Instrumental sensory analysis in the food industry

Part 1: Electronic noses

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Using human senses to evaluate food quality is a firmly established element in the processes employed by the food industry for ensuring quality and developing products. However, human sensory analysis is increasingly being supplemented by instrumental sensory analysis. Efforts are being made to mimic human sensory systems using electronic equipment and sensitive detection technologies (sensors, gas chromatography, etc.) that then can help to prepare for or complete human sensory tests. Instrumental sensory analysis is growing in importance, particularly in areas in which there is regular requirement for standardised and rapid analysis. This article and the parts that follow provide information on the current possibilities and technologies in the field of instrumental sensory analysis. Part 1 of the series focuses on 'electronic noses'.

Instrumental sensory analysis – definition

In addition to trained panels of human testers who use their senses to evaluate food and drink, there are now technical instruments designed to analyse individual sensory characteristics. Although only humans are able to deliver comprehensive sensory testing results – because of how they can combine sensory impressions in their brains and draw on past experiences – the equipment, processes and technologies of instrumental sensory analysis have become standard in many fields. Their possible applications are growing in number, particularly in areas in which there is regular requirement for defined, reliable and rapid analysis. Human sensory analysis, a time-consuming process that involves random sampling, can now be supported by technology-based chemical and sensory analysis and potentially also at line testing systems.

Instrumental sensory analysis encompasses the use of devices to capture:

- **Appearance (visual impact),** e.g. spectrophotometers, colorimeters, and electronic eyes for color and shape evaluation
- **Smell,** e.g. sensor-based electronic noses, gas chromatographs or ion-mobility spectrometry based electronic noses
- **Taste,** e.g. electronic tongues
- **Texture, consistency, mouthfeel or viscosity,** e.g. texture analysers, viscosimeters, rheometers, crustometers

1. How an electronic nose captures smell

The term odour encompasses all natural and synthetic substances that are identified by the olfactory system as smell. Odour is not a property of the material or substance itself, however. It is rather the sensory impression of the 'smeller'. The word scent is often used as a synonym for odour, but this should be restricted to the odours produced by plants and animals for the purposes of communication. Most odours take the form of volatile organic compounds (VOCs) that man has learnt to recognise throughout the course of evolution. Odour-producing substances helped us to find food, form relationships and detect danger, so we remember them. However, human beings are not exclusively dependent on chemical composition when it comes to perceiving smell. Substances that are chemically similar are often perceived differently because of our past experiences and as a result of selection and filtering in the brain.

Electronic noses are instruments designed to analyse odours and VOCs that are either already gaseous or have evaporated from a liquid or solid. They were first used in 1984 by the US Coast Guard to identify volatile substances in emergency situations. Today, they are used not only in the food industry but also in medicine, the automotive industry, agriculture, cosmetics and waste and sewage management. Up until now, interest in instrumental sensory analysis and electronic noses has been driven by the fact that the conventional method of analysis using sensory panels has several drawbacks. The use of trained testers can – depending on frequency of deployment and level of training – be very expensive. Also, it often takes a long time to perform the tests, and each tester can only work for a relatively short period of time because they get tired or become adapted to the smells. What's more, perceptions differ from individual to individual. Conversely, electronic noses measure VOCs and gases primarily on the basis of chemical composition and so are not swayed by the same subjective perceptions as humans. Therein lies the main difference between the two systems: sensors measure VOCs, they do not perceive odours.

2. Definition and history

An electronic nose is "a system that is designed to measure and analyse VOCs (as found in odours and fragrances) and gases. Various analysis methods and techniques are used for this purpose, and these are what differentiate the categories of electronic nose. For example, there are electronic noses that are based on sensors or gas chromatography (GC), those that use mass spectrometry (MS) or ion-mobility spectrometry (IMS), and those that use a combination of these techniques. The electronic signals or data measured using these methods are then analysed by means of chemometrics (multivariate statistics). The term 'electronic nose' therefore encompasses the 'identification' of odours through measurement of chemical substances, the capturing of the resulting analytical data and the final interpretation of this data. It should be noted, however, that electronic noses have no capacity to offer interpretations of odours. They can only provide data on VOC concentrations, i.e. both the odourless and odour-producing elements."

