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Invited Review Article: An odor-sensing system—powerful technique for foodstuff studies

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This work examines gas sensor array technology combined with multivariate data processing methods and demonstrates a promising potential for rapid, non-destructive analysis of food. Main attention is focused on detailed description of sensor used in e-nose instruments, construction, and principle of operation of these systems. Moreover, this paper briefly reviews the progress in the field of artificial olfaction and future trends in electronic nose technology, namely, e-nose based on mass spectrometry. Further discussion concerns a comparison of artificial nose with gas chromatography-olfactometry and the application of e-nose instruments in different areas of food industry. © *2011 American Institute of Physics*. [doi:10.1063/1.3660805]

NOMENCLATURE

AGS	Amperometric gas sensors
ANN	Artificial neural network
BAW	Bulk acoustic wave
BP-ANN	Back-propagation ANN
CA	Cluster analysis
CART	Classification and regression trees
CCA	Canonical correlation analysis
CDA	Canonical discriminant analysis
CP	Conducting polymer
CP-ANN	Counterpropagation ANN
DA	Discriminant analysis
DCM	Dichloromethane
DFA	Discriminant function analysis
DHS	Dynamic headspace
DMMP	Dimethyl methylphosphonate
EC	Electrochemical cell
EN	Electronic nose
FAIMS	High-field asymmetric waveform ion mobility spectrometry
FCM	Fuzzy C-means algorithm
FDA	Factorial discriminant analysis
FFA	Free fatty acids
FID	Flame ionization detector
FO	Fiber optic
FW	Feature weighting
GA	Genetic algorithm
GC	Gas chromatography
GC×GC	Two-dimensional gas chromatography
HCA	Hierarchical clustering analysis
HPLC	High performance liquid chromatography
ICA	Independent component analysis
IMS	Ion mobility spectrometry
INDEX	Inside-needle dynamic extraction
IR	Infrared
KNN	K-nearest neightbour algorithm
KSOM	Kohonen SOM
LDA	Linear discriminant analysis
LOD	Level of detection
LVQ-NN	Learning vector quantisation neural network
MAPLE	Matrix-assisted pulsed laser evaporation
MDA	Multiple discriminant analysis
MDS	Multidimensional scaling
MEMS	Micro-electro-mechanical systems
MOS	Metal oxide semiconductor
MOSFET	Metal oxide semiconductor field effect transistor
MS	Mass spectrometry
MVA	Multivariate analysis
NOSE	Neotronics olfactory sensing equipment
O	Olfactometry
OD	Olfactometric detector
ORs	Olfactory receptors
PARAFAC	Parallel factor analysis
PARC	Pattern recognition
PCA	Principal component analysis
PDMS	Polydimethylsiloxane
PID	Photo ionization detector
PLS	Partial least squares
PLS-DA	PLS-discriminant analysis
PNN	Probabilistic neural network
PTFE	Polytetrafluoroethylene
P&T	Purge and trap
QC	Quality control
QCM	Quartz crystal microbalance
QDA	Quadratic discriminant analysis
QLSR	Quadratic least squares regression
RBF	Radial basis function
RP-HPLC	Reverse phase - HPLC
SAW	Surface acoustic wave
SCA	Spectral clustering analysis
SHS	Static headspace
SHSA	Static headspace analysis
SIMCA	Soft independent modeling of class analogy
SLDA	Stepwise linear discriminant analysis
SOM	Self-organizing map
SPME	Solid-phase microextraction

SPR	Supervised pattern recognition
SVM	Support vector machine
TDNN	Time-delay neural networks
TOFMS	Time-of-flight mass spectrometry
TSM	Thickness shear mode
TSMR	Thickness shear mode quartz resonator
UV	Ultraviolet
VOCs	Volatile organic compounds
WPTER	Wavelet packet transform for efficient pattern recognition

I. INTRODUCTION

The need to provide proper quality for food products is becoming one of the main priorities in food processing technology.[1] One of the outcomes of such concern is the development and optimization of monitoring and control methods, both concerning food stocks, their processing as well as final products. The analysis of compounds responsible for taste and smell (the entirety of taste-aromatic sensations), carried out through classic sensorial analysis[2] or with the use of instrumental methods[1–3] constitutes a valuable source of information about the quality of a given product.

Excluding classic instrumental techniques (mainly chromatographic), in food analysis, two types of equipment based on electronic sensors are increasingly being employed. Depending on the type of analytes, e-nose and e-tongue instruments are regularly utilized.[4] The first performs an entirely aromatic analysis (volatile compounds) in the gaseous phase, without separating the aroma into individual aromatic components. The second type allows for the determination of components of medium and low volatility in the liquid phase and complements the first one.[5] Both types of equipment consist of arrays of non-selective gas or liquid sensors and are provided with a pattern recognition system, capable of identifying simple or complex taste and aromatic profiles.[6] Such equipment is quick-acting, easy to operate and it does not influence the analyzed sample.[7] It is also an alternative to relatively costly food quality evaluation methods such as: gas chromatography coupled with mass spectrometry (GC-MS) and/or olfactometry (GC-O),[6–10] infrared spectroscopy (IR), and classical sensory analysis.[2] The last is still the most often used technique and is the determinant of food quality analysis, especially of semi- and final products. This method is characterized by many limitations,[13] such as the fallibility of the human factor (e.g., the sensorial sensitivity of the evaluating person, his/her state of health, comfort or fatigue), low reproducibility and repeatability of results, as well as the unfeasibility of identifying compounds affecting taste and no possibility of performing a quantitative analysis.

Such numerous drawbacks of sensory analysis help explain the development of alternative methods for the evaluation of the sensory quality of food,[14] mainly electronic nose and tongue instruments.[15–17] In this paper, attention is mostly given to e-nose instruments. A short history of the development of such devices, their construction and operating principles will be presented, as will be a review of the sensors and data analysis methods employed in these systems, and the possibility of e-nose instrument applications in food industry.

II. SENSATIONS OF TASTE AND SMELL

The basis of sensory evaluation of food products is formed by the sum of taste and smell sensations collected by human senses.

A. Sense of taste

Taste (gustatory) sensations received by humans and animals originate as a result of a substance having contact with specialized chemoreceptors called taste receptors, which are clustered in the taste buds present in the whole oral cavity (on the tongue, palate, throat, and tonsils).[18] Groups of taste buds are located on small papillae, which differ in number and shape, depending on their location. Adults have about 10 000 taste buds,[15] sited according to the taste to which they react, along the tongue (Fig. 1). There are about 50–150 rod-shaped taste cells inside each taste bud, responsible for the transfer of information to a neuron, which transmits a pulse to the brain.[15,18] Five types of taste receptors can be distinguished.[19,20] They correspond to given groups of chemical substances present in food and beverages. Receptors are sensitive to their proper tastes: bitter, sweet, salt, sour, and umami and placed in the appropriate section of the tongue (Fig. 1).[19] Each of the basic taste sensations has a different taste threshold (Table I) with sweet and salty materials having the highest. Sour substances have an intermediate threshold

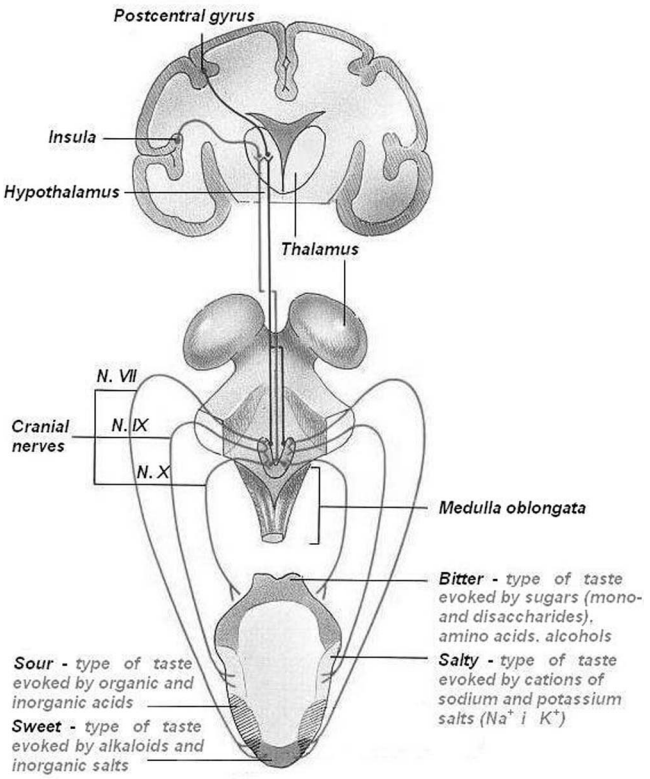

FIG. 1. Distribution of basic taste sensations and the taste pathways (umami is probably evenly distributed across the tongue).

TABLE I. Threshold levels for primary taste sensations.[a]

Taste	Substance	Taste threshold level ($M \times 10^{-6}$)
Sweet	Glucose	8 0000
	Sucrose	1 0000
Salty	Sodium chloride	2000
Sour	Hydrochloric acid	100
Bitter	Quinine	8
	Strychnine hydrochloride	1.6
Umami	Monosodium glutamate (MSG)	5

[a]References 18, 20, and 22.

TABLE II. Odor threshold of common odoriferous substances.

Substance	Odor threshold (in air)
Ethane	25 300 ppm
Butane	2700 ppm
Acetylene	565 ppm
Ethyl ether	5.83 ppm
Chloroform	30 ppb
Iodoform	20 ppb
Butyric acid	9 ppb
Methyl mercaptan	0, 4 ppt

value while bitter substances have the lowest one.[18,21] This probably relates with the fact that bitter serves a protective function against poisons (e.g., dangerous alkaloids), thus its sensitivity is high.[11–13]

The outlined taste sensations can be divided according to the taste-distinguishing mechanism into two groups:

- for sour and salty taste – hydrogen and sodium ions, respectively, which directly react with ionic channels by changing the membrane potential of receptor cells,[18,23]
- for sweet and bitter taste – there are protein receptor spots connected with the G protein, which, after forming a complex with a taste substance molecule, activate the G protein, leading to a series of chemical changes.[4]

Both these mechanisms finally cause the excitation of a nerve pulse, which travels through the nervous system to the brain.

B. Sense of smell

Sense of smell is one of two (along with the sense of taste) chemical senses. As a matter of fact, it is based on the ability to recognize default chemical compounds or their mixtures in the surroundings.[18,24] Smell sensory functions can be divided into following basic steps: determination of flavor in surroundings, sniffing, intensity determination of substance that is the source of flavor; or more complex: learning how to identify and differentiate flavors, remembering and integrating different flavors.[25] Ability of integrating different flavors is a very refined function of smell sense – it allows to predict and to learn connections of components that will combine to create a new flavor.[26]

The olfactory system used by humans is able to recognize and discriminate flavor compounds (about 10 000 chemicals) with high sensitivity and accuracy.[15,22] Levels of some odoriferous (smell producing) substances that can be detected by a normal healthy person are on the order of parts per trillion, with even stereoisomers can be distinguished.[22] For example, methyl mercaptan, a compound which gives garlic its characteristic aroma, has extremely low threshold of olfactory detection (less than 500 pg/L of air).[21] On the other hand, for substances such as acetylene, ethane and butane, odor thresholds are much higher[14] (Table II).

Unlike taste, it has not been easy to classify aromas into different groups. Researchers have suggested that the number of primary classes of olfactory sensations can be varied between 7 and 50.[22] Odorant molecules are generally light (relative molecular masses up to approximately 300 Da), small, polar, and often hydrophobic[13,14] organic compounds containing one or two functional groups.[27] Simple odors (e.g., an alcohol) contain only one type of odorant molecule while complex odors consist of hundreds or even thousands different chemical components each in varying concentration.[14,15]

Smell sense, in evolutionary point of view, is one of the oldest senses. The part of the human brain that handles the sense of smell is very much similar to its equivalent in reptiles, meaning the sense of smell evolved long before the segregation of mammals. Humans and other mammals are able to sense of high number of volatiles as having different flavor. This ability is caused by the existence of a large family of olfactory receptors (ORs) that number about 5×10^6 in human (as many as a mouse), 10×10^6 in rat, and $100–300 \times 10^6$ in dog (depending on breed).[28,29] ORs are seven-transmembrane domain G protein-coupled receptors, which are encoded by a large number of genes.[30,31] The amount of genes is estimated and varies from about 100 for fish, 1200–1500 for mice, 1300 for dog, to over 2000 for rat.[29,31,32] In case of human, Buck and Axel[30,33] identified 339 intact OR genes and 297 OR pseudogenes. This multigene family constitute 3% of whole human genome.[30,31]

The human nose is similar to a tri-cornered pyramid, partitioned by an internal wall, the nasal septum. It is formed by an orbital lamina perpendicular to the ethmoid bone at the top and by a tetragonal copula at the lower end.[21,26,34] The nasal cavity consists of two nasal tubes divided by a partition and of side walls with additional forms, turbinated bones and paranasal sinuses. At the front there are anterior nares, and at the rear the nasal fossa joins the nasal-pharyngeal fossa through choanae. The olfactory epithelium is located in the upper part of the nasal fossa, in the region of the nasal septum, the roof of the nasal cavity and at the front end of the superior nasal concha.[21,34] In humans, it covers an area of about 1–3 cm^2, i.e., many times less than in animals.[4,21,35] The olfactory epithelium is built of olfactory cells, basal cells, and sustentacular cells. An olfactory cell is a nerve cell (neuron) with two protoplasmic protrusions.[4] One of the protrusions is tipped with a bladder topped by olfactory hairs (cilia) protruding from among the basal cells above the epithelium's surface. The other protrusion conducts impulses from the cell body – it

functions as an axon. Olfactory cells are neurons with a double function: they are simultaneously chemical receptors and pulse-conducting cells.[21,26,34] The olfactory cells are in direct contact with the environment. This is the only place in the human organism in which nerve cells directly receive stimulus from the external world. Receptor cells are located on the sustentacular cells – associated with structural support.[34] A human being reacts on average to more than 100 thousand natural and artificial odors.[15,22,35] Only about 2% of an aromatic substance reaches the olfactory epithelium, which is a specific form of defense of the Ors.[21,34] To stimulate a single cell, less than 10 flavor molecules are sufficient. In the mucus layer, the hydrophobic molecules are being dissolved, which increases their concentration. This is the first mechanism of amplifying the olfactory signal. After the flavor molecule becomes bound with the protein cilia of the first neuron, the redundant molecules are removed through mucus efflux, enzymatic degradation in sustentacular cells, and permeation to the intercellular space and to the vascular system.[4,21,26] From the millions of olfactory cells containing about a thousand different protein receptors, olfactory information is transferred to the proper analyzer in the brain,[14,21,35] where their perception is estimated (i.e., undergoes the analysis of sensation features, which allows to distinguish the flavor and to determine its intensity).[24,36]

The senses of smell and taste are functionally connected[4,34] (Fig. 2) and they are firmly linked with the function of the digestive system. Their common links are confirmed by the fact that partial disconnection of the sense of smell, e.g., during a heavy attack of common cold, leads to a change in the perceived taste of a meal. All the other senses also have an impact on the perception of flavor, providing a huge information flow, which is continuously being processed.[24]

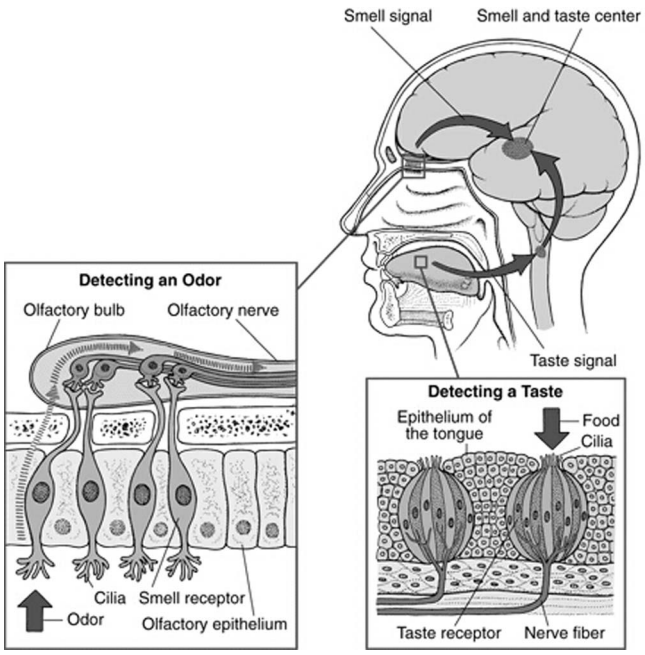

FIG. 2. Connection of olfactory and gustatory systems.

III. ELECTRONIC NOSE DEFINITION

The electronic nose (EN, synonyms: artificial nose, mechanical nose, odor sensor, flavor sensor, aroma sensor,[37] odor-sensing system[38] or multi-sensor array technology,[39] electronic olfactometry[40]) is an instrument which mimics the sense of smell. The device is designed to detect and discriminate among complex odors using array of chemical sensors. The sensor array, under influence of an odor stimulus, generates a characteristic fingerprints or smellprint. Using a database constructed on the base of patterns or fingerprints from human odors and trained pattern recognition system it is possible to classify and identify unknown odors. In recent years, the classical sensor types used for e-noses have been enhanced and complemented by other technologies introduced in this field. In last decade, beside chemical sensors, e-nose systems based on mass spectrometer or fast gas chromatography have been also introduced.[41]

A. Brief history of the electronic nose

The term "electronic nose" was introduced by Gardner in 1988 as the informal name of a device consisting of a set of chemical sensors connected with a pattern recognition system, thereby permitting to distinguish and discriminate simple and complex aromas.[38,42,43] However, the history of this technology is much older and goes back 40 years before the term had been introduced.

