CHAPTER 4

The test is in the tasting

Organoleptic Product Quality

Organoleptic is defined as "capable of being perceived by one or more sense organs", where the common senses are touch, hearing, smell, taste and sight. The perception of odour/taste is a key factor for product quality and usually derives from a combination of chemical components. Complex issues such as off-odours, off-taste, contamination in raw materials, intermediates and final products can be detrimental to the quality of a product, comfort and impact on health, and are major causes of consumer complaints worldwide. Emissions from polymers in the end application often cause nuisance smells ("plastic" or "rubber"-like) and affect air quality, especially in closed spaces, and taste performance in liquid packaging applications. As many of these materials are used in cars, trains, aircrafts, in buildings and factories, it is necessary to select polymers with low emission of (potentially hazardous) volatile compounds. This also calls for sensitive and selective ways to characterise volatile organic chemicals (VOCs) and to identify/taste odour sources both in product and process control. The economic impact of production variations is increasing dramatically and has led to rapid advancement in the field of characterisation of odours, off-taste and tainting.

Taste is the ultimate measure of the quality of a food product. Industry has invested countless years identifying contaminants that detract from the unique taste of high profile products. There are only five major taste receptor types – bitter, sweet, sour, salty and umami. As opposed to the low hundreds of uniquely discriminated tastes, with typical character impact compounds such as 2,3-butanediol ("butter") or isoamylacetate ("banana"), for odours this is in the order of the low thousands. Most of the odours are caused by organic volatile chemicals, rather than by particulates such as smoke or fog. Odorant molecules are typically hydrophobic and polar with molecular masses of up to about 300 Da. Gas chromatography has been, and still is, the instrumental method of choice for identifying the source of **off-odour**. In recent years, progress in sensor technology has enabled development of instruments ("electronic noses", e-noses or EN) that can mimic the human sense of smell and provide low-cost and rapid sensory information. These instruments cannot identify the chemical compounds responsible for odour, but can compare samples and categorise them, after proper training. Input from a sensory panel is required and constitutes the link between instrumental methods and real practice. They can thus be used as quick screening tools or for monitoring air streams to detect the presence of chemical compounds.

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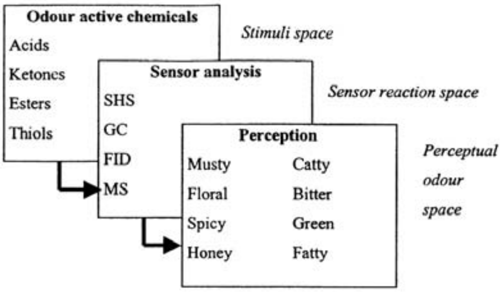

Fig. 4.1 Three-layer model of odour perception and mapping

Unlike a purely physical entity that can be clearly attributed to one isolated physical phenomenon (such as current, which is a flow of electrons, or colour, determined by photons impinging on a surface), odour is triggered by a multitude of different compounds interacting with millions of neurons. As shown in Fig. 4.1, odour perception is a multi-tiered phenomenon involving at least three dimensions: stimuli space (in which "odour active" chemicals are located), sensor reaction space (which maps the presence and quantity of odour active chemicals) and perceptual odour space (which maps output signals to a perceptual, mental, or mathematical pattern). It is of fundamental interest to determine whether the perceptual **odour space**, which is the target of e-noses, is a metric space. It is well known that the much simpler perceptual colour space gives no clear evidence for a metric function. In a non-metric space there are no "basic vectors". The existence of basic vectors would mean that there are "primary odours" out of which all existing odours can be synthesised. Intuitively it is understood that this is not the case. Then, if no primary odours exist, an "electronic nose" is not an analytical instrument either (an analytical instrument decomposes a compound entity into its individual constituents).

Trying to "image" an odour is thus difficult and presents a number of potential problems. Some of the limitations are of principal rather than technical nature; they cannot be overcome by perfecting sensor technology or by changing the "analysis" method altogether. It has been argued by Stoll [1] that there is no generally applicable "distance function" and hence no possibility to do measurements (that would correspond to the mathematical definition of that term) in perceptual odour space. In the absence of a generally applicable co-ordinate system there is also no common frame of reference for "odour data" measured for different types of sensors. Consequently, vendor- and technology-independent databases of odour are unlikely to ever become a reality. Nevertheless, experiments show that there is a strong correlation between odour perception and patterns derived from sensor signals. Properly calibrated electronic noses based on multiple chemical sensor arrays can provide an excellent aid in classifying and characterising odours. The implication then is that, while no metric for odour space in general can be assumed to exist, for a limited "sub-regime" pertaining to one particular type of odours there may well exist one. It is then the point how to find a metric sub-space for a given odour problem.