The first electronic nose, developed in 1982 by Persaud and Dodd at the University of Warwick, mimicked the human olfactory system. It consisted of three metal-oxide sensors that reacted to the odour-producing substances that flowed past them, similar to the way in which olfactory cells in the human nose are activated. The results were derived from the signal patterns. In the 1990s, a more technologically advanced electronic nose became established, with modified MOS applications and with polymer sensors. For some years now, innovative approaches have been making an increasing use of ion-mobility spectrometry, including in combination with gas chromatography. These and various other technologies make the electronic noses available on the market today suitable for all kinds of applications. Intensive research is still being carried out on the optimum techniques for measurement and analysis.

3. Design and types of electronic nose

In principle, an electronic nose is made up of three components: a system that extracts and prepares the sample, a detection system and a system for capturing and analysing data.

3.1 Extracting and preparing samples

The models for extracting and preparing samples range from manual and automatic to 'in line', i.e. those that are directly integrated into a process.

3.2 Detection devices

Detection devices, sometimes used in combination, include: sensors, gas chromatographs (GCs), different types of mass spectrometer (MS), e.g. ion-mobility spectrometers (IMS).

3.2.1 Sensors

In order for as broad a range of gases as possible to be measured, various types of sensors (sometimes known as sensor arrays) are used. The International Union of Pure and Applied Chemistry (IUPAC) defines chemical sensors as "devices that transform chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal." The different types of sensor have both advantages and disadvantages because of how they differ in terms of substrate, VOC-sensitive layer, input variable, working temperature, lifetime, decontamination (regeneration), selectivity and sensitivity.

Metal-oxide sensors

Metal-oxide sensors, also known as semiconductor metal-oxide sensors, consist of a carrier (ceramics, silicon) and a metal-oxide film (tin, zinc, titanium, iron, cobalt, nickel). They come under the category of electrical sensors. During the measurement process, VOCs and gas molecules are adsorbed by the metal-oxide film, thereby changing its electrical resistance. This change is translated into a signal. The OdorChecker made by the company 3S GmbH in Saarbrücken, Germany, combines this technology with other systems and a targeted temperature-control method. The FOX and GEMINI systems, developed by Alpha MOS, are also based on sensor array technology. FOX has 18 sensors and GEMINI has six.

The benefits of the metal-oxide sensors are as follows: they are cheaper, they have a low sensitivity to moisture and their switching technology is simpler. The disadvantages: high operating temperature and therefore higher energy consumption, limited selectivity[1].

Polymer sensors

Polymer sensors, which also come under the category of electrical sensors, are made of conductive plastics that adsorb VOCs and gas molecules. As their material swells, it loses conductivity. This change is translated into a signal. Advantages: broad selectivity, high sensitivity and stability, low operating temperature. Disadvantages: polymer sensors are highly sensitive to hydrogen, which can distort measurement results, and their functioning is impaired by oxidation after a certain period of time.

Other types of sensor include **MOSFETs** (metal-oxide-semiconductor field-effect transistors), which, like polymer sensors, are also classed as electrical sensors, and 'quartz microbalance' or **QMB[2] sensors**. The latter are piezoelectronic crystal sensors – mass-sensitive sensors in which the oscillation of a polymer-coated quartz disc changes depending on the VOCs or gas molecules it is exposed to. These changes are then translated into a signal.

3.2.2 Chromatography and spectrometry

Gas chromatography (GC), mass spectrometry (MS), ion-mobility spectrometry (IMS) and proton-transfer-reaction mass spectrometry (PTR-MS) are, in addition to the sensors described above, also used to assess odours. In addition to

1 Ability of a sensor to measure a concentration of a substance in presence of other interfering substances
2 Quartz microbalance

evaluating the overall odor fingerprint as sensor-based instruments, they have the advantage of giving more detailed information about the various molecules entering the composition of the odor: chemical characterization, quantification of concentration and sensory characterization (database connection). Further, beside the sensivity an improvement of the speed of analysis is possible, which could lead to an higher sample throughput and an higher proportion of substances that can be identified. For some applications there are also sensors available that will respond only to one particular substance or substance class. The HERACLES II electronic nose, developed by Alpha MOS, uses ultra-fast flash gas chromatography (cf. fig. 1). The VOCscanner, a product of the Hamburg-based VOCscan company, is based on mass spectrometry for VOC analysis into the ppb/ppt range.