In 1961 Moncreiff described a mechanical olfactory instrument.[44] This started a series of research on a system imitating the human olfactory system. More and more attention has been paid to redox reactions of aromatic compounds occurring at electrodes, to conductivity of these compounds and to many other aspects. In 1964, another artificial olfactory system was presented by Wilkens and Hartman. Theirs system relied upon the electrochemical effects of odorants at a number of electrodes.[45,46] The first e-nose instruments were very primitive.[46,47] Despite this fact, it has been found that the chemical reactions between markers and various sensors can be appropriately processed (a chemical signal into an electrical one) and sufficiently amplified,[41] so that a quantitative analysis of volatile compounds at relatively low concentrations can be performed. The first report on the subject of an intelligent model of an artificial nose was published by Persaud and Dodd[48] in 1982. The aim of the first artificial noses was an attempt to detect various volatile compounds in a similar way to how the human olfactory system acts.[40,48] In order to duplicate in principle the of operation of the human nose, work was conducted on some essential aspects:[38,48]

- developing an e-nose sampling system,
- filtering the gaseous samples,
- using biochemical sensors, which could react to volatile compounds and generate a signal which could be detected and amplified, and
- developing an appropriate system for analyzing data from sensors (e.g. artificial neuron networks), which would allow for recognition of volatile flavor compounds.

The high interest in developing sensing systems led to significant progress and a breakthrough in the field of sensor design and was confirmed by numerous patents on sensor arrays suitable for the control of safety of food and beverages, microbiological measurements and medical applications.[47,49] Along with the technological progress and new possibilities for applications of the e-nose instrument, the first commercially available electronic nose instrument appeared in the early 1990-ties of the last century (AlphaMOS 1993, Neotronics and Aromascan 1994, Bloodhound and HKR Sensorsysteme 1995). Afterwards, a new type of artificial olfactory system – MS-based e-nose instrument was developed in the end of the 1990-ties.[40,50,51] Nowadays, rapid development of these systems focuses on reduction of time of volatile fraction analysis, increasing sensitivity and the simplification of instruments.

Previously, classical sensor-based e-nose instruments used static headspace as isolation technique of aroma compounds, which is certainly not sensitive enough to deal with complex food matrices.[52] In addition, gas sensor array systems have problems with drift, stability (as a result of humidity or influence of CO_2), frequent calibration, sensor poisoning, profile masking by some major components of the sample (e.g., ethanol), low sensor-to-sensor and instrument-to-instrument reproducibility, and high power consumption (e.g., MOS sensors operate at high temperature).[52–55] Current work concerning of MOS sensors has focused on micromachining to reduce power consumption, optimization modeling and sample pre-treatment to avoid poisoning.[54,56] In case of MOSFET sensors, recent development of these devices is directed to appliance of new construction materials allowing to operate at higher temperatures (possibility of detection of high boiling compounds and reduction of recovery time). For example, Wingbrant *et al*. elaborated silicone carbide based MOSFET devices.[57] The other group of sensors introduced by Curie brothers is piezoelectric sensors,[54] especially QCM and SAW sensors. Actual work is concentrated on extending of variety of coatings for these sensors for different applications,[58,59] miniaturization of sensor array (e.g., fabrication of multichannel QCM by Abe *et al*.)[60,61] and searching for more reproducible QCM and SAW sensors. On the other hand, introduction of e-nose instruments based on MS solve typical problems, found with conventional e-noses, such as sensor poisoning, profile masking, the strong influence of moisture, and the nonlinearity of signals.[40,53,55] Table III presented below shows current commercial e-nose instruments available on international market.[35,41,62–65]

IV. CONSTRUCTION AND OPERATING PRINCIPLES OF THE ELECTRONIC NOSE

The only aspect by which the electronic nose resembles the human sense of smell is its function.[47,66] The similarity results from the fact that the sensors analyse gaseous samples (like ORs) and send a signal to the pattern recognition (PARC) system, which is equivalent to brain function.[5,14] However, the operating principles, number of sensors and their sensitivity and selectivity are different.[67] For these reasons, many scientists prefer to call the electronic nose by other terms: flavor sensor, aroma sensor,[37] odor-sensing system[38] or multi-sensor array technology.[39] Usually, an e-nose instrument consists of sensors, electronics, pumps, a conditioning unit, flow-meter etc. and software for this equipment is needed for data processing and statistical analysis.[47,67] Four basic elements can be distinguished in this system (Fig. 3).

The first component is the sampling system, which eliminates all undesirable factors that could affect sensor response and ensures a stable and repeatable headspace (volatile fraction being in equilibrium with solid or liquid sample) of gas sampling environment.[68] The electronic nose instruments presently available on the market have two separate chambers in the sample-collecting system. Temperature and humidity are constantly monitored both in the sample chamber and in the sensor chamber, while the analysis is running. After headspace sampling, ambient air is applied to both chambers to prevent potential contamination (residue from previous sample and environment).[64,69] Moreover, the sample chamber must be made from non-adsorbing and inert materials, to avoid wall-memory effect.[68]

The second element is the sensing system; it is comprised by a group of several sensors measuring different flavor properties with various selectivity,[22,54,67] or by a single detecting device (e.g., a mass spectrometer) carrying out a series of measurements of a given aroma profile, or a combination of these two types.[49,70] The type and number of sensors play a key role in determining the applicability of the e-nose instrument.[64]

The third element is the data acquisition system, where the signal is processed. A distinguishing feature of this system is the recording method of the sensor response signal.[54,63] Some aromas change their profiles over time, depending on whether they are static or dynamic.[64] Thus, a data series formed by averaging signals from a sensor is more suitable. It can provide more information on aromas and an identification process for flavors is more simple and reliable.[69]

The pattern recognition system is the fourth element of an electronic nose instrument. It identifies the odor profile by comparison with known profiles from the database.[71,72] It associates each pattern to one of many possible reference classes. Odors are characterized on the basis of greater or lesser similarity of given features and they are assigned to a given class. The probability of correct identification of the odors is calculated.[73]

The sample injection stage should be primed by passing a reference gas or pure dry air through the sample and sensor chambers. This operation sets the sensor signals to a constant basic level and removes residues and impurities remaining from a previously analyzed sample.[35,64] In this way, a basic line is established. Sampling may be performed in various ways, such as headspace sampling, diffusion methods, bubbling or initial enrichment (pre-concentration).[65] The sample is placed in the sample chamber where it can be heated for headspace liberation of aromatic compounds, if necessary.[64]

The gas is pushed by a vacuum pump through a plastic or stainless steel pipe from the sample chamber to the sensor chamber or pulled in case of portable instruments.[35,63,64] The sensor array which is exposed to odor compounds is stimulated by the physical or chemical reactions of these

TABLE III. Examples of commercially available electronic nose instruments, models and technologies.[a]

Manufacturer	Model name	Technology basis	PARC method
Agilent Technologies (www.home.agilent.com)	4440A Chemical Sensor (or HP 4440)	MS	PCA
Airsense Analytics GmbH (www.airsense.com)	i-PEN, i-PEN3, PEN-2, PEN3	10 MOS sensors	ANN, PCA, LDA, DFA, PLS
	GDA 2	MOS, EC, IMS, PID	Different PARC methods available
Alpha MOS (www.alpha-mos.com)	FOX 2000, 3000, 4000, 5000	6, 12, 18 or 24 MOS sensors	ANN, PCA, DFA, PLS
	PROMETHEUS, RQ Box	MOS, EC, PID, MS	ANN, PCA, DFA, PLS
	HERACLES	Ultra Fast GC (2 FID detectors)	Radar plot, SQC, PCA, DFA, PLS, SIMCA
Applied Sensor (www.appliedsensor.com)	iAQ-2000, iAQ-100, iAQ-engine	MOS sensors	ANN, PCA
	VOCcheck, NST 3210, NST 3220, NST 3320	MOS, MOSFET, IR, QCM	ANN, PCA
Bloodhound Sensors Ltd. Scensive Technologies Ltd. (www.scensive.com)	Bloodhound BH114, Bloodhound ST214	14 Carbon black-polymers	ANN, CA, PCA
ChemSensing Inc. (www.chemsensing.com)	ChemSensing sensor array	Colorimetric sensors	. . .
Dr. Födisch AG (www.foedisch.de)	OMD 1.10, OMD 98	MOS sensors	. . .
Environics Oy (www.environics.fi)	MGD-1	IMS	PLS
Electronic Sensor Technology (www.estcal.com)	zNose model 4200, 4300, 4500, 7100	Ultra Fast GC/SAW	SPR
GSG Mess- und Analysengeräte GmbH (www.gsg-analytical.com)	MOSES II	8 QCM, 8 MOS	ANN, PCA
HKR-Sensorsysteme GmbH (www.hkr-sensor.de)	QMB6, MS-Sensor	QCM, MS	ANN, CA, PCA, DFA
Illumina Inc. (www.illumina.com)	SNP genotyping services	FO	ANN
Marconi Applied Technologies (www.marconitech.com)	eNose4000, eNose5000	CP, MOS, QCM, SAW	ANN, DA, PCA
Microsensor Systems Inc. (www.microsensorsystems.com)	Hazmatcad, VapourLab, Eagle	SAW or GC	. . .
Osmetech Plc (www.osmetech.plc.uk)	AromaScan A32S	32 CP sensors	PCA, ANN, PLS
RST Rostock System-Technik GmbH (www.rst-rostock.de)	SamDetectFF2, SamDetectFF2D, SamDetectGFD1	6 MOS sensors, QCM, SAW	ANN, PCA
Sacmi Imola S.C. (www.sacmi.com)	EOS 507, 835, Ambiente	6 MOS sensors	LDA
Shimadzu Co. (www.shimadzu.com)	FF-2A, FF-2020	MOS	PCA
Smart Nose (www.smartnose.com)	SMart Nose 300	MS	PCA, DFA
Smiths Detection Group Ltd. (www.smithsdetection.com)	Cyranose 320	32 CP sensors	PCA

[a]Notes: ANN – Artificial neural network, CA – Cluster analysis, CP – Conducting polymer, DA – Discriminant analysis, DFA – Discriminant function analysis, EC – Electrochemical cell, FID – Flame ionization detector, FO – Fiber optic, GC – Gas chromatography, IMS – Ion-mobility spectrometer, LDA – Linear discriminant analysis, MOS – Metal oxide semiconductor, MOSFET – Metal oxide semiconductor field effect transistors, MS – Mass spectrometer, PCA – Principal component analysis, PID – Photo ionization detector, PLS – Partial least squares regression, QCM – Quartz crystal microbalance, SAW – Surface acoustic wave, SPR – Supervised pattern recognition.

compounds with the active material in sensors. This leads to changes in the electrical properties of the sensors, such as conductivity.[65,73] These changes are converted into an electric signal. An instantaneous response is thus created. The intensity of the response depends upon the kind of odor.[63,73] Before measurement, it is important to maintain constant, stationary conditions of the sensor's environment. Usually, it is recommended to turn on the e-nose instrument for two or three days for stabilization. The response of the sensor array is recorded and sent to the data-acquisition system.[35] Before transferring the data to the pattern recognition system, the electric signal is processed and averaged in the data acquisition system.[22,65] The period of time during which the odor compound acts upon the sensor is called the *response time* of the sensor array[65] (Fig. 4).

The next stage is the process of sample scrubbing with the use of a carrier gas. Its purpose is the removal of olfactory substances from the whole system. This process takes anywhere from several seconds to a minute.[35] Finally, for the last step, the reference gas is passed through the whole e-nose system to prepare it for the next measurement. The time period of cleaning up of the apparatus with scrubbing gas and the reference gas is called recovery time.[14,42,63] After this operation, the sensors return to their base state.[65] Each odor is accompanied by a characteristic reference response of the sensor array, its fingerprint.[49,74,75] In regard to that fact, carrying out many measurements it is possible to create a reference library of known odor profiles. The total response of the sensor array is unique for a specific odor, which is the base of distinguishing odors by the system.[65] Like the human sense of smell, the e-nose instrument can "learn" new references, by adding and storing them in the database. Such systems can link "freshly learned" references with appropriate odor profiles.[74,76]

The appropriate training process allows for effective identification process. Sensors are designed for specific groups of chemical substances.[65] In spite of this, their

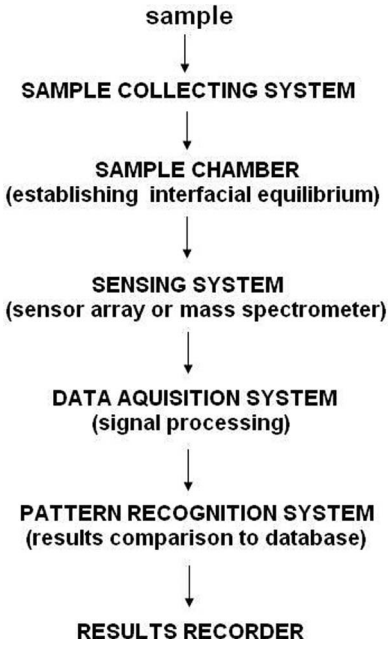

FIG. 3. Electronic nose construction scheme.

response can be actuated by a broader spectrum of compounds. However, the pattern of response is unique for each odor profile.[64,74] To carry out a training procedure of the e-nose instrument, a large number of known samples are analyzed and they can be subsequently divided into classes.[22,27] The next step is the validation of the procedure to check its correctness.[49]

To the end of XX century, the majority of systems were intended for laboratory use. Many of them were heavy, large, and relatively expensive.[35] They are very helpful in many applications, but they have two main disadvantages. They do not allow an *in situ* analysis, and in some applications they are incapable of determining all volatile compounds essential for a given analysis.[77] In order to solve this problem, a number of manufacturers have started to design a portable, miniaturized version of the e-nose instrument.[35,78] Several commercial versions of such products are available on the market and can be hold in one hand.[79,80] Size of these instruments varies from

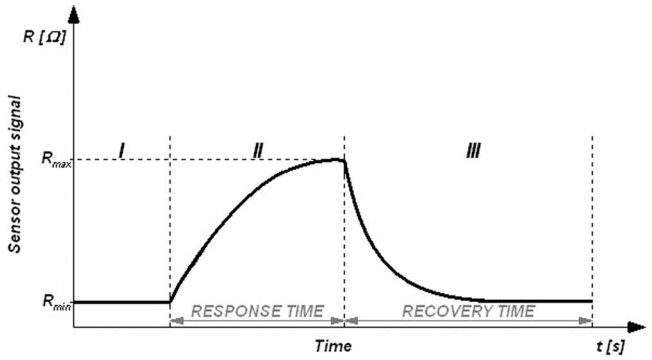

FIG. 4. Characteristic of the response of e-nose chemoresistive sensor (MOS or CP) to an odorant. R_{min} is the baseline resistance and R_{max} the resistance in the odor (I – flow of reference gas, II – measuring sample headspace, III – recovery step) (Refs. 14, 42 and 65).

a few to over a dozen centimeters.[79,81] Nowadays, such instruments are less expensive. It is also important that such a portable instrument contains a sample chamber, as many of them do not have one. This adversely impacts the feasibility of obtaining repeatable results, because impurities originating in the environment may influence the response of the sensor array.[64,68]

V. SENSOR ARRAYS IN ELECTRONIC NOSE SYSTEMS

Sensors are the main, most important elements of an e-nose instrument. Their function is to provide information on measured parameters.[35,64,75] This process is a transformation of one form of energy into another. The output signal may take the form of mechanical, electrical, magnetic or chemical energy, as well as heat and radiation.[26,41,43,63,74]

The sensors on an electronic nose system should be selectively sensitive to odors which may be present in a given kind of tested sample[82] (for a specific application, e.g. samples of air, food, explosives etc.). They can be divided into five categories: conductive, piezoelectric, electrochemical, optical (smell-sensing) sensors, and those based on gas chromatography and mass spectrometry. The first two groups of sensors substantially differ from the others so that they may be classified in still another way.

Sensors can be divided into two classes: "hot" and "cold" sensors.[47] The first can operate at higher temperatures, but their range of application is severely constrained. Their advantage is reduced susceptibility to humidity.[39]

A. "Cold" class conductivity sensors

We can distinguish three types of conductive sensors: conducting polymers (CP),[66] MOS,[83–85] and MOSFET.[7,86] Their resistance changes when exposed to volatile organic compounds (VOCs). The operating principle relies on changes in some properties of the material from which they are made, as a result of an action of a gas or odor, which leads to a change in resistance of these sensors. The mechanism causing the resistance change is different in each type of sensor, but the construction and placement of individual elements in conductive sensors is basically the same[47,65] (Fig. 5).

1. Conducting polymer sensors

Intrinsically conducting materials, conducting polymer composites and metal oxides are three of the most commonly utilized classes of sensing materials in conductivity sensors. Interaction of a gas/odor with these conducting materials leads to a change in resistance in the sensor. The mechanisms that lead to these resistance changes are different for each material but the structure and layout of these sensors are essentially the same.

a. Intrinsically conductive polymer chemiresistor arrays The conducting layer in this type of sensor was until recently made from organic conducting polymers

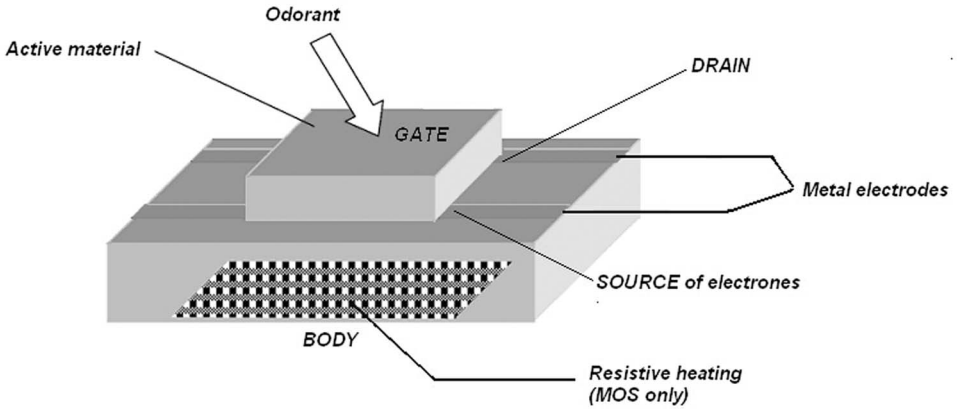

FIG. 5. Simplified scheme of conductive sensors.