The lack of a "primary odour" system means that, for some time to come, each instrument/sensor type will be constrained within the "feature space" it spans. GC- or MS-based "noses" do not score any better than multi-sensor systems in this respect. Chances are enhanced with the application of different sensor and transduction principles simultaneously. The gap between stimuli and perceptual odour spaces must be bridged by cross-validation with a human sensory panel for each type of application.

Odour problems in polymers generally arise from:

(i) outgassing of residual monomers, process solvents or chain transfer agents;
(ii) low-MW oligomers, oils and waxes trapped in the polymer;
(iii) thermal degradation of the polymer during processing, end-product manufacturing and use;
(iv) additives with high vapour pressure (*e.g.* BHT and 2-hydroxy-4-octoxybenzophenone);
(v) degradation or interaction of additives in the polymer formulation;
(vi) volatiles produced during curing of thermosets, adhesives, sealants, *etc.*;
(vii) radiation sterilisation of plastic packaging;
(viii) trace impurities;
(ix) chemical reactions with the environment (*e.g.* hydrolysis, oxidation); and
(x) external sources.

Apart from residual monomers and process solvents, some common types of outgassing are formaldehyde vapours (from urea-formaldehyde resins), emissions from car interiors, synthetic carpets, *etc.* The contribution of a compound to release an odour from a polymer is determined by the odour threshold, molecular weight and polarity. Processing conditions also have some impact; accurate degassing during compounding is absolutely necessary. For typical processing temperatures of most common polymers, *cfr.* ref. [2]. **Production variables** have a potential effect on polymer odour in PE manufacture [3]. The type of polymerisation process (low-MW waxes), the activity and level of metal catalyst residues, solvents, oxidation of the polymer and additives may all contribute to odour formation. Incorporation of fillers can also lead to considerable odour generation in compounds, although fillers do not smell. The reason for this effect probably can be found in the interaction of active sites and/or heavy metal traces of the filler with the polymer or the stabilising system. Yet, in most cases the polymer pellets produced are not to be blamed; odour/taste problems often arise from critical processing conditions of the polymer. Organoleptic properties are not to be measured on granulate but on the end-product.

The source of odours can not always even be assumed to be related to the polymer, the additives formulation, or manufacturing process. Other sources of odours that may be picked up during storage, handling, transport and usage should be considered, *e.g.* contamination from repeat-use containers, cross-contamination from storage silos, odours emanating from other products stored in warehouses, possum/cat urine contamination, *etc.* Controlling the odour generation of compounds is particularly important for automotive applications, household appliances, food and drug packaging, and affects indoor air quality in offices and homes. Many odour problems in polymeric materials are related to the formation of breakdown products, in particular aldehydes and ketones with very low odour thresholds. Thermal oxidation of PE yields various aldehydes, thermal degradation of PET leads to acetaldehyde and poly(hydroxy butyrate) yields crotonaldehyde. Erucamide yields nonanal upon thermal degradation, whereas de-esterification of nucleating agents such as dibenzylidene sorbitol gives 4-methylbenzaldehyde.

Off-odour may be classified as a common type of **failure**. Base packaging material can itself contain solvent residues, either from coatings or, where the base packaging material is a laminate, from an adhesive. Such solvent residues can be ethyl acetate, toluene and THF, all of which have strong odours. Printing inks also often contain solvents with well-defined odours. A criterion for selection of a solvent for use in packaging manufacture, *e.g.* for printing inks, is a high odour threshold (OT) value (10-100 mg/m^3). There are no generally agreed maximum levels for residual solvents in food packaging. The total level of residual solvents should preferably not exceed 30 mg/m^3; for some of the more odorous solvents, such as isopropyl acetate, individual levels should be less than 5 mg/m^3. Some types of packaging, particularly printed materials, can have detectable odours immediately after production but lose much of the odour during normal storage before use. Samples of such packaging should only be taken after the normal storage period. For substances of known chemical nature and origin, quantitative measurements can be carried out to confirm the cause of the odour. Where the off-odour is due to impurities, reaction products, or contaminants, the task of identification can be difficult. Potential odour problems related to additives are listed in Table 4.1.

The standard definition of **taint** (ISO, 1992) is a taste or odour foreign to the product; off-flavours involve an internal deteriorative change. Common sources of taints and off-flavours may derive from direct contact (*e.g.* liquid packaging systems, pallets, cleaning materials), water and aerial contamination (*e.g.* flooring materials, paints, insulation materials), chemical or microbial reaction (*e.g.* autoxidation reactions). Examples of some common chemical taints are phenols in flooring materials, halophenols and -anisoles in bleached paper/board materials, hydrocarbons (*e.g.* residual styrene monomer in PS), acrylates in UV-cured inks and varnishes, *etc.* Taints are derived from a wide variety of chemicals (phenols, halophenols, haloanisoles, sulphur containing compounds, alcohols, hydrocarbons, esters and ethers, amines, chlorinated hydrocarbons, carbonyl compounds, furans and oxygen-ring compounds, fatty acids, *etc.*).