Ion-mobility spectrometry (IMS) is increasingly being used as an alternative to the aforementioned technologies. IMS is a physical analysis method that makes it possible to detect trace amounts of gaseous organic compounds (µg m³). The measurement principle is based on the amount of time it takes for gaseous ions to pass through a homogeneous electrical field at atmospheric pressure. Gaseous analyte molecules are ionised at atmospheric pressure and separated in an electric field. This allows the substances to be both identified, by means of the mobility measurements, and quantified, with the intensity of the signals revealing the level of concentration. This method is used in the Analytical-IMS (A-IMS), developed by G.A.S. Gesellschaft für analytische Sensorsysteme mbH in Germany, and in the Lonestar Portable Gas Analyzer, made by Owlstone Ltd. in the UK. The miniaturisation of the technology has also been a plus, as it has allowed a portable measurement system to emerge.

Fig. 1: HERACLES, Alpha MOS

Fig. 2: FlavourSpec®, G.A.S., Dortmund

Combining a GC with an IMS not only enables a higher sample throughput (because of the increased analysis speed), but also exploits the selectivity of the GC and the high sensitivity of the IMS to identify individual VOCs or their 'fingerprints'. It's how the G.A.S. FlavourSpec® – in an analysis time of three to 15 minutes – is able to produce a 3D spectrum 'fingerprint' of a gas, liquid or solid sample (cf. fig. 2). Of particular note here is the physical measurement principle, which delivers reproducibilities comparable to traditional high-end analysis systems (GC, GC-MS, HPLC). A further characteristic of these systems is their extremely high sensitivity, which eliminates the need to pre-treat or concentrate the sample but enables specific organic compounds within the detection range of the human nose to be detected and quantified.

3.3 Data capture and analysis systems

Product-specific software systems are used to capture and analyse data and to visualise results. They are integrated into the respective gas measurement systems and some can be supplemented with the purchase of a reference database. This makes it easier to calibrate the electronic nose, as there is an existing 'odour memory'. An example of this is the AroChemBase, a database developed by Alpha MOS that consists of more than 44,200 compounds for the classification of molecules. Around 2,000 of these come with sensory attributes. AroChemBase will be soon extended with NIST database information. G.A.S. offers an expandable NIST-based library for a similar purpose. NIST stands for the National Institute of Standards and Technology, an organisation in the US that maintains an internationally regarded chemical compound library. It is based on the Kovats Retention Index of 82,337 compounds analysed by gas chromatography, and includes their formulas and chemical abstract registry numbers.

4. Odour measurement principle of …

4.1 Sensor-based electronic noses

4.1.1 Calibration and odour measurement

In order for an electronic nose to capture a broad spectrum of substances, it is usually made up of multiple sensors (also called a sensor array) with varying selectivity and sensitivity towards gaseous compounds. The technology employed by these sensors mimics human olfactory cells, generating electronic signals based on the odour sample and using computing power to interpret this by comparing it with a reference pattern. Instrumental odour analysis basically involves two steps – measurement and method. The samples are extracted in a process that either follows a precise set of rules or is specific to the device. Then, depending on requirements and whether this is possible, water, oil, dust and other irrelevant and potentially disruptive gases and VOCs are removed. After this, the different types of VOC (volatile, semi-volatile, etc.) are separated out and transferred to the sensor array, where the responses of the sensors are measured in various ways. The reactions of the sensors to the gas generates a specific signal pattern ('fingerprint').