(CPs). CPs are usually synthesized by chemical or electrochemical oxidation process.[41] The most widely used sensor coating monomers are polypyrrole, polyaniline, polythiophene, polyacetylene.[64,87] Poly(phenylvinylene), poly(3,4-ethylenedioxythiophene), poly(*N*-vinylcarbazone), poly(thienylenevinylene), and many others have also been investigated.[88] The presence of a conjugated π-electron system, which extends over the whole polymer, is the characteristic feature of CP materials.[65,89]

Presently, electrical conductors diffused in an organic insulator are used.[64,87] Conductance decreases with a reduction of conducting paths (due to physical swelling of the material) through which charges are transported, and so the resistance of this layer rises.[13,72,74] This conductivity changes may, or may not, be linearly dependent on the concentration of analyte presented to the sensor, depending on the particular transduction mechanism involved in the conducting polymer of concern.

The sensitivity of a single sensor to a given odor is described by the measurement of the so-called gas-polymer partition coefficient.[64] CP based sensors are characterized by an order of magnitude lower sensitivity than MOS sensors.[89] Nevertheless, measurements at the ppm and sub-ppm level have been reported for some analytes with suitable electronic circuitry (sensitivity in the range from 0.1 to 100 ppm).[64,74,90] Usually, they are employed at low temperatures, such as room temperature,[91] thus they do not need heating and are simple in operation. Besides, they are stable and their recovery and response time is short (especially for polar compounds) and inversely proportional to the thickness of the polymer.[89,90] They are also easy to manufacture, have good mechanical properties and can be used in a portable instruments.[41] Their major disadvantages are: high susceptibility to humidity[64] which may mask their response to VOCs and sensor drift due to oxidation of the polymers over time.[54,63,65]

The general application of CPs is their utilization as chemiresistors, CPs for field- effect transistors and semiselective coatings for piezoelectric crystals.[54]

b. Conductive polymer composite chemiresistor arrays

The detecting layers of sensors may also be created from composites of a conducting polymer in which both the conducting and the insulating materials consist of organic polymers.[64,87] Alternatively, the conducting layer may consist of an inorganic conductor such as carbon black, Ag, Au, and the insulating phase is formed by an organic material capable of expansion,[75] usually consisting of 80% (w/w) insulating polymer and 20% (w/w) of carbon black.[65,79,90,92]

The transduction mechanism of the carbon black composite sensors has been described on the basis of percolation theory. Upon exposure to an odorant, the composites swell to varying degrees depending on the polymer-odorant interactions, and this swelling results in a change in the conductivity of the composite film. Each sensor element in the array, consisting of a chemical unique insulating matrix, responds differently to a given odorant, resulting in a distinctive pattern. For example, an electronic nose that uses an array of 32 polymer-carbon black composite sensors, constructed at The Jet Propulsion Laboratory was able to identify and quantify a broad range of target compounds and distinguish isomers and enantiomers.[93] Thin-film chemical sensors based on the carbon-black polymer nanocomposite recently developed reliably detect chemical warfare agents.[94] This e-nose system was exposed to dimethyl methylphosphonate (DMMP) and dichloromethane (DCM) in parts per million concentration levels.

B. B "Hot" class conductivity sensors

1. Metal oxide semiconductor sensors

MOS sensors have many advantages, therefore they are the most popular sensors used in electronic nose instruments available on the market. They are relatively inexpensive, stable in time (it is possible to carry out many analyses without significant changes of basic parameters, which ensures high repeatability of results), have high sensitivity (from 0.1 ppb to 500 ppm)[54,95,96] and chemical resistance and are easy to operate.[83,97] For the first time MOS sensors were utilized as household gas alarms in the 1960s in Japan.[41] Basically, these sensors comprise a ceramic support tube containing a platinum heater spiral onto which metal oxide semiconducting film is coated onto the external side of the tube.[65,98] The oxide coating may be either n-type or p-type semiconductors. The n-type semiconductor (tin dioxide, zinc oxide, titanium

dioxide, tungsten(VI) oxide, gallium(III) oxide or iron(III) oxide) respond to oxidizing gases (such as O_2, NO_2, Cl_2) and its thermal or photolytic excitation promotes reactions with oxidizing molecules due to an excess of electrons.[99] The p-type semiconductors (nickel or cobalt oxides) respond to reducing gases (such as H_2, CH_4, CO, H_2S) and their excitation result in deficiency of electrons that increases the reactivity with reducing compounds.[47,65,100] From chemical point of view, catalytic reactions of volatile gas molecules on the surface cause the transfer of charges, which leads to a change in the electrical resistance of the sensors.[64,67] Strictly speaking, when an odorant molecule finds itself in the vicinity of the sensor, the resistance (at the contact boundary) changes proportionally to the concentration of the odor substance.[35]

The MOS sensors are usually doped with small amounts of catalytic metal or metal oxide additives, especially noble metals (Pt, Pd, Cu, Au),[47,100] which change the response characteristics of the semiconductors. The doping substances help to diminish the humidity and temperature dependence and to improve the sensitivity and the selectivity.[99] However, excessive doping can negatively influencing on sensor characteristic, e.g., reduction of sensitivity.[65] Selection of the catalytic additives and operating conditions make possible to adapt e-nose instrument to given application with sufficient low detection limit.[98] For example, Yu *et al*. assembled tin dioxide nanobelts with low-power microheaters for detecting nerve agent – DMMP. This research showed that sensitivity of MOS sensors for DMMP detection can be enhanced to sub-ppb level by doping the nanobelt with CaO.[101] Another studies connected with doping of MOS sensors have been carried out by Capone *et al*. They developed the array of differently doped solgel tin oxide sensors (Pd-, Pt-, and Os-doped SnO_2) for the classification of different olive oils.[102]

The metal oxide film thickness classifies sensors into thin (6–1000 nm) and thick (10–300 μm) film sensors. The thickness is only related to the fabrication method (physical or chemical vapor deposition, evaporation and spraying for thin films vs. screen printing or painting for thick films) but also with the response (faster for thin films), sensitivity (higher for thin films), reproducibility (higher for thick films), and cost (lower for thick films).[65,98]

MOS sensors operate at high temperatures, between 300 and 500 °C, which averts the effect of humidity on the results of the analysis and shortens the response and recovery time.[64,74] It entails the provision of an additional element – a heater – to the electronic nose system. The consequence of high operating temperature of first e-nose instruments was very high consumption of electrical energy.[65] For this reason, consuming less energy sensors with a thin layer of metal oxides were utilized. Nowadays, these type of sensors are small and despite of high operating temperature, their power consumption is relatively low (tens of mW), making them useful for portable instruments.[41,54,103] For example, development of TiO_2 nanobelts, with low-power microheater device that consists of two adjacent silicon nitride (SiN_x) membranes, which can operate at 500 °C with only 3.8 mW power consumption.[101]

Unfortunately, MOS sensors exhibit low sensitivity to sulfur-based odors[64] and ethanol; furthermore, they are susceptible to poisoning by these compounds due to the formation of durable, irreversible combinations with metal oxides.[26,35,47]

2. Metal-oxide semiconductor field-effect transistors

Metal-oxide semiconductor field-effect transistors have been applied as gas sensing elements since some of the earliest e-noses. The MOSFET structure commonly utilized for e-nose applications (Fig. 6) consists of a metal gate on top of an oxide layer, typically SiO_2, and a p-type silicon base with n-doped channels on either side of the gate.[65,104] Such sensors work on the principle that their threshold voltage changes on interaction of the gate material, typically noble metals (e.g., Pt or Pd) with certain analytes, due to corresponding changes in the work functions of the metal and the oxide layers. The changes in the work functions occur due to the polarization of the surface and interface of the catalytic metal and oxide layer when gas interacts with the catalytically active surface.[35,105,106] It has been observed that the change in the threshold voltage is proportional to the concentration of the analyte and is used as the response mechanism for the gas.[65]

The sensitivity and selectivity of sensors of this type may be adapted to specific applications through appropriate choice of the type and thickness of the catalytic metal, as well as through choice of the operating temperature.[47,105] For example, sensors with thick metallic layers are effectively used for the detection of hydrogen sulfide, as opposed to sensors with more porous thin layers, which are designed to detect amines, alcohols, and aldehydes.[47,104,107] The limit of detection of MOSFET sensors, with Pd, Pt, and Ir gates, for sulphides and amines is 0.1 ppm.[107] Response time of these devices is different and varies from milliseconds up to 300 s.[57,108]

The production techniques of MOSFETs permit the obtainment of small and inexpensive sensors,[63,106] allowing a relatively high repeatability of results of the analyses in which they are used. In spite of the high sensitivity and selectivity of these sensors, their operating conditions (the environment) have to be under constant control, which excludes their application in portable instruments.[105,106] The MOSFET sensors selectivity and sensitivity can be affected by the working temperature (75–200 °C), kind of metal gate and microstructure of the catalytic metal.[99,109] They are not capable of detecting to full range of substances of interest, which is the deciding factor against their use in commercial e-nose systems.[35]

C. "Cold" class piezoelectric sensors

This group of piezoelectric sensors includes two basic types: quartz crystal microbalance (QCM) or bulk acoustic wave (BAW) and surface-acoustic-wave (SAW) devices. They are used in electronic nose instruments as devices detecting changes in mass, although they can measure temperature, mass changes, pressure, force, and acceleration.[35,110]

The main difference between SAW devices and QCM equipment is that the wave created by the former propagates along the surface of the sensor, while in the latter type through the whole volume of the sensor.[65,111] The operating principle

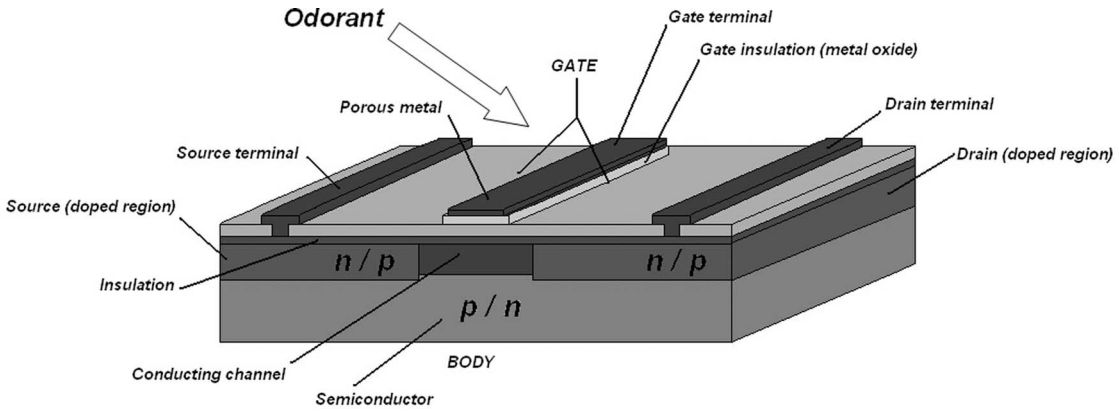

FIG. 6. Structure of MOSFET sensors.

of both types of devices is similar and is based on a change in the mass of the piezoelectric sensor occurring during its exposure to odorous compounds (adsorption/absorption of the compound on/in the layer), which causes a change in the resonant frequency of the sensor.[47,65,110–112]

1. Bulk acoustic wave sensors

QCMs (BAW or thickness shear mode (TSM) devices) are the simplest type of piezoelectric sensors. They are built from a single quartz crystal (several millimeters in diameter) and two disks covered with sputtered gold, acting as electrodes and connected with wires (Fig. 7).[64] The mass of the gas molecules being absorbed on the surface of the sensor is measured by the change of resonant frequency and the signal's frequency varies between 5 to 30 MHz.[35,37,47] A three-dimensional wave is created which travels through the whole bulk of the crystal.

The membrane, which covers the crystal absorbs molecules of the odorous compounds as it comes into contact with the vapor. At that instant, the mass of the polymer disk (on the surface of the crystal) increases, the resonant frequency decreases – it is an inversely proportional relation.[113] For example, when a QCM sensor made from a crystal with a diameter of 166 μm oscillating (resonating) with a frequency of 10 MHz gains 0.01% of its mass, the resonant frequency decreases by 1 kHz.[35] Therefore, the frequency changes allow for the identification of odors. After performing a measurement, an appropriate reference gas should be passed through the e-nose instrument so that the resonant frequency of the QCM sensor returns to its initial state.[113]

QCM sensors are produced with the use of MEMS technology. Their advantage is the possibility of producing very small elements, for example layers of 10 nm to 1 mm thickness[37,47,65] as well as the potential to considerably shorten the response and recovery times, even to 10 s.[65,114] The disadvantage of such miniature devices is their instability, caused by the increased surface-to-volume ratio. Increasing the surface-to-volume ratio increases the signal-to-noise ratio, but on the other hand lowers the accuracy of the measurements.[35,113] Furthermore, the temperature dependence and interface circuitry cause main difficulties with applying these sensors in e-nose instruments.[65]

QCM devices are very sensitive and can operate effectively in analysing compounds at the ppb level.[63,115] They have found application in the military sector because of the possibility of measuring mass changes with a resolution to 1 pg. Because of this, they are used to detect trace amounts of explosive materials and other hazardous substances.[35]

Moreover, QCM sensors exhibit linear responses in a broad range.[65,113,115] They are characterized by high sensitivity to vapors of organic compounds, for example: for aliphatic primary amines in the range of 7.5–48.2 Hz/mg/l.[116] There is also the possibility of matching a QCM polymer sensor to a given application.[115,116] It is worth mentioning that the commonly used packing of chromatographic columns can also be used as absorbing material in this type of sensors.[35]

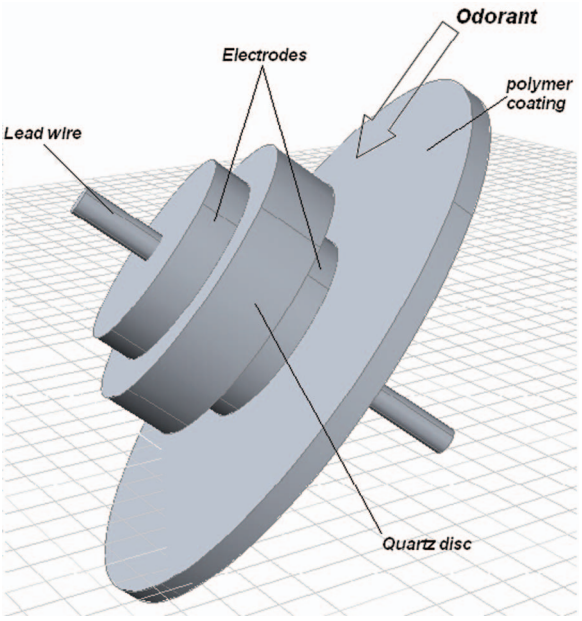

FIG. 7. Structure of a bulk acoustic wave sensor.

2. Surface acoustic wave sensors

A number of differences between SAW and BAW sensors exist, in spite of the fact that they belong to the same group of sensors – piezoelectric sensors. In a SAW sensor,

an acoustic wave travels along its surface, not through the whole bulk of the sensor.[47,117] Also, the operating frequencies of SAW sensors are considerably higher (in the range 40 MHz–1 GHz),[47,64] which does not adversely affect their sensitivity, even with the smallest mass changes.[35] In turn, this favorably influences the signal-to-noise ratio, which increases slightly with an increase of the surface-to-volume ratio.[54,113]

A SAW device is built from a piezoelectric substrate with an input (transmitting) and output (receiving) transducers placed on its surface. The membrane, which is selective to volatile compounds, is placed between these transducers and most often made from polymers, lipids, Langmuir-Blodgett films or self-assembled monolayers.[64,65,113] At the instant when the alternating current is applied to the input transducer (the transmitter), a two-dimensional acoustic wave is emitted, which travels along the surface of the crystal.[63,118] Depending on thegeometry of the acoustic structure and on the frequency scaling, SAW sensors can produce different types of waves: Rayleigh waves, surface transverse waves, Bleustein-Gulyaev waves, and Lamb and Love waves.[99] The substrate must be made from a material with piezoelectric properties, therefore it is most often made from: zinc oxide (ZnO), lithium niobate ($LiNbO_3$), lithium tantalite ($LiTaO_3$) or quartz.[26,47,63,65,111] Otherwise, SAW devices operate like QCM devices. A membrane absorbs the odor compound molecules. From the sensing point of view, the adsorption of volatile on the sensor changes the properties of the chemically interactive material that affect both: the phase velocity and the propagation loss of the acoustic wave.[54,99] The result of that is a frequency shift whose magnitude is related to the amount of material adsorbed onto the layer sensor.[54,113,117]

SAW devices are flat. They are produced by the microelectronic industry using the photolithographic method in which thin layers (20–30 nm)[119] are deposited using airbrush techniques.[47,110] Because of this, they are much cheaper than QCM sensors and can be produced in greater quantities, as the production process does not require the use of three-dimensional MEMS methods.[35,63] Alternative techniques utilized in manufacture of SAW devices are screen printing and spin coating techniques.[120] Pique *et al.*[121] utilized matrix-assisted pulsed laser evaporation (MAPLE) for depositing polymer thin films onto SAW sensors and found the performance to be comparable to that of SAW sensors coated by standard spray coating methods. MAPLE technique allows for deposition of solvent-free polymers onto a range of substrates. Moreover, the research conducted by Nicolae *et al.* shows that use of MAPLE direct write technique allows for fabrication SAW sensors 3–5 times more sensitive and having 10–40 times lower detection limit than sensors deposited by spray coating.[122]

The sensitivity of SAW sensors depends on the type of membrane employed. The layers in sensors of this type can be made from various substances, formerly used as packing in GC columns.[47,111] The broad choice of such layers results in a considerably broader spectrum of odors capable of identification.[37,65,113] Typically, more than one such variant of SAW device is needed to analyze a mixture of odor compounds.

