Pollien, and C. Milo, "Solid-phase microextraction method development for headspace analysis of volatile flavor compounds.," *J. Agric. Food Chem.*, vol. 48, no. 6, pp. 2430–7, Jun. 2000.
- [5] T. Dewettinck, K. Van Hege, and W. Verstraete, "The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater.," *Water Res.*, vol. 35, no. 10, pp. 2475–83, Jul. 2001.
- [6] O. Gonzalez-Rios, M. L. Suarez-Quiroz, R. Boulanger, M. Barel, B. Guyot, J.-P. Guiraud, and S. Schorr-Galindo, "Impact of 'ecological' post-harvest processing on the volatile fraction of coffee beans: I. Green coffee," *J. Food Compos. Anal.*, vol. 20, no. 3–4, pp. 289–296, May 2007.
- [7] C. Yeretzian, A. Jordan, R. Badoud, and W. Lindinger, "From the green bean to the cup of coffee: investigating coffee roasting by online monitoring of volatiles," *Eur. Food Res. Technol.*, vol. 214, no. 2, pp. 92–104, Feb. 2002.
- [8] F. Mestdagh, T. Davidek, M. Chaumonteuil, B. Folmer, and I. Blank, "The kinetics of coffee aroma extraction," *Food Res. Int.*, Mar. 2014.
- [9] J. S. Ribeiro, M. M. C. Ferreira, and T. J. G. Salva, "Talanta Chemometric models for the quantitative descriptive sensory analysis of Arabica coffee beverages using near infrared spectroscopy," *Talanta*, vol. 83, no. 5, pp. 1352–1358, 2011.
- [10] J.-K. Moon and T. Shibamoto, "Role of Roasting Conditions in the Profile of Volatile Flavor Chemicals Formed from Coffee Beans," J. Agric. Food Chem., vol. 57, no. 13, pp. 5823–5831, Jul. 2009.
- [11] E. Comini, C. Baratto, I. Concina, G. Faglia, M. Falasconi, M. Ferroni, V. Galstyan, E. Gobbi, A. Ponzoni, A. Vomiero, D. Zappa, V. Sberveglieri, and G. Sberveglieri, "Metal oxide nanoscience and nanotechnology for chemical sensors," *Sensors Actuators B Chem.*, Oct. 2012.

- [12] S. Kandasamy, a. Trinchi, M. K. Ghantasala, G. F. Peaslee, a. Holland, W. Wlodarski, and E. Comini, "Characterization and testing of Pt/TiO2/SiC thin film layered structure for gas sensing," *Thin Solid Films*, vol. 542, pp. 404–408, Sep. 2013.
- [13] D. Zappa, E. Comini, R. Zamani, J. Arbiol, J. R. Morante, and G. Sberveglieri, "Preparation of copper oxide nanowire-based conductometric chemical sensors," *Sensors Actuators B Chem.*, vol. 182, pp. 7–15, Jun. 2013.
- [14] E. Comini, C. Baratto, I. Concina, G. Faglia, M. Falasconi, M. Ferroni, V. Galstyan, E. Gobbi, A. Ponzoni, A. Vomiero, D. Zappa, V. Sberveglieri, and G. Sberveglieri, "Metal oxide nanoscience and nanotechnology for chemical sensors," *Sensors Actuators B Chem.*, no. 2010, Oct. 2012.
- [15] M. Falasconi, I. Concina, E. Gobbi, V. Sberveglieri, a. Pulvirenti, and G. Sberveglieri, "Electronic Nose for Microbiological Quality Control of Food Products," *Int. J. Electrochem.*, vol. 2012, pp. 1– 12, 2012.
- [16] E. Ongo, M. Falasconi, G. Sberveglieri, a. Antonelli, G. Montevecchi, V. Sberveglieri, I. Concina, and F. Sevilla III, "Chemometric Discrimination of Philippine Civet Coffee Using Electronic Nose and Gas Chromatography Mass Spectrometry," *Procedia Eng.*, vol. 47, pp. 977–980, Jan. 2012.
- [17] E. N. Carmona, V. Sberveglieri, and A. Pulvirenti, "Detection of microorganisms in water and different food matrix by Electronic Nose," 2013 Seventh Int. Conf. Sens. Technol., pp. 699–703, Dec. 2013.
- [18] V. Sberveglieri, E. Comini, R. Emilia, V. Amendola, and R. Emilia, "Electronic nose for the early detection of different types of indigenous mold contamination in green coffee," 2013 Seventh Int. Conf. Sens. Technol., pp. 465–469, 2013.
- [19] V. Sberveglieri, E. N. Carmona, E. Comini, A. Ponzoni, D. Zappa, O. Pirrotta, and A. Pulvirenti, "Research Article A Novel Electronic Nose as Adaptable Device to Judge Microbiological Quality and Safety in Foodstuff," *Biomed Res. Int.*, vol. 2014, pp. 1–6, 2014.