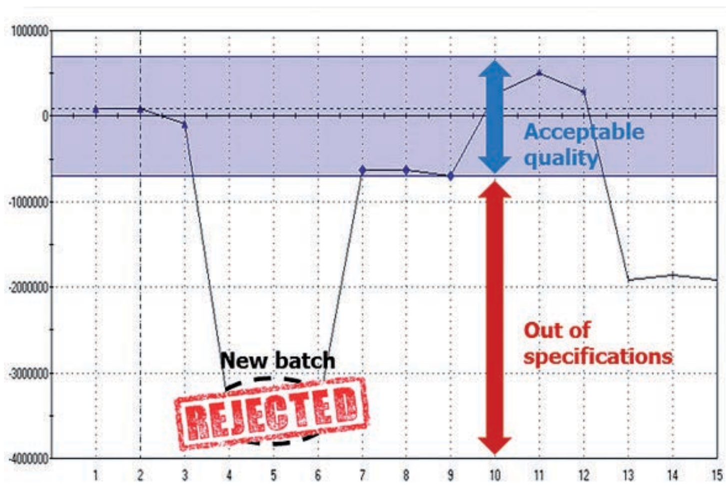
For the second step, the analysis of the signal, pre-classified measurement readings are needed. These take the form of existing standard signal patterns and are needed to 'train' or calibrate the electronic nose before use. In order, say, for a bad odour to be identified, it has to undergo a standard sensory test by a panel of human experts – who interpret the smell as bad – and instrumental sensory analysis so that the relevant signal pattern can be recorded. Such information enables the electronic nose to compare its signal patterns with the reference patterns and to classify them accordingly.

4.1.2 Data analysis

After the VOCs have been measured, the data is analysed. This can be done using either statistical analysis or intelligent analysis. In the statistical approach, the signal patterns are evaluated using probability models. Examples of this method include discriminant analysis, principal components analysis, linear calibration and cluster analysis. The intelligent analysis approach favours the use of non-linear methods – such as artificial neural networks or 'fuzzy' pattern analyses – that have the ability to learn, to organise themselves and, to a certain extent, mimic the human brain.

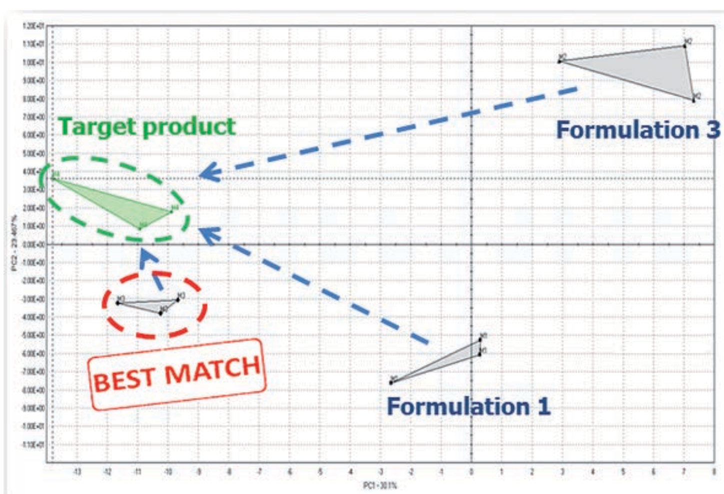
Figures 3 and 4 show possibilities for the visualization of results in quality assurance and product development tasks.

Fig. 3: Quality assurance analysis result



Quelle: Alpha MOS, Toulouse

Fig. 4: Product development analysis result



Quelle: Alpha MOS, Toulouse

4.2 Electronic noses based on GC and GC-MS as well as combined GC-IMS systems

4.2.1 Odour measurement

For more than 65 years, gas chromatography (GC) has been a widely used, high-performance analysis method for providing qualitative and quantitative measurements of complex mixtures of volatile compounds. It works by separating a gaseous substance into individual chemical compounds. A combination of GC with mass spectrometry (MS) broadens the spectrum of application because chemical compounds are not only quantified but also – through comparison with libraries of data or standard substances – characterised, which enables unknown compounds to be rapidly and reliably identified.

The method for measuring VOCs using gas chromatography (GC) coupled to an ion-mobility spectrometer (IMS) is based on a separation of the mixture in the column and then an additional separation of the ions in the spectrometer by times of flight. Many systems are equipped with an automatic headspace sampler to make it as easy as possible to take and prepare samples, and to make sample handling, injection and analytical parameters accurate and reproducible. Before the odour is measured, the sample matrix is extracted using gas chromatography. This involves delivering the substance mixture to the separation column selected for the application and passing it, together with a carrier gas (helium, nitrogen or purified air), through a thin, coated capillary in which the solid (silica gel soaked with alcohol) or liquid (liquid film/capillary columns) stationary phase is located. As the mixture passes through the column, its individual compounds bind more or less well to the stationary phase depending on their physical properties (their polarity). The mobile phase – the flow of gas – carries the less weakly adsorbed analytes ahead of those that are more strongly adsorbed, thereby separating the individual substances of the mixture.