The quantity sensitivity is low, at the ppm level.[63,117] The sensitivity varies from 0.5 to 12 Hz/mg/m^3, depending on the employed polymer coatings.[119] The response time is relatively short.[64]

A disadvantage of both types of devices – SAW and QCM – is their complicated and expensive electronics, as well as their sensitivity to humidity and temperature changes.[64,74] Moreover, replacement of a damaged SAW sensor and batch-to-batch reproducibility of characteristics are difficult to achieve.[37,47]

D. Electrochemical sensors

Electrochemical gas sensors, including mainly amperometric and potentiometric (both with liquid and solid electrolytes) sensors are also widely used in e-noses technology.[123]

The common characteristic of amperometric gas sensors (AGS) is that measurements are made by recording the current in the electrochemical cell between the working and counter electrodes as a function of the analyte concentration. A current at the working electrode is generated when the analyte is typically reacted electrochemically, that is oxidized or reduced. This reaction is performed typically at a fixed potential controlled by a potentiostat. The amperometric gas sensor is one of the most widely used sensors for toxic gas detection[41] (e.g., for carbon monoxide, nitrogen oxides, hydrogen sulphide, sulphur dioxide). They are commonly used in mining operations for personnel protection monitoring and in industrial hygiene and safety applications.[113]

As opposed to the amperometric sensors, potentiometric sensors use the voltage at zero current that is typically representative of an equilibrium electrochemical process. The signals arise because an electrochemical reaction can occur at electrodes, or at membranes in solid, liquid, or condensed phases. The generated signal is an electromotive force that is dependent on the activity of the analyte, and is described by Nernst's equation. A solid electrolyte electrochemical sensor uses solid electrolyte instead of the liquid electrolyte. Such sensors are typically designed to operate at high temperature and can operate in either a potentiometric or amperometric mode.

Generally, electrochemical gas sensors with liquid electrolyte operate at room temperature, have low power consumption and are very robust, but are still quite bulky. Important advantage of electrochemical sensors is their moisture resistance.[64] Moreover, electrochemical gas sensors do not age and the relation between the concentration of a given odor compound and the obtained signal is linear. The disadvantages of these sensors, from the standpoint of their application within electronic nose instrument, are their size and relatively high selectivity for a limited number of simple gases.[124]

E. Smell-seeing (optical) sensors

Optical sensor systems measure the modulation of light properties. In general, optical instruments are more complex but offer a variety of different measuring possibilities.

Different operation modes were developed using changes in absorbance, polarization, fluorescence, optical layer thickness, color or wavelength (colorimetric). Olfaction instrument based on optical sensors benefited from scientific developments in other fields ranging from optical technologies developed by the telecom industry.

Identification of odors with the help of an e-nose instrument is possible due to the employment of appropriate optical sensor arrays containing various chemo-responsive dyes.[64,125] In connection with this, the sensitivity of such sensors depends upon the type of dye or the mixture of dyes used, and on the type of polymer supporting them.[65] The availability of a broad range of dyes which may find application in sensors, leads to low cost and a simple fabrication procedure of smell-seeing sensors.[125] This diversity of choice also contributes to the high selectivity of these sensors.[35,126,127] Moreover, it is possible to use dyes in affinity to a single specific volatile compound. A very wide range of sensitivities is achievable in optical sensors, which is impossible to attain in other types of sensors used in e-nose instruments.[63,113]

The simplest optic sensors use color-changing indicators, such as metalloporphyrins or more generally chemically responsive dyes, to measure absorbance with a light-emitting diode and photodetector system upon exposure to gas analytes. In a colorimetric sensor arrays (CSA) a thin films of multiple dyes that change color depending on intermolecular interactions are applied. The CSA is digitally imaged before and after exposure and the resulting difference map provides a digital fingerprints for single or mixture of odor-producing substance. On this base a detector for toxic different gases (e.g., Cl_2, F_2, HCN, SO_2, NO_2) was developed by Suslick *et al.*[128–130]

An advantage of optical gas sensors is their short and linear response (e.g., for ammonia response time – less than 15 s, linear dynamic range – 180 ÷ 18 000 ppm).[91–93] In contrast to many sensors employed in e-nose instruments, they are characterized by resistance to the influence of toxic compounds, therefore they can be used to detect such compounds. The examples are metalloporphyrins, which change color under the influence of these substances. It allows for the visualization of odors and their identification by comparison with a reference basis.[64] The whole system operates thus analogously to a litmus paper which permits the determination of the approximate reaction of the solution.

Due to the hydrophobicity of the dyes and membrane, such sensors are not affected by changes in relative humidity. Older electronic-nose methods relied on sensors whose response originated from weak and highly nonspecific chemical interaction, while newer systems are based on stronger dye-analyte interactions. Different studies showed the ability of such system to discriminate among analytes in complex mixtures, including 100 volatile organic compounds,[133] sweeteners,[134] soft drinks,[135] and beers.[136]

The fluorescence methods, working in similar setup detect not the absorbance but the light emission at a lower wavelength, are more sensitive than colorimetric sensor array. Such sensors, commonly known as optical waveguide sensors, are built from glass fibers covered with a thin (2 μm),[65] chemically active material containing a fluorescent dye in polymer matrix.[35,63,113] The properties of the polymer supporting fluorescent dye, i.e., polarity, hydrophobicity, porosity, and a tendency to expand, have a significant influence on the sensor response.[63,113,126,127] An example is provided by polyaniline sensors, which have shown to be sensitive in the determination of low ammonia concentrations at the ppm level.[65,132] Furthermore, the addition of alumina can improve the detection limit of the sensor (e.g., LOD for 2,4-dinitrotoluene – 23 ppb).[125,131]

It is obvious that fluorescence-based optical-fiber array systems have their drawbacks. The lifetime of fluorescent dyes is limited due to the photo-bleaching process.[35,65] Therefore, periodic calibration of sensors is necessary with respect to the repeatability of results. An additional disadvantage is the high complexity of the supporting electronics connected to the sensors, which leads to a considerably higher cost of the e-nose instrument.[65,113,137]

VI. GAS CHROMATOGRAPHY AND MASS SPECTROMETRY-BASED ELECTONIC NOSES

Early technologies of e-noses repudiated techniques based on chromatography because of the considerably long time of analysis. The development in this field has led to many new possibilities.[63,138] New type of such systems, so-called fast GC,[64,139] are characterized by similar parameters, namely, time of analysis and data processing, to classical ones based on sensor array. It make possible to apply such instruments to the same applications, which are handled by stationary versions of e-nose systems based on sensor array. An electronic nose, based upon fast GC, is able to simulate a sensor array containing hundreds of orthogonal (nonoverlapping) sensors. Chemical analysis of any odor is accomplished in 10 s by a very fast separation of chemicals in sampled vapors. For a chromatographic system, chemical sensor space is defined mathematically by assigning unique retention time slots to each sensor.[140,141] Furthermore, in case of using GC version of such instruments, the typical problems (e.g., sensor poisoning, sensor drift) connected with sensor array are omitted.[53,142] The other attitude for this issue is the idea of appliance the instruments based on MS. Advantages resulted by the use of a MS cause rise a new generation of e-nose instruments.[55] Analogically to e-nose based on GC, the MS-based e-nose instruments use individual mass fragments from mass spectra as a sensor signals.

A. GC/SAW

The principle of operation of the GC/SAW system was described on the example of commercially available zNose 4500. This instrument measures the concentration of volatile constituents. This concentration is proportional to the frequency of the wave travelling in the SAW sensor.[139,140] The result of the analysis is in the form of a profile of volatile constituents of the sample.

The analysis of volatile compounds can be divided into two main stages in which tight control of time and temperature is needed, which ensures precision and reproducibility of measurements.[139,143] In the first stage – sample collection

– the gaseous sample is entered the system, where it is preconcentrated and injected as a "short pulse" into a capillary chromatographic column. The carrier gas (pure helium) transfers the compounds to the SAW sensor. In the second stage – analysis – the helium stream is reversed and directed to a trap, before passing to the SAW sensor.[138,139,143] After starting the analysis, a ten-millisecond current pulse is applied to the trap, which heats up quickly and intensely, releasing volatile compounds in a very short time.[138,143] The volatile compounds are again transferred to the GC column, trapped and focused at a relatively low temperature (about 40 °C). From this moment, the column temperature rises linearly to maximum temperature, which leads to the release of chemical compounds and their movement along the chromatographic column.[139,140,143]

The SAW sensor consists of an uncoated 500 MHz acoustic interferometer or resonator bonded to a Peltier thermoelectric heater. Because there are no coatings applied, the SAW sensor detector is stable and very sensitive (part per billion for volatiles and part per trillion for semi-volatiles).[141,143] The GC/SAW is sensitive enough to recognize drinking water contaminants by testing the headspace of water sample.[139,143]

The main advantages of GC/SAW instruments are the very short time needed for analysis (about 10 s), portability, high precision and accuracy (RSD within 1%–2%).[138,141] Moreover, it can operate in a wide range of concentrations, which allows for the analysis of solid, liquid, and gaseous samples. Operation and calibration of GC/SAW systems are characterized by simplicity.[95–97] An additional benefit of this technique is the possibility of obtaining not only a qualitative, but also a quantitative results. This ability is visualized as a "fingerprint," called a VaporPrint.[141,143]

The main foundation of fast GC is to be simple and fast in use. These facts are connected with some limitations in comparison to conventional GC. To increase the separation speed during analysis, different parameters have to be adapted: increase of the carrier gas flow rate, an increase of the temperature-program heating rates, a reduction of the column length, a reduction of the column diameter, a reduction of the thickness of the stationary phase, and the use of a faster carrier gas. Such operations decrease of the resolution and the sample capacity. It is also important to note that these optimizations increase the demands on the detector technology used in terms of sensitivity or speed.[144] Another disadvantages of fast GCs are connected with their abilities as portable instruments. Despite the development in fast GC technology, in comparison to portable sensor array e-noses, the fast GC instruments still are heavier and sizeable. The necessity of use of gas supply is main factor that increase size of this equipment. However, the 300 analysis can be conducted using relatively small gas bottle.

B. MS-based electronic nose

Instruments based on mass spectrometry have been developed relatively recently and they constitute an alternative to conventional electronic nose instruments employing sensors.[55]

Their advantage is that the analyzer of mass does not exhibit problems typical with a sensor array, such as sensor poisoning, profile masking by some constituents, susceptibility to moisture, and nonlinearity of the response signal in some operating ranges.[52,55,70]

Using this type of systems, the headspace analysis of a sample is performed in two ways: static (SHS-MS) or dynamic (DHS-MS).[100–102] The first step is injection of the gaseous sample, which subsequently is ionized in the mass spectrometer ionization chamber. Afterwards ions are separated according to the different ratio of mass-to-charge (m/z).[55] In such a way a mass spectrum is obtained, which characterizes the given type of sample. It constitutes a volatile profile of sample, often called the "signature" or the "fingerprint."

Most electronic nose instruments available on the market are used for qualitative analysis of daily products or substances, which could pollute the environment. It has been observed, however, that these devices can be also used for quantitative analysis.[52,70,146] The advantage of this technique in comparison with GC-MS is the much shorter response time and wider range of application. On the other hand, it provides less information than GC-MS.[52,55,147] For this reasons, both mentioned techniques are complementary. For example, MS-based e-nose instrument (SMart Nose) has the power to assess rapidly the infant milk formula quality as a qualitative tool whereas the SPME-GC-MS can identify the VOCs produced and quantify them.[146,147]

The MS-based electronic nose system has an unquestionable advantage over the commonly used e-nose instruments equipped with sensor arrays, in particular when adaptability and sensitivity are taken into account.[40,55,70,148] In a classical electronic nose instrument, the number and type of sensors have to be specified according to requirements of a certain application. The adaptability of MS-based e-nose instrument is much higher than classical one.[40] They can be adjusted to particular applications, simply by selecting the optimum set of fragment ions. Moreover, these systems can be used to determine the differences between samples.[29,100–103] As opposed to traditional e-nose instruments, MS-based systems are not susceptible to interferences from the sample, especially ethanol and water, which reduces the sensitivity to other constituents.[55] However, they are relatively expensive, as their price exceeds several times the cost of gas-sensor-based e-nose systems. Another inconvenience is the inability to use them for online measurements and as portable instruments.[40,55] Moreover, some specific applications (e.g., fatty food matrices) require appropriate sample preparation (e.g., pre-concentration of VOCs), which extend the time of analysis and cause the additional errors associated with this step of the analytical process. It should be also understood that the mass fingerprinting system is not a universal system and the lack of flavor stability of products during analysis may lead to inconsistent mass fingerprints for the same type of sample.[52]

1. Ion mobility spectrometry and high-field asymmetric waveform ion mobility spectrometry

Ion mobility spectrometry (IMS) is known as a fast and sensitive technique for the detection of trace substances. The

working principle of IMS is lain in filtering of ions as in the case of mass spectrometry. The separation of ions of target molecules is based on the differences in mass/charge (m/z) ratio and their different mobilities. Different collisions with particles of drift gas, determinated by size and shape of target ions, and m/z ratio has a direct influence on the separability of ions. Thereby, the collisions between the ions and the ambient air molecules is utilized, and the measurement can be performed under normal pressure.[53,144,148]

Generally, a gas phase sample is ionized by help of UV-light, β-radiation or partial discharges. The ions move in a weak electrical field towards a detector. During their drift they collide with a drift gas flowing in the opposite direction and therefore are slowed down depending on their size, shape, and charge. As a result, different ions reach the detector at different drift times, which are characteristic for the ions considered. The number of ions reaching the detector is a measure of the concentration of the analyte. The method enables the identification and quantification of analytes with high sensitivity (ng/L range). Those characteristics of the method are preserved even in air with up to 100% relative humidity.[149]

High-field asymmetric waveform ion mobility spectrometry (FAIMS) separates and filters ions generated by various atmospheric pressure ionization methods.[150,151] FAIMS is similar to conventional IMS in that it uses the motion of ions produced by an applied electric field to achieve separation. Further, this ion motion occurs in a drift gas, typically at one atmosphere. The major difference between the two techniques is the magnitude of the electric field and its method of applying. In conventional IMS, a low constant electric field, generally less than 200 V/cm, is applied parallel to the direction of separation, and is used to move the ions through the drift gas inside the spectrometer. In FAIMS, a much higher electric field, generally greater than 10 000 V/cm, is applied perpendicular to the direction of separation and the drift gas is used to move the ions in the direction of separation. The electric field in FAIMS is also not constant, with an asymmetric waveform alternating between periods of opposite polarity.[150–152]

The suitability of the both techniques for application in the field of food quality and safety, including storage, process, and quality control as well as characterization of foodstuff, was investigated in recent years, e.g., monitoring of production process of cheese or beer fermentation, characterization of alcoholic products (beer, wine), quality control of packaging materials during the production of polymeric materials.[148,149]

VII. COMPARISON OF GAS CHROMATOGRAPHY-OLFACTROMETRY AND ARTIFICIAL NOSES

Gas chromatography with olfactometric detection (GC-O) was proposed by Fuller *et al.*[153] in 1964. It was proven to be a valuable technique for the determination of odor active compounds from a complex matrices.[154] Nowadays, GC-O has been found as a competitive technique for e-nose instruments in the field of analysis of volatile fraction of food products. A comparison of both systems is presented in Table IV.

TABLE IV. Electronic nose vs gas chromatography-olfactometry.[a]

	E-Nose	GC-O
Advantages	Relatively short time of analysis	Simple construction of olfactometric detector
	Preparation of sample is not required	Possibility of identification of high number of odor active compounds in complex mixtures
	Separation of sample constituents is not required	Possibility of fast classification and differentiation of food products on the base of aroma profile
	Short recovery time	Relevance of single compounds for the aroma assessment
	Portable version is available	Possibility of using GC detectors for qualitative and quantitative analysis
	High sensitivity and reproducibility	Possibility of parallel analysis of the same sample by several panelists
	Recognition of simple and complex odors	
	Objective analysis of whole aroma	
	Low sensitivity to moisture using MS-based e-nose system	
Disadvantages	Sensors suffer from ageing	Time consuming
	Possibility of sensor poisoning (e.g., MOS sensors can be poison by sulphur compounds)	Sample pretreatment (isolation and enhancement) is required
	Sensors are susceptible to moisture	*In situ* analysis is impossible
	In some cases less sensitivity than human olfactory system	Limitation of number of measurements per day
	Complexity of training of e-nose sensors and elaboration of appropriate data analysis	Lower reproducibility
	Limited specificity of sensors	Complicated comparison of results from different laboratories
		Data could be affected by different chromatographic behavior of analyzed compounds
		Requirement of trained olfactive panelists
		Detection of the end of the odor region is difficult

[a]References 64, 154, 160, and 161.

The GC-O technique makes possible a sensory evaluation of the eluate released from chromatographic column. The aim of that is determination of aroma-active compounds.[155] In this case, the human nose plays the role of a chromatographic detector. Appropriately trained evaluator or sensory panel sniff the eluate from the GC column and relate the aromatic impressions to the retention times. It should be mentioned that the human nose is able to detect and distinguish some volatile compounds already at the amount of 10^{-17} g, while the detectors commonly used in gas chromatography require at least 10^{-13} g to identify a compound.[63]

The discussed technique allows a simultaneous qualitative and quantitative evaluation of the flavor of each analyte separately (after separation in a chromatographic column). In other words, it provides the possibility of determination of eluting compounds appearing in the sample above the threshold of sensory detection, describing the intensity of olfactory sensation and the time of sensory activity.[155] Separated analytes are recorded at the chromatographic spectrum ("fingerprint," olfactogram) using a dedicated slide potentiometer (shifting the position of the potentiometer slider according to the change in odor intensity leads to the creation of peaks – the so-called finger-span method). Sensory evaluation of odors is facilitated with the use of a specially constructed device, so-called olfactometric port. Furthermore, in most of the presently used chromatographs, it is possible to employ the olfactometric detector (OD) with other conventional types (especially mass spectrometer (MS) or flame-ionization detector (FID)).[156,157] Simultaneous detection is realized by dividing the eluate stream in an appropriate ratio so that it reaches both detectors. This ensures a comparison of both signals.[155] With regard to this fact, application of GC-O/MS allows for description of odors and their connection with identified compounds by mass spectrometer. The only shortcoming of such solution is the possibility of divergence between the retention times at chromatograms and olfactograms. It is caused by differences in length of interfaces between gas chromatograph and detectors, and by pressure conditions under which detectors work (vacuum for MS, atmospheric pressure for OD). This problem can be overcome by installing a restrictor (in the form of a narrow bore capillary) before the mass spectrometer to increase the pressure drop between the interface and the flow splitter, as well as through careful selection of the flows of the carrier and auxiliary gases.[158]

An important part of the GC-O apparatus (Fig. 8) is the olfactometric port, which permits sniffing the separated volatile compounds. In most cases, a cone made of either PTFE or glass and fitted to the shape of the human nose is used for the purpose. The eluate from the column is fed into the olfactometric port through an appropriately designed capillary transfer line. The transfer line length is long enough to ensure comfortable position for the evaluator during the detection procedure and to avoid any discomfort due to the nearness of hot GC parts. Further, the transfer line is heated during the analysis, to prevent the condensation of semi- or low-volatiles on the capillary walls.[155,156]

The eluate supplied to the olfactometric port may cause drying of the nose mucous membrane of the olfactory panelist (particularly during long-lasting analyses). An appropriate addition of an auxiliary gas (mostly humid air) is often used to avoid the problem. In cases where the analyzed eluate is sufficiently concentrated, it is often split into multiple streams leading to individual olfactometric ports and analyzed by several evaluators simultaneously. In this way, more objective results can be obtained.[159]

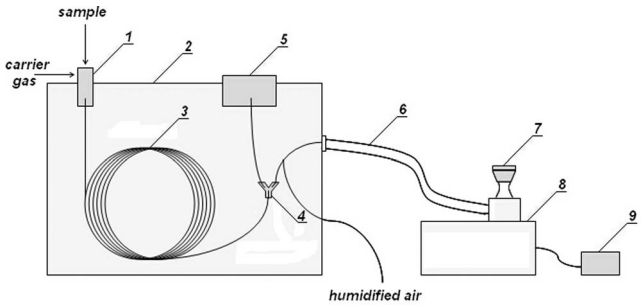

FIG. 8. Scheme of GC-O system.

VIII. DATA ANALYSIS METHODS

The response of multisensory e-nose systems is very complicated. Thereby, proper utilization of such seemingly chaotic information is not as easy as reading the indications of a classic single-sensor analyzer, e.g., for the detection of methane in coalmines and in household gas-fittings. For this reason, it is necessary to apply special data analysis methods.

The analysis of the artificial nose signal includes signal processing and pattern recognition. These steps can be further divided into four processes: preliminary analysis (preprocessing), feature extraction, classification, and decision making (Fig. 9).[35,63]

Preliminary analysis includes balancing the sensor's drift, averaging the transient responses of the sensor array and a reduction of the effects of a previous measurement upon the current one.[162] The information on a measured value provided by the sensors is an unprocessed response, full of noises, which are removed during the feature extraction process. The statistical analysis techniques controlling the feature extraction step can be divided in two groups: quantitative methods and pattern analysis methods.[35,144] The quantitative methods are supervised and therefore work on the database of known samples. Pattern analysis techniques may be either unsupervised, such as cluster analysis (CA) and principal component analysis (PCA), or supervised, such as discriminant function analysis (DFA) or canonical correlation analysis (CCA).[63,144,162–164] However, the more common classification of commercially available techniques for sensor signal analysis can be presented in the form of three main groups:[47,91]

- graphical analysis,
- multivariate analysis, and
- network analysis.

The choice of PARC method depends on the kind of data obtained as well as the type of result that is required. Another ground of differentiation for the statistical methods could

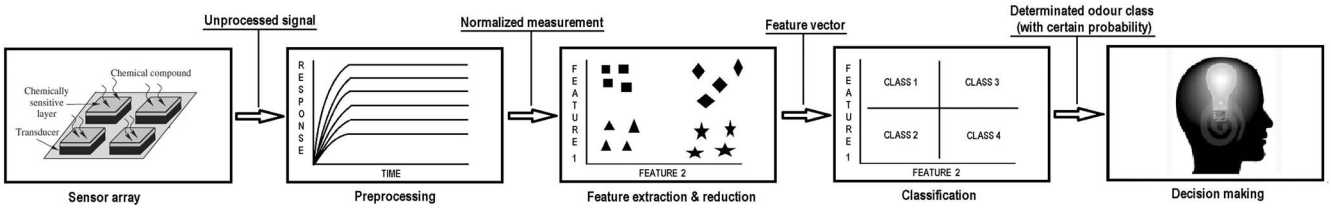

FIG. 9. Signal processing and pattern recognition in the electronic nose.

be: linear/nonlinear or supervised/unsupervised techniques (Table V).[38,165,166]

The simplest method of data analysis is a graphical data presentation in the form of a raw data histogram, or a "odor fingerprint" or polar diagrams. They are used mostly for the detection of samples which differ considerably from the other ones.[63,160,164] Figure 10 shows an exemplary comparison of three hypothetical distributions of signals received from 12 sensors, which could be obtained in the course of an analysis of samples A and B and that of a standard mixture. The histogram shows great similarity in the odor of sample A to the odor of the standard and a significant difference between the aromas of standard and sample B. Similar information can be obtained from the polar diagram presented in Fig. 11 (Ref. 26).

A more complicated method of analysis of sensor array signals involves statistical calculations. Many multivariate analysis methods, such as PCA, CA, multidimensional scaling (MDS), linear discrimination analysis (LDA), partial least squares method (PLS) can be employed.[144,164]

The multivariate data analysis is based on a reduction of data, which could be linked by one or two relations ($z = f(x)$ or $z = f(x,y)$). Due to this fact, results can be checked using a graphical form on two- or three-dimensional spot diagrams (Fig. 12).[167] The distances between spots representing the compared "objects" are a measure of mutual similarity/dissimilarity. Odor maps provide the possibility of differentiation of complicated flavor mixtures. They are divided into zones or regions, which indicate similar olfactory sensation of the same type of samples.

TABLE V. Patter recognition methods mainly utilized in e-nose instruments.

Statistical method	Supervised	Linear
Principal component analysis (PCA)	−	+
Hierarchical clustering analysis (HCA)	−	+
Partitional clustering algorithms	−	+
Spectral clustering analysis (SCA)	−	+
Linear discriminant analysis (LDA)	+	+
Discriminant function analysis (DFA)	+	+
Canonical discriminant analysis (CDA)	+	+
Canonical correlation analysis (CCA)	+	+
Feature weighting (FW)	+	+
Partial least squares regression (PLS)	+	+
Independent component analysis (ICA)	+	−
Blind source separation (BSS)	+	−
Artificial neural network (ANN)	+	−
Radial basis function (RBF)	+	−

LDA is one of the most frequently used classification procedures. It has found usage in many applications where it turned out to be successful. The method maximizes the variance between categories and minimizes the variance within categories.[166,168]

For comparison and to visualize the relationships between different samples and sensors, PLS is commonly used. It produces projections that arrange the information from the whole data table in a few dimensions of a data matrix with many variables and objects.[169] The dimensions extracted in PLS are chosen in such a way to optimize the ability to use them to predict a dependent variable from many independent variables.[164,165]

In many cases, the use of more complex methods of data collection and analysis is justified. Systems resembling the human olfactory system are neurocomputers – electronic models of neural networks and/or computer programs simulating their operation. They are known as artificial neural networks (ANN).[49,91,165] Both solutions allow for data analysis, where distribution is totally unpredictable. The ANN program is contained in its structure – in connections between elementary network units, whose significance changes as a result of "learning."[160] Due to training, the networks gain the ability to classify information sets on various objects, even when the differences between them have not been indicated by humans. A specific set of signals coming from e-nose sensor array can be linked with a similar set, which occurred during analysis of standard[49,63,165,166] (e.g., a specific kind of coffee or perfume, the aromatic trace of a criminal).

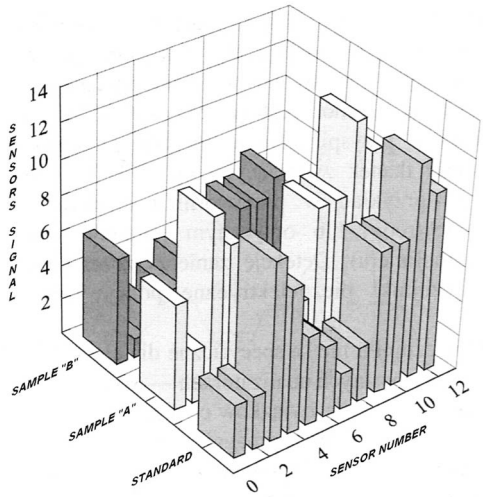

FIG. 10. Hypothetical histogram of responses from 12 sensors to the effect of a standard mixture and samples A and B.

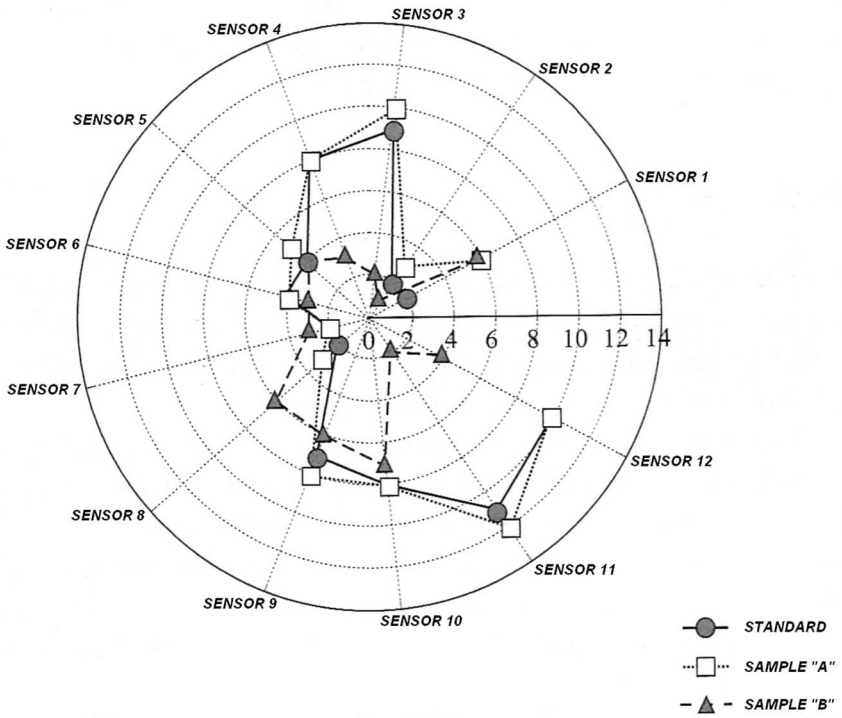

FIG. 11. A polar graph of responses from 12 sensors to the effect of a standard mixture and samples A and B.

The elementary units of the technical model of a neural network, "neurons," are very simple electronic devices (their links are synapse equivalents).[170] Neurons in the network are situated in layers, forming a hierarchic structure. The layers are parallel to each other and they can appear in different numbers (generally a three-layer network is sufficient to process a signal with good efficiency).[63,166,170,171] Each of the neurons has many "inputs" and one "output." The electrical signal arriving at each of the inputs is multiplied by a numerical value, a so-called "weight."[164,171] The magnitude of the output signal (S_y) depends upon the input signals (S_x), their weights (W_n) and the "input-output" function $S_y = f(S_x)$ (Fig. 13).

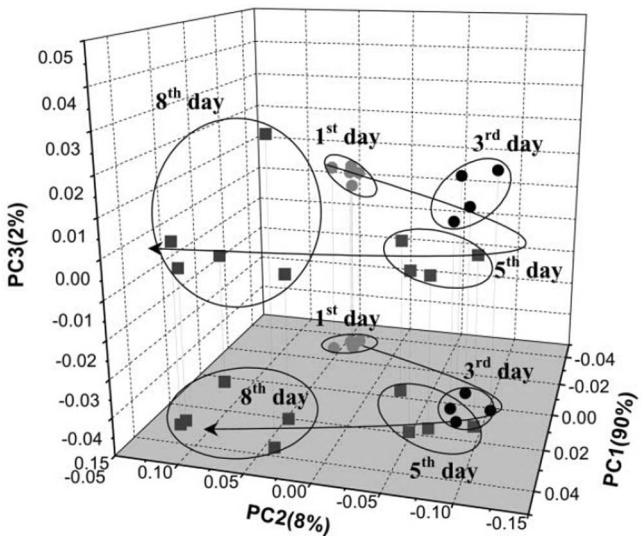

FIG. 12. PCA results – 3D diagram of rancidity of UHT milk in a function of time (Ref. 167).

IX. APPLICATION OF E-NOSE INSTRUMENT

The areas of application for an e-nose instrument are those in which odor plays an essential role or determines the quality of analyzed products. In addition to the food industry, the following potential branches of artificial nose application should be pointed out: plastics processing, environmental protection,[172] air[173,174] and water monitoring,[175] various branches of the chemical industry including explosive materials,[176] cosmetics, pharmaceutical, petrochemical, paper,[177] packaging industries,[42] as well as the alcohol industry,[178] liquid-gas distribution and bottling plants, and criminological and medical tests.[179–181] The range of use of e-nose instrument is broad and includes: quality monitoring of raw materials and processed products,[169] monitoring of production processes,[182] evaluation of freshness and ripeness of food products,[183,184] shelf-life investigations,[185] authenticity assessment of premium-class products,[47] detection of microbial pathogens,[186] classification of odors and perfumes.[187]

A. Application in food industry

Most of the scientific publications regarded to the artificial nose utilization are focused on food analysis.[7,47,64,82] The food industry is the largest and most promising market for such systems. Applications of the e-nose instrument in the food industry include: quality control of foodstuffs, control of the cooking process, non-destructive ripeness and freshness evaluation, inspection of fish-processing, monitoring of

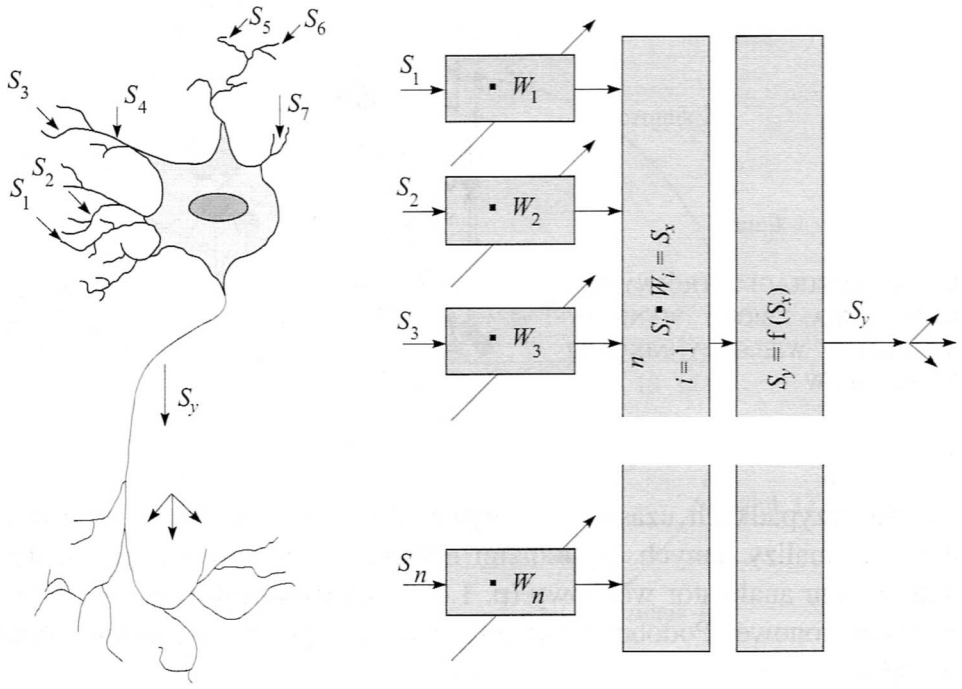

FIG. 13. Principle of operation of ANN – comparison with a biological neuron.

fermentation processes, checking the rancidity of mayonnaise, determination of origin of fruit-vegetable juices, classification of alcoholic beverages (e.g., wine, vodka, beer), detection of poisonous compounds content in packaging, inspection of beverage containers.[37,41,52,64,69] In some cases, e-nose instruments can complement or absolutely displace evaluators carrying out sensory analysis of food products.

In the next subsections, examples of application of odor-sensing systems in the food industry are discussed in more detail for selected products and summarized in Table VI.

1. Dairy products

In the literature, there are many articles dedicated to e-nose instruments applied to the food and beverage investigations and other concerning environmental, agricultural or medical topics. However, the number of studies focused on dairy products is still very limited, probably due to the complexity of their matrices. Some papers describe the use of e-nose instruments in monitoring of diary products in terms of quality and production processes, ageing, or spoilage.[76,123] Moreover, in some cases (e.g., microbial spoilage detection) sensory analysis is inadvisable because of the possibility of toxification of panelists. Because of this reason, the e-nose instrument constitutes an appropriate solution.