From the separation column (elution), the carrier gas passes straight into the ion-mobility spectrometer. Here the analyte gas is ionised. These ions are accelerated by an electric field that moves them through a longitudinal drift tube containing an opposing 'drift gas' (air or nitrogen). Each substance has a unique pattern of ions, which during their flight are separated from each other in accordance with their molecular mass and geometric structure. A detector fitted with an electrometer then measures and amplifies the charges of these ions. This enables VOCs in gases and in the headspace of solid and liquid samples to be quickly and selectively identified.

4.2.2 Data analysis

The measurement result is provided by the individual substance signals that are detected and quantified in accordance with the calibration of the system. Alternatively, a 'fingerprint' of the detected volatile compounds can be produced, which can then be processed using various data analysis systems. The measurement result can therefore either take the form of the actual concentration of the analysed substance or a complex odour impression based on similarity and comparison with reference patterns (reference database).

5. Potential applications of electronic noses in the food industry

Numerous projects have been described that demonstrate how electronic noses are being used successfully and in clearly defined processes by producers of food and beverages to help their sensory departments and tester panels in quality assurance and research and development. There are examples of them being used to monitor storage conditions and product freshness and to improve quality by detecting defects. Moreover, trials have been run to see if they can test shelf life, detect the geographical origin of ingredients and products, and identify abnormal flavours. Electronic noses are also being deployed to monitor and optimise production processes. The following examples show how they are being used for different product groups.

Beer: sensor-based electronic noses have been used to detect the **manufacturing method/process technology** employed to make different beers. Lagers and ales [3] were identified with an error ratio of just 3 per cent, whereby the measured difference was not based on odours, but on the changes in concentration of organic and inorganic compounds. For such analysis to be successful, samples have to be properly prepared. Enrichment methods such as dynamic headspace analysis or solid-phase microextraction are used to reduce the concentration of ethanol and water vapour so that there is no negative impact on the measurements.

And for a number of years now, a GC-IMS-based electronic nose system has been used to monitor the brewing process and to measure concentrations of diacetyl and pentanedione – products of beer fermentation – in the µg/L range. It is also sometimes possible to measure fermentation byproducts directly from the gas phase.

Fish: electronic noses have been used to detect **spoilage** of cod via the indicator trimethylamine[4].

Meat: electronic noses have been used to **test the shelf life** of roast chickens packed in a modified atmosphere and to compare the results with those of microbiological and sensory analysis and gas chromatography. A high correlation was shown between the results given by the microbiological analysis and those obtained from the electronic nose.

Oil: electronic noses have been used to reveal the origin of olive oils. Note that the quality of olive oils is influenced by **geographical provenance**, olive variety and cultivation method, and it can be difficult to tell if a product is authentic.

Fruit: a method has been devised to **record how flavour develops** during the post-harvest ripening process. To do this, an electronic nose's sensors were coated with a material that was selective for substances that promote ripening. Using this method, it was possible to classify apples based on their ripeness.

These research projects give a brief overview of the broad range of applications that can be addressed by electronic noses in the various sectors of the food and beverage industry. In many production areas, the monitoring of odours and flavours plays a key role in quality control. When it comes to providing sensory assessments of food and drink products, electronic noses frequently present the ideal solution for supporting specialists with their 'trained noses'. Human sensory analysis often only takes the form of a spot check, whereas electronic noses can be used to permanently monitor the various odours, including foreign odours and VOCs, thereby ensuring compliance with defined criteria relating to product quality. This is particularly applicable to the following tasks:

3 The difference is in the yeasts: ales are brewed with top-fermenting yeasts, lagers with bottom-fermenting yeasts.
4 As fish decay, more of these amines are released.