The electronic nose instruments are widely being used for analysis of dairy products, mainly milk,[167,209,241,242] various types of cheese,[208,221,243–246] and yogurts.[76,123] A group of Italian scientists[167] have carried out measurements on pasteurized and UHT (ultra-high temperature) milk after different degrees of ageing. Milk samples, from one-day to eight-day ones, were analyzed by an e-nose instrument equipped with an in-house developed MOS sensor array (five SnO_2 thin film sensors, of which four were doped with Ni, Os, Pd, and Pt) and classified by the PCA method. The samples were incubated 15 min at 30 °C, then the headspace was transferred in a flow of nitrogen to the injector and introduced into sensor chamber with a temperature of 250 °C. The response and recovery time of sensors was 2–3 min.[102]

The e-nose technology also allows for shelf-life determination and discrimination of off-flavors in milk and milk products. Marsili has paid attention to these problems in numerous papers.[247–250] He employed the SPME-MS-MVA system (solid phase microextraction, mass spectrometry, multivariate analysis) to determine the shelf-life of 2%-fat pasteurized milk and full-fat chocolate milk. Milk samples containing 5 μl of an internal standard (10 μg/ml chlorobenzene) were extracted using the SPME technique (75 μm carboxen/PDMS fiber) at 50 °C for 20 min. During analysis, the injector temperature was set at 275 °C, and the transfer line changed between 150 and 180 °C. The analysis lasted less than 7 min. Using the PLS method, the shelf-life of 2% milk and chocolate milk samples was determined with an accuracy of $\pm$0.62 and $\pm$0.88 days (correlation coefficient of 0.9801 and 0.9832 for milk and chocolate milk, respectively).[250]

The study of boiled off-flavors originating in the pasteurization process in UHT milk was performed by Mulville.[251] For this purpose he used the NST 3320 equipped with MOSFET, MOS, and QMB sensors. Samples of 0.5%-fat boiled milk of different dilution were analyzed. 40 ml of each solution were placed in 100 ml bottles and incubated for 30 min at 20 °C. During this stage, the sample headspace was introduced to the injector by a 60 ml/min flow of ambient air (filtered in activated charcoal). PLS analysis was capable of discriminating down to 10% of boiled milk, in comparison with 30% for sensory analysis.[251]

The artificial nose can be a useful tool for classification of bacterial cultures and detection of spoilage in milk

TABLE VI. Application of e-nose instruments in the food industry.

Application	Sample	Object of study	Sample handling	Sensors	Data analysis method	Ref.
FOOD PROCESS MONITORING	Wine-must	Discrimination between fermentation stages	SHS	AromaScan A32S: 32 CP	PCA	188
	Iberian hams	Spoiling during the curing process	SHS	16 Tin-oxide thin films	PCA, PNN	189
	Milk fermented with *Lactobacillus casei* strains	Discrimination between genotype strains and odor intensity scores	INDEX/ SHS	SMart Nose: MS	PCA	190, 191
	Australian red wines	Spoilage caused by *Brettanomyces* yeast	SHS/ SPME (for MOS) & SHS (for MS)	HP 4440: MS FOX 3000: 12 MOS	PCA, PLS, SLDA	192, 193
	Tomato *cv.* Cencara	Dehydration processes of tomato slices	SHS	Air Sense: 10 MOS	PCA	182
	Mangoes (*Mangifera indica* L.)	Discrimination between harvest maturities within a ripening stage Discrimination between ripening stages within a maturity stage Discrimination between fruit varieties	SHS	FOX 4000: 18 MOS	DFA	183
	Black tea	Estimation of optimum fermentation time	SHS	8 MOS	TDNN, SOM	194
	Grains	Odor classification	SHS	NST 3210: 4 MOS, 1 IR, 10 MOSFET	ANN	169
	Coffee	Quality classification	SHS	FOX 3000: 12 MOS	ANN	195
FOOD FRESHNESS EVALUATION	Cod-fish fillets	Discrimination between storage periods	SHS	LibraNose: 8 TSM FreshSense: 5 EC	PLS-DA	196
	Fresh/cold smoked Atlantic salmon (Salmo salar)	Spoilage classification at different temperatures	SHS	AromaScan A32S: 32 CP FishNose (GEMINI): 6 MOS	MDA, PLS, PCA	197
	Fresh tilapia fillets (*Oreochromis niloticus*)	Discrimination between storage times of fillets under different treatments	SHS	eNose 4000: 12 CP	DFA	198
	Oysters (*Cassostrea virginica*)	Prediction models for odor changes in shucked oysters	SHS	EEV model 4000: 12 CP	DFA	199
	Eggs	Establishment of freshness categories	SHS	4 Tin-oxide sensors	PCA, FCM, SOM, ANN	184
	Ground beef/beef/ sheep meats	Rancidity detection, spoilage classification and bacteriological parameters prediction	SHS	FOX 3000: 12 MOS 6 Tin-oxide sensors	QLSR, PCA, SVM, PLS	200
	Meat	Determination of storage time	SHS	NST 3210: 4 MOS, 1 IR, 10 MOSFET		201
FOOD SHELF-LIFE INVESTIGATION	Pinklady apples, Jonagold apples	Discrimination of type of apples Discrimination between ripening stages Discrimination between shelf-life durations and storage conditions	SHS, SPME	21 MOS, 12 QMB, LibraNose: 7 QMB, MS	PCA, ANN, PLS, Radial plots	185, 202, 203
	Tomatoes (*Lycopersicon esculentum* Mill.)	Discrimination between cultivars, ripening states, storage shelf-life times during two storage treatments, prediction of fruit quality characteristics	SHS, SPME	LibraNose: 5 QMB, MS, PEN-2: 10 MOS	PCA, LDA, PLS	204–206
	Peaches (*Prunus persica* L.)	Discrimination between cultivars and between ripening states during shelf-life	SHS	PEN-2: 10 MOS	PCA, LDA, CART	207
	Crescenza cheese	Definition of the threshold of the shelf-life at different storage temperatures	SHS	NST 3320: 10 MOFSET + 12 MOS	PCA, CA, LDA	208

TABLE VI. (Continued.)

Application	Sample	Object of study	Sample handling	Sensors	Data analysis method	Ref.
	Milk	Determination of shelf-life	SHS	FOX 4000: 18 MOS	PCA, vectors norm. analysis	209
	Extra virgin olive oils	Evaluation of the oxidative status at different storage conditions	SHS	NST 3320: 10 MOFSET + 12 MOS	PCA, LDA	210
	Refined raspeed oil	Evaluation of lipid autooxidation under different storage conditions	SHS	FOX 4000: 18 MOS	PCA, PLS	211
FOOD AUTHENTICITY ASSESSMENT	Tequila, whisky, vodka and red wine	Discrimination between the four types of beverages, Discrimination of wines from different regions	DHS	FOX 4000: 18 MOS	PCA	178
	Italian wines	Recognition and quantification of adulterations	SHS	4 Thin-film MOS	PCA, BP-ANN	212
	Spanish wines	Classification of wines varieties, origins and ageing	SHS, P& T, SPME	16 Tin-oxide sensors, 8 Tin-oxide sensors, ZnO, SAW, MS	PCA, PNN, SIMCA	213–216
	Virgin olive oils	Detection of adulterations	SHS	FOX 3000: 12 MOS	LDA, QDA, ANN	217
	Extra virgin olive oils	Discrimination between geographical origins	SHS	MS, NST 3320: 10 MOFSET + 12 MOS	PCA, SLDA, LDA, CP-ANN	218,219
	Orange juices	Discrimination between geographical origins	SHS	FOX 3000: 12 MOS	PCA, FDA	220
	Emmental cheese	Discrimination between geographical origins	SHS	SMart Nose: MS	PCA	221
	Swiss unifloral honeys	Discrimination between botanical origin of honey	SHS, SPME, INDEX	SMart Nose: MS	PCA, DFA	145
	Aceto Balsamico Tradizionale di Modena'	Classification of different aged products	SHS	MS	PARAFAC, PCA, SIMCA,WPTER	222
	Coffee	Authenticity assessment Differentiation between coffee blends	SHS	FOX 4000: 18 MOS Lab-made: 6 MOS	ANN	47
	Beer	Identification of brand	SHS	Lab-made: 12 CP	PCA	223
	Mushrooms	Differentiation between species of freeze-dried mushrooms	SHS	Lab-made: 5 MOS, AromaScan A20S: 20 CP		224
	Cola	Brand comparison	SHS	FOX 2000: 6 MOS	CA	225
OTHER APPLICATIONS	Virgin olive oils	Discrimination between quality grades Qualitative and quantitative information about negative and positive sensory attributes	SHS	FOX 3000: 12 MOS, 8 CP, MS	PCA, KSOM, SIMCA, PLS	226,227
	Italian dry red wines	Prediction of sensorial descriptors, Correlation with sensorial descriptors and GC/MS profiles	DHS, SHS, P& T	PEN-2: 10 MOS, 16 thin film tin-oxide sensors	GA, PLS	228,229
	Oranges and apples	Evaluation of post-harvest quality	SHS	LibraNose: 7 TSM	PCA, PLS, PLS-DA	230
	Peaches and nectarines from several cultivars	Evaluation of the sensorial features typical of each class	SHS	LibraNose: 7 TSM	PCA, LVQ-NN	231
	"Xueqing" pears	Quality indices prediction (firmness, soluble solids content and *p*H)	SHS	8 MOS	MLR, ANN, PLS	232,233
	Apricots (*Prunus armeniaca*)	Discrimination between varieties	SHS-GC	FOX 4000: 18 MOS	PCA	234
	Apples	Discrimination between cultivars and kinds of apple	SHS, SPME	14 Tin-oxide gas Sensors, 8 Micro-SAW oscillators	PCA, PLS, BP-ANN, Radial plots and visual inspection of signals	235,236
	Longjing green teas	Discrimination between different quality grades	SHS	PEN-2: 10 MOS	LDA, PCA	237

TABLE VI. (Continued.)

Application	Sample	Object of study	Sample handling	Sensors	Data analysis method	Ref.
	Onions (*Allium cepa*)	Influence of edaphic factors on bulbs quality	SHS	AromaScan A32S: 32 CP	PCA	238
	Hams	Discrimination of different types of hams	SHS	16 Tin-oxide thin film sensors	PCA, PNN	67
	Chinese vinegars	Identification of several commercial vinegars	SHS	9 Doped nano-ZnO thick film sensors	BP-ANN with *k*-NN	239
	Diverse food products	Discrimination between foods, e-nose sensors selection	SHS	MOSES II: 7 QMB, 8 MOS, 4 EC	PCA	240
	Packaging	Quality assessment of modified atmosphere packaged poultry meat Off-odors assessment of film packaging Examination of cardboard papers Detection of off-odors in canisters of pharmaceutical inhalant	SHS	NST 3320: 12 MOS, 1 IR, 10 MOSFET, humidity sensor, FOX 2000: 6 MOS, NST 3210: 4 MOS, 1 IR, 10 MOSFET, AromaScan A32S: 32 CP	MDA, PCA, PLS, ANN	39, 42, 238

products. Production of volatile compounds (i.e., ethyl butanoate, ethyl 3-methylbutanoate, ethyl hexanoate, acetic acid, acetaldehyde, ethanol) by some bacterial strains such as *Bacillus cereus*, *Bacillus pumilus*, *Pseudomonas perolens*, and *Pseudomonas fragi* is the basis of these type of studies.[252] Significance of indication of microbial milk spoilage by e-nose instrument is its identification of not only undesirable off-flavors but also the potential of milk toxification.

A group of scientists from Bedford, UK utilized the e-nose instrument (model BH-114 from Bloodhound Sensors Ltd., Leeds, UK) equipped with 14 conducting polymer sensors, to study the early detection of spoilage bacteria and yeast in skimmed milk.[252] The samples were prepared by mixing inoculum in the amount of 10^3–10 cells/ml (evaluated spectrophotometrically and under a microscope) with 15 ml of 10% skimmed (defatted) milk in polypropylene 50 ml bottles. All samples were incubated at room temperature for 30 min to obtain a state of equilibrium; in some cases the samples were further incubated at 30 °C. Then the phase was transferred to the feeder in a stream of air cleaned on carbon (rate of flow: 200 ml/min). A DFA analysis allowed for the discernment of correctly unpolluted milk, milk with added butyl alcohol (check sample), and milk with varying content of *Staphylococcus ureus* bacteria cells or *Kluyveromyces lactis* yeast (after 2 and 5 h of incubation). With the use of DFA analysis, milk with various concentrations of *Pseudomonas aureofaciens*: 10, 3.5 × 10, 8 × 10 cells/ml was correctly classified. Moreover, using a PCA analysis, proper classification of milk containing the individual strains of *S. aureus*, *B.cereus*, *Pseudomonas* spp., *K.lactic*, *C. pseudotropicalis*, unspoiled skimed- , and check milk was achieved. Also, the application of a three-layer neural network (ANN) permitted the differentiation of four out of the five mentioned bacteria and yeast cultures, after prior incubation at 25 °C for 5 h.[252]

Similarly, Marsili[248] described the possibility of applying SPME-MS-MVA as an e-nose instrument for the classification of bacterial species of *Pseudomonas fluorescens*, *Pseudomonas aureofaciens*, and *Pseudomonas putrefaciens* in milk. All of them had a Cheddar cheese-like aroma.

Apart from milk, yoghurt and kefirs studies, the e-nose instrument has become a useful tool in checking various type of cheese. It was used mainly to determine the degree of ripeness, for quality evaluation and classification of cheeses according to their geographical origin and their type, as indicated by numerous papers.

For example, Jou and Harper have begun tests to distinguish five different brands of cheese – including four Swiss brands (pungent, mild and with fat content of 0% and 30%) and one Norwegian (Jarlsburg cheese).[253] For this purpose, they used the FOX 2000 equipped with 6 MOS sensors. Samples of ground cheese (5 g) were placed in glass vials and incubated at 40 °C for 30 min. The sample headspace was transferred in a stream of carrier gas – compressed air (rate of flow 250 ml/min) to the sensor chamber. The analysis results were recorded in 1 min, after which the sensors were regenerated and returned to their basic state, which lasted 7 min. DFA permitted proper classification of the tested cheeses, consistent with sensory analysis and SPME/GC-FID. The second procedure was based on a measurement of the intensity of selected volatile fatty acids: acetic, propionic, butyric, isovaleric, and hexanoic acid, which are compounds that have an essential effect on the odor of brands of Swedish cheese.

An electronic nose system based on MS (Smart Nose, LDZ, CH) equipped with a Combi PAL autosampler (from CTC Analytics AG, CH) was used for classification of Emmental cheeses on the base of their geographical origin.[221] As a comparison method, dynamic headspace gas chromatography followed by flame ionization and mass spectrometry (DHS/GC-MS/FID) was employed; it served to detect volatile compounds which could constitute geographical origin markers. The analysis comprised 20 cheese samples (ripening period: from 2.5 to 4 months) from various European countries: Austria (Vorarlberg – 3 samples), Germany (Allgäu – 3 samples), France (Bretagne and Savoie – 3 samples each from these regions), central Finland (2 samples), and Switzerland

(6 samples). 4 g of ground cheese were incubated at 90 °C for 30 min and then analyzed; the analysis lasted only 3.5 min due to the use of a multiple-vial incubating device. In order to distinguish Swiss cheese brands from non-Swiss ones, the PCA analysis was used. In this way, 90% of Swiss cheese and 91% of the remaining samples were correctly classified. Moreover, it has been shown that there is a possibility of distinguishing Swiss cheese from cheese originating outside of Switzerland region – the classification was correct within 90%–100% and 83%–100% for Swiss and other European cheese, respectively. Furthermore, an analysis carried out by the GC-MS/FID method permitted the detection of volatile compounds more or less characteristic for cheese brands coming from one or two regions. As an example, on the basis of content of butan-2-one, 3-hydroxybutanone, butan-2-ol, and octene in the tested samples, Swiss cheese brands were distinguished from the remaining brands (the compounds mentioned above can be regarded as markers).

Gursoy *et al.*[243] made an attempt to employ an ion mobility-based electronic nose instrument, type MGD-1, to discriminate ripeness and geographical origin of yellow cheeses. To this purpose, 24 samples of cheese with various age of ripening (3, 6, and 9 months) acquired on the local market in Finland and 9 samples of Emmental cheese coming from different European regions (Germany, France, the Netherlands, Finland, and Switzerland) were investigated. Cheese samples of 2 g were placed in 250 ml conical flasks and incubated at 55 °C (with the addition of 50 g of $CaCl_2$ – for reduction of humidity of the gas sample). Next, the headspace sample was transferred in an air stream (2 l/min) to the ionization chamber (IMCELL™) at 35 °C. Data analysis was carried out by the PCA method. Nine-month cheeses were clearly distinguished from the other less ripened cheeses (Fig. 14). PCA diagram indicated that the discrimination of 3 and 6 months old cheeses was unresolved. Moreover, the MGD-1 system was capable of properly classifying cheeses of various geographical origins and also detecting the spoilage of Emmental cheese caused by the fermentation of lactic acid esters to butyrate.

Similarly, a research group from Denmark has investigated changes occurring during ripening of Danish blue cheese.[254] Tests were carried out on 96 samples of cheese (fat content >50% of dry mass) produced in the 35th, 37th, 39th, and 43rd weeks of 2001. The cheese was melted at 4 °C during a whole night, and subsequently 20 g was homogenized with 20 ml of 5% NaCl solution (w/v). 5 ml of the obtained suspension were placed in a 10 ml vial and incubated at 50 °C for 10 min. 500 μl of sample headspace was injected by the HS-100 autosampler (from CTC Analytics AG, CH) to the sensor chamber (rate of flow 150 ml/min). The analysis was carried out by means of the FOX 3000 (from Alpha M.O.S., FR) equipped with 12 MOS sensors. After analyzing each sample, the sensors were regenerated by passing dry air (with maximum humidity of 0.5%). Apart from this, cheese samples were subjected to a chemical analysis which consisted of: determination of volatile compound content (GS-MS), determination of soluble peptides (RP-HPLC) originating in the ripening process ($pH = 4.6$) and free fatty acids (FFA) (GC-FID). Tests have shown that the e-nose instrument can be a useful tool in monitoring the process of cheese ripening, providing results close to those obtained with chemical analysis methods. It was difficult, however, to discriminate explicitly between 2-week and 4-week cheeses because their aromatic profiles were very similar, as in the case of FFA profiles. Furthermore, cheese samples with this degree of ripeness have a very similar composition of the volatile fraction and similar content of *p*H 4.6 soluble peptides. Information obtained through the application of an e-nose instrument can constitute a model which allows for the prediction of results of other chemical analyses, in particular FFA determination and peptides soluble at *p*H 4.6 (with high accuracy).

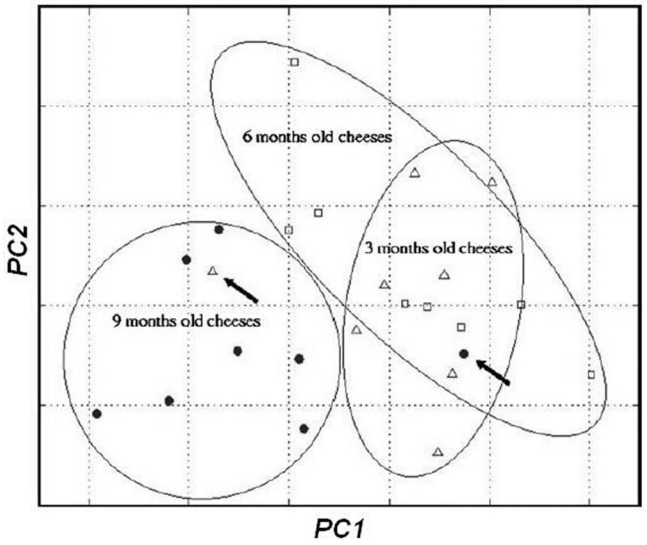

FIG. 14. Score plot obtained by using PCA to MGD-1 e-nose data for Emmental cheese samples with three different ripening stage: Δ −3 months old cheese, □ −6 months old cheese, and ● −9 months old cheese.[243]

2. Meat and fish

The majority of publications of foodstuff analysis by e-nose instrument are related to meat[42,200,255–257] and fish products.[258,259] It is worth to mention that one of the first domain of applications of e-nose technology was fish studies. Most of them are connected with quality control (QC). QC has great importance within the meat industry. Using e-nose instruments, it is possible to monitor the meat from the raw material throughout the process and to the final product by analyzing VOCs released from the meat matrix.[256,260] Sensory quality, shelf-life, spoilage, off-flavor, taints, and authenticity can be monitored by these instruments. In addition, the electronic nose can be useful when the product development is taken into consideration.[261] This section describes the applications of these systems for meat quality assessment, where fast detection methods are essential for appropriate product management. The given examples suggest the possibility of using e-nose technology in meat handling.

Many of them are published by Berdagué from France.[262–265] His research was based on the use of the Alabaster UV device equipped with MOS sensors, a stainless-steel measurement chamber, a UV lamp, and air in- and outlet connected to a fan. The first tests were conducted in

cooperation with Talou and they have shown that this simple system allows to discern the degree of maturity of dry non-spiced sausages and to detect differences in the composition of meat products.[262] The Berdagué research team also started the research on discrimination of microorganisms. For this purpose, the FOX 2000 device was used, which enabled correct classification of 90.5% of the analyzed bacteria species by headspace analysis. Different bacteria strains used in medicine or their pathogenic varieties often found in meat products have also been found and correctly classified.[263]

Olafsdottir *et al.*[186] investigations conducted with the use of 12 MOS sensors (FOX 3000) have confirmed their usability in the detection of meat spoilage and the contamination of meat products, after performing an appropriate optimization of the method, i.e., employment of additional surface acoustic wave sensors.

Winquist *et al.*[201] used a NST 3210 Emission Analyzer for the analysis of ground beef and pork samples. Various data-processing algorithms have been applied, including an artificial neural network algorithm. It has been found that every type of standard recognition software, due to data obtained from the measuring device, permits the differentiation between given types of meat. More difficult was to determine the storage period of meat products. It has been found that only artificial neural networks based on appropriate learning methods are suitable for this purpose.[201] On the contrary, Shiers *et al.*[256] did not achieve positive results in monitoring the spoilage process of minced beef using an e-nose instrument based on CP sensors. This failure could be attributed to the high susceptibility of the employed sensors to moisture and the low sensitivity to small amount of volatile compounds generated during meat taint.

Similar to the case of beef and pork products, MOS sensor systems (two- or six-sensor versions) have been successfully employed for the determination of the spoilage degree of the different fish species: haddock, cod, redfish,[259] and smoked salmon.[266] Samples of the first three species of fish were stored at room temperature or in ice, the smoked salmon samples in a temperature of 5 or 10 °C for four weeks. The obtained results were sufficient to confirm the usefulness of the e-nose instrument for the evaluation of fish freshness.[259] In the case of research on the freshness of smoked salmon, a prototype has been developed, suitable only for direct analysis of smoked salmon samples, the so-called FishNose prototype based on the GEMINI device from Alpha MOS Company.[266] Optimization of this system has been carried out by the OPTOTEK Company. Analysis of standards proved that the FishNose system was not sensitive to the compounds caused the smoke flavor such as guaiacol, but was more sensitive to the volatiles such as butanone, originating from spoilage process of smoked salmon. Local prediction modelling based on samples from a single producer possessed better performance than a global model based on products from different producers to predict quality features like sweet/sour and off-flavor, and microbial counts based on the FishNose six sensor array system. The equipment and the methodology developed for one specific application – rapid quality control of smoked salmon, were characterized by high sensitivity, short time of analysis with simultaneous high repeatability of results (error limit of 5% with respect to the real sample).[266]

3. Beverages

An e-nose instrument is often used in the analysis of beverages, particularly alcoholic drinks such as wine,[193,267,268] vodka,[40,269] and beer.[223,270] Among them, it finds the greatest appreciation in investigations of wines, where it forms a tool to determine the vintage, botanical and geographical origin, and differentiation of wine classes, as confirmed by Lozano *et al.*[213–215] and Martí *et al.*[216] E-nose systems used during the last 20 years in the analysis of alcoholic beverages can be divided into two main types: classic instruments based on gas sensors and new ones using mass spectrometry.[40,269,270] In general, MS based systems have an advantage over classic ones, particularly with regards to stability, sensitivity, and versatility. Moreover, their greatest advantage over classic devices in the analysis of alcohols is the fact that high ethanol content in a sample does not influence on the results.

A group of Italian scientists[271] used the e-nose instrument to distinguish between two wines of the same name (Gropello red wine), but coming from two different vineyards. A system of MOS sensors was used, adapted to distinguish between wines of the same type. The usefulness of the abovementioned device has been confirmed as an alternative analysis tool, which may replace routine wine tests carried out by olfactory panel. A standard wine distinguishing analysis did not give satisfying results in this case, which may result from the same content of free SO_2. The sensors of the e-nose instrument were sensitive to a broad range of chemical compounds. A statistical analysis of output signals from the sensors gave a much greater possibility of discerning wine coming from different wineries, in comparison with traditional sensory analysis. However, García *et al.*[267] verified the suitability of the e-nose instrument to recognition and discrimination four red wine brands (Bodegas Centro Españolas, Tomelloso, Ciudad Real) produced from the same variety of grapes and the same geographical origin, stored in the same cellar. Studied samples were: *Allozo 2002* (young wine), *Allozo Crianza 2000* (aged for a year in American oak barrel and 6 months in bottle), *Allozo Reserva 1998* (aged for 18 months in American and French oak barrel and 18 months in bottle), and *Allozo Gran Reserva 1997* (aged for 24 months in American and French oak barrel and 36 months in bottle). In this case, the e-nose instrument was equipped with 16 MOS sensors. Multisensor array was organized in five blocks and each one was composed of several elements: 1st block formed by SnO_2 of different thickness, 2nd and 3rd blocks doped with Cr and In, respectively, as sandwich structure and 4th and 5th blocks doped with Cr and In, respectively, as a superficial layer. Doping levels are different and were expressed as sputtering time in seconds. Two different sample preparation techniques for volatile compounds extraction: static headspace and dynamic headspace (purge-trap concentrator system), were used. PCA and PNN were employed as the tool for data processing (Fig. 15). The conducted wine studies showed that purge and

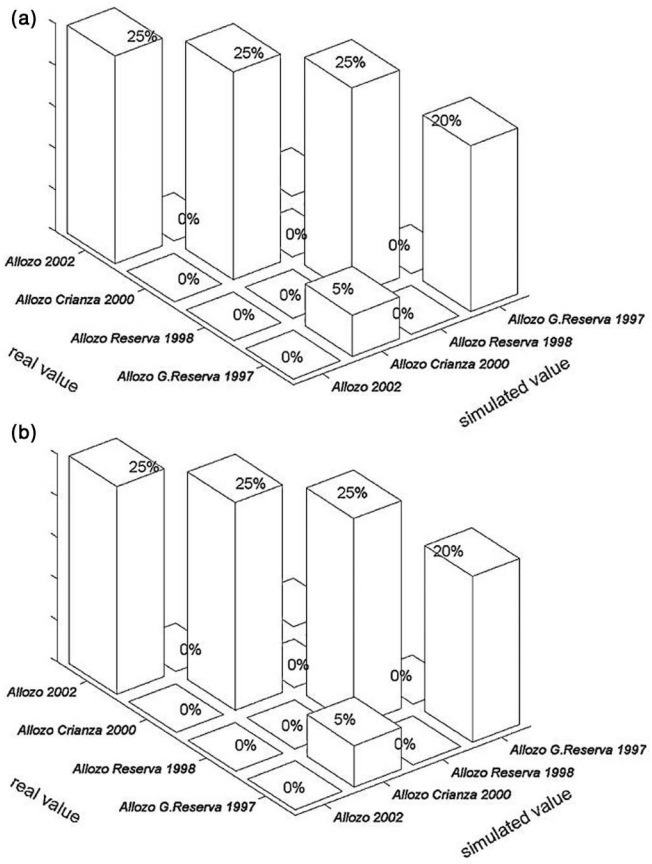

FIG. 15. Classification of four types of wine: *Allozo 2002*, *Allozo Crianza 2000*, *Allozo Reserva 1998*, and *Allozo Gran Reserva 1997* performed by a PNN for two sampling techniques: (a) static headspace, (b) dynamic headspace.[267]

trap method allow for a better classification of the different wines (success rate of 95%). The obtained results proved that it is possible to use e-nose instruments for the identification and differentiation of red wines originating from the same vineyard as well as from the same geographical origin and same variety of grapes.

A research group from Spain[268] analyzed the aroma of white wine by means of an e-nose system equipped with MOS sensors. The usability of this equipment in discerning 29 typical aromatic compounds occurring in wine of this sort was checked. Using statistical methods, PCA as well as PNN, in spite of the strong effect of ethanol, the system could properly discern the wine components with high accuracy, which was minimum 97.2% for PCA and 100% for PNN. These results confirm the usefulness of the accommodated e-nose system for the determination of both the origin and type of wine grapes used for production of the wines on the basis of differences in aromatic profiles. Moreover, the same group of researchers confirmed the suitability of the e-nose instrument to determine the degree of maturity of wines. The research discussed above is significant because of the possibility of detecting adulterations connected with vintage and origin of wine.

Another approach was used by Australian scientists, who applied an electronic nose system based on mass spectrometry. The aim of Cynkar *et al.*[272] research was checking the usefulness of such equipment by chemometric methods to monitor the degree of wine taint caused by *Brettanomyces* yeast. The tests included fast analysis of two Australian wines (Cabernet Sauvignon and Shiraz). PCA and stepwise linear discrimination analysis (SLDA) were used. The SLDA analysis allowed to correctly classify 67% of samples in three categories resulting from various concentrations of 4-etylphenol in wine samples: above 500 μg/L, in the range from 200 to 500 μg/L, below 100 μg/L. The results obtained for samples of spoiled and unspoiled wine differed considerably, which allowed them to be discerned.

Identification of various alcoholic beverages (beers, wines, vodkas, tequilas, and whiskies) was undertaken by researchers from Mexico and France. Razzago-Sanchez *et al.*[269] investigated 21 different alcoholic beverages using an e-nose instrument with 18 MOS sensors. PCA and DFA allowed the identification of differences between various alcohol types and their classification, independent of the ethanol content in its composition (Fig. 16). Furthermore, the use of dehydration and dealcoholization allowed for the identification of alcohols of the same type (e.g., of beers from different breweries having the same alcohol content).

Besides testing alcohol products, the e-nose instrument finds application in the analysis of non-alcoholic beverages, particularly juices.[273–276] Researchers from Alpha MOS (Clanchin, Lucas) carried out analyses of apple and orange juice using the e-nose instrument.[277] The results thus obtained were in agreement with those obtained from sensory analysis. The applicability of the e-nose instrument as a new tool for routine quality and safety checks of the above-mentioned food products and for differentiation of juice brands of the same or similar juice type has been shown.

A group of scientists from Canada[278] has investigated the usefulness of the electronic nose instrument in testing the freshness of orange juice. They have shown that the differentiation of fresh juice from spoiled (deprived of aromatic compounds by passing inert gas through the juice sample) by means of this device is relatively simple. However, if the juice has been adulterated through addition of appropriate essences containing aromatic compounds characteristic for orange juice (e.g., hexanal, d-limonene, nonanal, α-pinene, linalol, acetaldehyde, ethyl butanoate), the possibility of detecting and distinguishing genuine orange juice from an adulterated one is practically impossible.

Gobbi *et al.*[279] checked the usefulness of the commercial electronic nose EOS835 (Sacmi Imola scarl, Italy) for early detection of Alicyclobacillus spp bacteria in two aromatized nonalcoholic beverages. These bacteria are known to beverage producers as organisms that have the ability to survive the pasteurization process and generate compounds which pollute the final product. The e-nose instrument easily differentiated polluted products from those free from these bacteria, much earlier than a trained group of estimators detected these bacteria's metabolites in beverages by means of sensory analysis. Aside from this, detection of bacteria metabolites at the level of 200 ppb using the HPLC method was unattainable, in contrast to the electronic nose instruments, which confirms the potential of these instruments as a tool for early detection of pollutants of the above type.

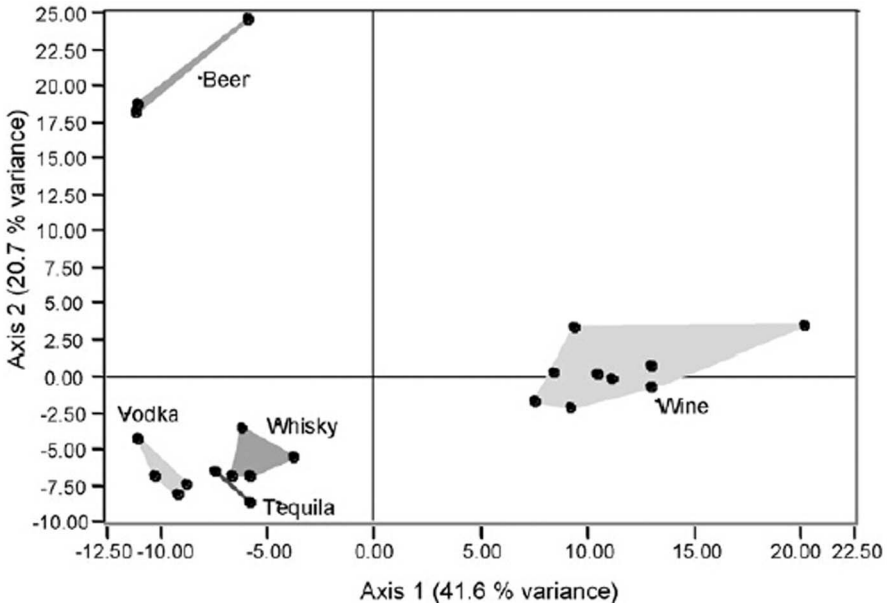

FIG. 16. The DFA map of the whole data (optimal array of 3 sensors) for different alcoholic beverages.[269]

4. Fruit and vegetables

The electronic nose instrument finds greater and greater application in the fruit and vegetable processing industry, particularly in horticulture and agriculture, where it is successfully used in monitoring the aroma of apples,[280] peaches,[207,231] pears,[281] melons,[282] oranges,[230] bananas,[283] tomatoes,[204–206] cucumbers,[284] and other fruits and vegetables.[285–288] It is a useful tool for the evaluation and monitoring of the ripening stage of fruits and vegetables, in the estimation of their quality, determination of their origin and classification according to the type of cultivation.

For example, a research group from Spain[288] has developed a system based on an array of 12 SnO_2 sensors and an artificial neural network for classification of fruit samples with regard to their ripeness (green, ripe, and overripe). The e-nose instrument was meant to be a tool allowing monitoring of the ripening process while simultaneously not destroying the samples. The test material consisted of three kinds of fruit: peaches (collected during three different periods, from July to August; white variety), pears (stored for a month in a controlled environment – 2.5% O_2 and 2.5% CO_2; Spanish variety "blanquilla") and apples (from the same crop as peaches). Slices of the fruit were placed in a concentration chamber. After a certain time (usually 1 h), 150 ml of headspace was sampled with a chromatographic syringe and injected into the sensor chamber where the sudden concentration change caused changes in the electrical conduct of the sensors. The time of analysis, from the moment of injection to the moment of sensor stabilization, was about 10 min. Each time, both chambers were cleaned with synthetic dry air after measurement. Comparison methods were traditional techniques which destroy the sample: firmness measurement (penetrometer), determination of fruit juice *p*H (*p*H meter), and of soluble sugar in Brix degrees (refractometer). The results obtained confirmed the suitability of such a design of the e-nose system to monitor the degree of ripeness of fruit, in particular peaches and pears (accuracy better than 92%). Contrary to this, the accuracy for apples was lower. Furthermore, the system was capable of correct prediction of the days number of the fruit storage from the moment of harvesting (in the case of peaches the maximum error was 1 day). An additional advantage of the discussed e-nose model was its concentration chamber, which provided stronger sensor signals and the possibility of simultaneous measurement of a greater number of fruit samples.