- Monitoring of packaging quality and detection of foreign odours from packaging materials
- Monitoring of freshness and product quality through identification of 'off odours', such as the rancidity of meat
- Identification of bacterial contaminations or levels of mycotoxins in bread and baked goods
- Identification of fermentation defects, e.g. caused by foreign yeast cultures in dairy products
- Monitoring of storage conditions and shelf life,
- Flavour evaluation and stability,
- Authenticity tests, e.g. geographical origin of ingredients and/or materials

6. Providers of electronic noses based on different technologies (selection)

Electronic noses based on different technologies are developed and sold by a number of companies. A selection of them are listed in table 1.

Table 1: Overview of technology providers (selection)

Company	E-Nose	Technology	Applications
AlphaMOS www.alpha-mos.com	FOX GEMINI ULYS, ULYS-O HERACLES RQ BOX (on-site e-nose) Airsense	MOS MOS GC, GC-Olfactometry Ultra Fast GC MOS, PID, electrochemical cell IMS	Food & beverage, plastics & packaging, flavors & fragrances, cosmetics, pharmaceutical industry, environmental sector
3s GmbH www.3s-ing.de	3S-OdorChecker (portable)	Pellistors, semiconductor gas sensors	Quality control in various sectors
GSG measurement and analysis equipment www.gsg-analytical.com	MOSES II VOCmeter	QMB, MOS, calorimetric sensor 8 QMB, 4 MOS	Example applications: perfume oil, coffee, plastic Quality control in the food, plastic, textile, pharmaceutical and chemical industries
G.A.S. Gesellschaft für analytische Sensorsysteme mbH www.GAS-Dortmund.de	FlavourSpec BrethSpec GC-IMS A-IMS UV-IMS	GC and IMS	Quality control of raw ingredients, intermediate products and end products, process control and monitoring in the food and drink industry, flavouring production and medical research
Owlstone Ltd. www.owlstonenanotech.com	Lonestar	FAIMS (Field Asymmetric Ion Mobility Spectrometry)	Quality control, purity control, identity control in the food industry, freshness tests
VOCscan www.vocscan.com	VOCscanner®	Mass spectrometry	Conformity and quality control, process optimisation and control, benchmarking in product development, correlations with sensory panels, medical diagnosis

7. Summary and outlook

In summary, it is clear that the different electronic noses offer benefits over the traditional sensory panels and human sensory analysis in terms of objectivity, reproducibility and long-term viability. These benefits are to be expected mostly in areas in which products that should preferably be very homogeneous are subjected to routine, standardised testing so that their gas/gas mixtures can be identified and clearly described. Because electronic nose tests can quickly tell you whether the quality of a product is good or bad, they are often used to pre-select samples that are then subjected to more intensive analysis.

The use of electronic noses in the food industry can sometimes be limited by the fact that there is a need to analyze many products with very complex flavour profiles. The variance between these can often be immense, making it somehow difficult to properly calibrate the electronic noses and therefore can limit the identification of particular substances. Also the calibration as such, could require a some know-how and practical experience. While sensor-based electronic noses can only be used for overall comparisons without compounds characterization, their implementation in quality control environment might be sometimes simpler than GC e-noses which require higher skills to interpret chromatography data. But the GC-based instruments are more suitable for applications in which chemical information about specific compounds is needed or also for analyzing matrices with a predominant compound such as alcoholic drinks (ethanol can be isolated and the analysis focused on aroma compounds). These factors have to be taken into account before using sensor- or GC-based electronic noses.

The electronic nose systems based on IMS or GC/IMS have a different physical working principle, however, and are positioned between traditional human sensory analysis and high-end mass spectrometry. By and large, these do not suffer from the commonly occurring 'typical drift', which leads to non-reproducible results, meaning that their results are more reliable than those produced by other analytical measurement systems. Moreover, the high selectivity and sensitivity of IMS-based detection systems (µg/L range) enable measurements to be taken directly from the gas phase (like in the human nose), thereby eliminating the time-consuming process of preparing and concentrating the samples. Consequently, such systems do not necessarily need a laboratory. They can usually be deployed where the raw ingredients come in, within the production process itself or at the final checks stage. Simple handling is an additional benefit of these systems.

In conclusion, the different electronic noses offer the food processing industry compelling additional options in quality assurance, product development and product monitoring, on the proviso – as with other projects in the food technology sector – that the project objective and the challenge to be solved are clearly formulated and their associated parameters are precisely specified.

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