In a similar way, Italian scientists[207] classified four different peach cultivars and estimated their ripening stage during shelf-life by using a commercially available portable electronic nose PEN2 (Win Muster Airsense, DE), equipped with 10 MOS sensors. Fruit samples coming from the garden of the Mario Neri farm in Imola (4 varieties: "Earlymaycrest,", "Maycrest," "Springcrest," "Silver Rome") were placed in 1-liter hermetic glass jars closed by a screw cap with a silicone/PTFE membrane. After reaching a state of equilibrium ($20 \pm 1\,^{\circ}C$, 1 h), the headspace sample was pumped through the sensor chamber for 1 min (flow intensity 300 ml/min). After analysis of the sample, the system was blown by 3 min. with filtered air to assure its return to basic state. Each peach sample was tested three times and averaged results were used in the statistical analysis – PCA, LDA, and CART. Results obtained by means of the e-nose instrument were compared with results of traditional methods of ripeness evaluation such as measurement of ethylene content (GC-FID) and colorimetric estimation of color. An evaluation of the ripeness degree of fruit by means of PCA and CART, as well as diagrams resulting from the e-nose instrument (collected during the ripening process) indicated evident changes occurring during the storage period. The loading analyses have shown that the subassembly of several sensors (W5S, W2S, W1S) can successfully detail all these changes, but only one of them – W5S – is suited for the classification of peaches into three categories:

unripe, ripe, and overripe. CART analysis permitted a classification of peach samples into appropriate groups with an error of 4.87% determined by cross validation and also determining the limiting values of parameters of sensor W5S, indispensable for classification of fruit into the three mentioned classes. The results of research have shown that just this sensor of the e-nose instrument can constitute a fast-acting and non-destructive tool suitable for monitoring the ripeness degree of peaches directly in gardens, parking houses or retail shops.

Another important aspect in quality control of harvested fruit is the detection of defects occurring mainly during storage and processing. The most important among them are: mealiness (caused by extreme ripeness), damaged peels, (caused by mechanical factors or temperature), and contagions which have an essential influence on the choice of the product by customers. Therefore, it is important to eliminate these faults and to ensure high quality, and for this purpose the e-nose instrument can be a useful tool. This possibility has been checked by Natale *et al.*[230] They carried out investigations of aroma changes caused by mealiness and peel defects in oranges and apples (divided into 3 groups: 1–3, 7–14, and 24–30 days) during the storage period, using one of e-nose prototypes (LibraNose series) based on 7 TSMR. Fruit samples, after enclosing them in tight vials (equipped with inlet and outlet valves) were kept at 30 °C for 20 min to obtain phase equilibrium, after which headspace was introduced to the sensor chamber. Analysis time, including measurement and recovery time, was 15 min. Data were analyzed using chemometric methods – PCA and PLS. In both cases – apples and oranges – the e-nose prototype used was capable of effectively detecting defects in the harvested fruit. It permitted the determination of storage time, as confirmed by PLS analysis for oranges (error about 2%), and also detection of defects caused by extreme ripeness (mealiness) and mechanical defects (e.g., cuts) in case of apples. A quantitative analysis has shown that an increase in mealiness does not change the headspace composition of fruit but only the concentration of volatile compounds. In turn, in the case of mechanical defects in fruit, apart from a change in concentration resulting from direct exposition of the fruit flesh to oxygen, the headspace composition was changed.

The laboratory-assembled electronic nose system based on MOS sensors was used to non-destructive evaluation of quality of blueberries. The device allowed for the detection of soft and damaged fruit in packaging at a 5% level of damage and differentiation of four out of five ripeness classes: ripe-green and green-pink (1), blue-pink (2), blue (3), and ripe (4). Moreover, the correlation response of sensor array with berry firmness, color, *p*H, and acidity allow to distinguish 10 varieties of berries. The e-nose system can be useful for quick and non-destructive determination of the quality and type of packed fresh berries.[289]

Similarly to the analysis of fruits, the artificial nose can be used to monitor the storage step and differentiate vegetable cultivars, as has been checked by Berna *et al.*[204] For this purpose, 45 tomato samples have been investigated (variations: Tradior, Clotilde, and S&G 40-292) by means of two systems: an e-nose instrument equipped with QCM (EN) sensors and one based on MS (MS-EN). SPME was used for comparison, linked with GC-MS. Initial experiment has shown changes in the aromatic profile of two different tomato varieties during storage (1, 8, 12, and 19 days). Results of PCA analysis for EN have shown that changes in the signals from sensors with storage time are insignificant, therefore discerning samples after 1 day from those after 8 days was practically impossible. On the other hand, results of measurements carried out with the use of MS-EN have shown clear changes in the aromatic profile of tomatoes, in the course of their storage. Analysis of results from GC-MS by the PCA method allowed for the identification of volatile compounds (β-phellandrene, 6-methyl-5-hepten-2-one, 1-nitropentane, and 2-methylbutanol) whose concentrations change during storage, are easy to detect and thus allow to determination of the degree of ripeness of tomatoes. A second experiment has demonstrated that MS-EN easily differentiated tomato varieties, contrary to EN with which it was difficult to attain by means of two-dimensional relationships.

5. Other applications

a. Coffee Roasted coffee has one of the most complicated aromatic profiles among the whole variety of food products. Present knowledge resulting from scientific research confirms the presence of over 600 volatile compounds in coffee headspace. Gardner, one the best-known specialists in the field of electronic nose instruments, used a laboratory-designed system based on 12 MOS sensors for the classification of three commercially available coffee brands (two of the Arabica type, Robusta, a mix of both) with various mix compositions and with various roasting levels.[195] All three coffee varieties have been properly classified, while the e-nose instrument was capable of more correctly distinguishing coffee with different roasting levels than of different blend. The author stressed the need for improving the procedure and the equipment, through obtain higher selectivity and stability of sensors. It will assure potential use of an electronic instrument for on-line quantitative process control in the food industry.

Similarly, Fukunaga *et al.* used a device equipped with 6 MOS sensors for the analysis of various coffee blends. It has been found that the sensor output signals were closely linked to the roasting level of the coffee. In addition, it has been found that coffee with a medicine-like aroma was more easily detected by means of an e-nose instrument than by GC-MS.[47]

Delarue *et al.*[15] estimated the applicability of MOS and CP sensors for the identification of instant coffee powder coated with a flavored oil. CP sensors were not able to discern aromatized coffee from non-aromatized coffee, which was caused by their high sensitivity to the presence of water and CO_2. Contrary to this, the MOS sensors allowed for the correct differentiation of the coffee samples. However, Shilbayeh and Iskandarani[290] made an attempt to use a system based on Figaro TGS800 series sensors with an integrated heating system which leads to the stabilization of their temperature and evaporation of aromatic compounds from their surface. The application of such a system together with

appropriate software allows for the correct classification of coffee varieties. The main factor differentiating the coffee samples was the mean response time of the sensors. Tests have shown that a smart electronic nose system can be useful for analysis of the volatile fraction of food products, in particular, for quality control of coffee.

b. Tea After harvesting season, tea leaves are exposed to the influence on various external factors. The most important among them is the oxidation process, i.e., fermentation of tea. Cut-off tea leaves are laid on the ground or on a belt conveyor, where the oxidation process is conducted under strictly defined conditions, i.e., at proper temperature, humidity, and defined air circulation. During this process, the leaves change color from green to copper-brown and aroma from grassy to floral. It is crucial that the fermentation process should be carried out for a sufficiently long time to achieve the highest tea quality. For this purpose Bhattacharyya *et al.*[291] have checked the usefulness of the e-nose instrument for monitoring the fermentation process of black tea. Their research has confirmed the possibility of using the system, characterized by high accuracy and repeatability. The method based on the e-nose instrument can find an application in the processing of black tea, because it is less arbitrary than obtaining the subjective opinions of many experts. The method can be applied off-line without using complex tests, which may change the sample composition. Such objective methods can be the basis of analysis of tea quality during its production.

The same research group used the e-nose instrument for assessment of final quality of finished tea.[292] The group found that the e-nose instrument can determine the quality of tea like sensory evaluators but with much higher accuracy, which leads to better classification. Moreover, the e-nose instrument made it possible to choose the optimal withering time of tea leaves. However, Dutta *et al*. analyzed 5 tea samples of different quality.[27,293] The tests were based on the use of an e-nose instrument to determine the aroma of the teas with the aim of broadening the possibilities of quality analyses of teas or totally replacing the presently used methods by the new technique. A system has been employed with an array of MOS sensors and various statistical analyses were applied (PCA, the FCM algorithm, the SOM method, RBF, ANN). The research team achieved a 100% correct classification of five tea samples of different quality. The results obtained have proven the applicability of the e-nose instrument for discerning the aroma of teas produced in various conditions. Similar research was carried out by Yu *et al.*[168] They evaluated the capacity of an e-nose instrument (PEN2) to classify the green-tea quality grade. Four tea groups (A120, A280, A380, and A600) with a different quality were analyzed. Using LDA, each variety of green tea has been correctly categorized to the proper quality grade. The method using the ANN allowed for the correct classification of 90% of all green-tea samples.

c. Grains The Swedish Farmers Supply & Corp Marketing Association[294] employed equipment from the Alpha MOS (FOX 3000) as a tool which could replace the presently used methods of grain quality evaluation (sensory analysis). The scientists used a 12 sensors device and were able to discern 80 wheat and barley samples with 80% correctness. It has been found that after proper optimization of the system and the method, the e-nose instrument can constitute a useful tool for grain analysis.

Borjessön *et al.*[169] used the e-nose instrument for the classification of grain with regard to their aroma and prediction of the degree of mustiness. The signals from MOSFET sensors were processed by ANN. A total number of 235 samples of wheat, barley and oat were sensory classified by at least two grain inspectors. Two types of classification methods were introduced: the first one divided the samples into four classes (mouldy, acid, burned, normal), the other one into two classes (good and bad – inspector opinion). The e-nose instrument correctly classified 75% of the samples in the four-class system, 90% in the two-class system. The second classification system allows for more correct classification in comparison with sensory evaluation by inspectors, which may create the basis for the introduction of this system into routine grain quality tests. An additional advantage in advocacy for the introduction of the e-nose instrument to grain industry is the fact that a person evaluating the degree of foulness of grains is subjected to infection by mildew spores, fungi, and bacteria. Jonsson *et al.*[294] also confirmed that the e-nose instrument is the best and indispensable tool for quality control of grains. Results obtained using of ANN allowed to classify the grains with sufficient accuracy into four classes: good, slightly moldy, moldy, and very moldy.

The usefulness of the e-nose system in determining the degree of grain mustiness was also proved by Magan and Evan.s[295] According to them, the e-nose instrument successfully identified grains tainted by fungi producing mycotoxines, confirming their presence.

d. Honeys Pollen, sensory analysis, and physicochemical studies are most often employed in quality and botanical/geographical origin assessment of honeys. As alternative it is possible to apply more objective and reliable instrumental techniques, especially chromatographic techniques, such as CG-O, GC-MS,[296] GC×GC-TOFMS.[297] They are relatively expensive, time-consuming and often cause destruction of the sample. Due to this, scientists look for alternative methods in investigating honey products. According to the literature, the e-nose instrument can be successfully used for this purpose. It has been used in classification of botanical and geographical origin of honeys, as well as for evaluation of their quality and authenticity. Ampuero *et al.*[145] employed MS-based e-nose system to distinguish unifloral honeys and to identify their botanical origin. Three different sample preparation techniques: static headspace analysis (SHSA), SPME, and inside-needle dynamic extraction (INDEX) were compared. Statistical methods, PCA and DFA, were used as a tool for the classification of honey samples in respect of their varieties, which were already determined by standard methods. Varieties of Swiss honeys: acacia, chestnut, dandelion, lime, honeydew, rape were analyzed. INDEX as well as SPME has shown the ability to considerably enrich volatile components during extraction, and what is more,

significantly heavier molecules were extracted than in the case of SHSA. The last of the mentioned extraction techniques has emerged as the best from the point of view of speed and reliability; what is more, results obtained with its use are convergent with results from the classic method of evaluation of the botanic origin of honeys (pollen analysis). Similar research was carried out by Benedetti *et al*.[298] They investigated 70 honey samples of different botanical and geographical origin, using an e-nose instrument equipped with 10 MOSFET and 12 MOS sensors. The sensors signals were analyzed by means of PCA and ANN. The second PARC method gave satisfactory results. The proposed methodology was simple, quick and did not require isolation of volatile compounds. For these reasons, this technique could find application in on-line quality control. The results also confirmed the usefulness of the e-nose instrument as a tool for determining the origin of honeys.

The problem of distinguishing of geographical origin of honeys was also investigated by Čačić *et al*.[299] Samples of chestnut (*Castanea sativa Mill*.) and black locust honeys (*Robinia pseudoacacia L.*) were subjected to analysis. The physical and chemical properties of honey and its botanic origin were investigated in an accredited laboratory. The geographical origin was determined on the basis of interviews with bee-keepers. The signals obtained from the e-nose sensors were processed using PCA and were used to determine differences between profiles of volatile compounds of honey samples with the same botanical, but different geographical origin. The results from PCA have shown that samples of honey from regions close to each other have a very close profile of the volatile fraction, contrary to honeys from regions far more distant, whose profiles were differentiated. This dependence indicates the possibility of using the e-nose instrument as a tool for determining the geographical origin of honeys.

Ghidini *et al*. checked the utility of the e-nose instrument for evaluating the authenticity and origin of honeys and compared this technique with traditional methods (sensory, chemical, and pollen analysis).[300] For this purpose, they tested 15 honey samples – fourteen from Italy (4 from Brescia and 10 from Sondrio) and one sample from China. The ISE Nose 2000 based on 12 MOS sensors (MOS-AOS system) equipped with a semi-automatic sampler (16 samples) was used. PCA and FDA were used as data analysis methods. The measurement results indicate that differentiation and evaluation of the authenticity of honey samples with the use of conventional chemical methods is very difficult. The use of the new, relatively cheap, fast and non-destructive e-nose technique is promising and probably after validation of a greater number of samples, it can find practical application. The analysis of 15 samples using the e-nose instrument was capable of distinguishing a variety of Chinese honey from Italian honeys and correct identification of the chestnut honey from the others. It demonstrated the suitability of e-nose instrument for differentiation of botanical and geographical origin of honeys.

X. SUMMARY

One of the main priorities observed lately in food technology is increased concern and care for safe food. In many cases the analysis of compounds responsible for taste-aromatic sensation, performed by using classical sensorial analysis or instrumental methods delivers a valuable information about the quality of a given food product. However, conventional flavor analysis techniques such as gas chromatography or gas chromatography-olfactometry, often do not provide reliable results, mainly due to the complexity of different food aromas and the subjectivity of human response to odors. Hence, the need for an instrument such as the electronic nose that combines high sensitivity and correlation with data from human sensory panels in food control still exists. Other advantages of e-nose instruments such as mobility, short time of analysis, low price, and ease of use cause that e-nose systems enter into increasing number of industrial enterprises for control and improvement of food quality far away from well-equipped chemical laboratories and trained specialists. Recent applications of electronic nose technologies have come through advances in sensor design, material improvements, and progress in microcircuity design and system integration.

It should be kept in mind, however, that the expenditure of work, time and financial outlay necessary to build, train and adapt (program) such equipment to appropriate applications are initially still very high. Nevertheless, costs borne at the production stage are returned quickly during the practical utilization of such a system. This is due to the superiority of e-nose instruments over classic sensory analysis and chromatographic techniques, resulting from simplified sample preparation, nondestructive influence on the analyzed sample, very short time of analysis and objective and repeatable results of analyses. Further utilization of the e-nose instrument is related to the relatively low operational costs, therefore the financial expenditures incurred are returned after a relatively short time.

A proper selection of an appropriate e-nose instrument for a particular application should include assessments of the selectivity and sensitivity range of individual sensors arrays for particulate target analyte, the number of unnecessary redundancy sensors with similar sensitivities, and various operational requirements (run speed or cycle time, recovery time between samples, data analysis) and result-interpretation requirements. Furthermore, it should be remembered that the proper functioning of gas sensors may be affected by several parameters, such as sensor poisoning, the strong influence of moisture, and the nonlinearity of signals. Because the e-nose gas sensors provide a large and complex amount of data the pattern recognition techniques, such as principal component analysis, linear discriminant analysis, and artificial neural network have to be used for data processing generated by each sensor.

As discussed in the review, there are many important and potentially exciting areas where existing e-nose instruments may be applied. Generally, electronic nose instruments are utilized since eighty's as aromatic quality sensors in the agricultural, environmental, medical, biotechnological, and food domain. In food control there are five major categories of their use: process monitoring, shelf-life investigation, freshness evaluation, authenticity assessment, and other quality control studies.

The classical e-nose instruments are based on an array of gas sensor as detection system and often they do not produce enough information for many recent real-work problems. Therefore, the observed tendency is to combine different types of gas sensors to produce hybrid systems. However, it should be realized that this involves more complex electronic and it is also necessary to normalize and standardize the different sensors outputs. On the other hand, to avoid typical problems connected with classical e-nose instruments, it is possible to use of e-nose systems based on MS or fast GC. The development of such instruments is directed to miniaturization and utilization as portable devices.

In spite of that fact, e-nose instruments are a fast, reliable, cost effective, in line, automatic, and operator friendly systems. Much more development is still required before their full potential can be reached.

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