Table 4.1 Potential odour problems related to additive types

Additive(s)	Polymer(s)	Origin of odours
• *Initiators:*		
α-cumylperesters	PVC	Acetophenone
• *Chain-transfer agents:*		
Methyl ethyl ketone;	LDPE	Residual chain-transfer agents
Mercaptans, dodecanethiol	PMMA	
• *Plasticisers:*		
DEHP	PVC	Hydrolysis products (*e.g.* 2-ethylhexanol)
• *Pigments:*		
Cadmium red, orange, yellow; ultramarine blue	Various	Acidity (H_2S)
• *Stabilisers:*		
Thioesters	Polyolefins	Sulphoxide conversion products
Organotin mercaptides	PVC	Organotin mercaptides
Red phosphorous	PET, PC	Hydrolysis (phosphine)
Ba/Cd heat stabilisers	PVC	Free fatty acids, phenols, residual solvents
• *Lubricants:*		
ESBO	PVC	Oxidation
Ca/Zn stearates	HDPE	Thermal decompositon (aldehydes)
• *Slip agents:*		
Fatty acid amides	LDPE	Oxidation (aldehydes, nitriles)
Oleamide	LLDPE, LLDPE/LDPE	Degradation
Erucamide	LDPE	Degradation
• *Nucleating agents:*		
Bis-toluidine sorbitol	PP	Decomposition (4-methyl-benzaldehyde)
• *Cross-linking agents:*		
Dicumyl peroxide	XPE	Decomposition (acetophenone, cumyl alcohol, cumene, α-methyl styrene)
• *Blowing agents:*		
Azodicarbonamide	Various	Thermal degradation (NH_3, isocyanic acid)

For purposes of **odour control**, deodorising powders (*e.g.* Abscents^{TM}, UOP) remove odour from the environment by an adsorption process. These materials exhibit extremely strong adsorption behaviour, reaching the adsorption limit at a partial pressure that is typically below the olfactory threshold of the odour. Organophilic molecular sieve-based deodorising powders are particularly effective for adsorbing low-MW organics, including ammonia, aliphatics, olefins, chlorinated hydrocarbons, aldehydes, ketones, sulphur compounds (mercaptans), alcohols, organic acids, esters, amines, indoles and aromatics; large multi-aromatic ring compounds are not adsorbed. Applications include removal of odours in cosmetics, body powder, personal care and plastics applications. In the application as a polymer additive, deodorising powders are recommended for use with reactive compounds like aldehydes and ketones in adhesives and coatings, and for removal odour from polyolefinic material such as containers, wraps, barrier film and bottles, as well as in elastomers and polyurethanes (in foot-soles). Antimicrobials, such as Irgaguard® B1000, are used for odour control of HDPE waste bins, as odour suppressant in flexible PUR mattresses and shoe insoles, and in PET textile fibres [4].

Packaging materials as a source of taints have been reviewed [5]. A monograph dealing with food taints and off-flavours is available [6]. For odour, tainting and outgassing problems with polymers, *cfr.* also ref. [3].

4.1 SENSORY ANALYSIS

Principles and Characteristics The only way to select compounds responsible for an organoleptic problem is the use of sensory analysis. Identification and clarification of off-odours is often connected with significant time and cost expenses (*cfr.* Table 4.2). Sensory analysis, which was born in the 1930s in the food-processing industry, is a science with clearly defined basic principles. The main advances are being made in analysing and interpreting sensory data, and in relating sensory data to instrumental data. Complex multivariate statistical analyses are often needed. The ambition of sensory metrology is to measure the senses. Sensory data are rarely universal.

Table 4.2 Difficulties connected with the solution of organoleptic problems

- Extremely low odour thresholds
- Same odour for numerous substances (*cfr.* ref. [6])
- Different odour depending on concentration (*cfr.* ref. [7])
- Very slow formation of off-odours
- Unexpected reactions (oxidation, condensation, dehydration, *etc.*)
- Long time required for diffusion through packaging materials
- Overlapping of odour active substances (unspecified global odour)
- High cost
- Exposure assessment

The threshold limits of chemical compounds can lie over a range of 10 orders of magnitude or more; saturated hydrocarbons have a high threshold limit and are relatively odourless, esters and unsaturated aldehydes and ketones are intensive odoriphores. Some extreme odour threshold (OT) values in air are 10^3 mg/m^3 for octane and nonane, and 10^{-4}-10^{-5} mg/m^3 for 1-octene-3-one and 1-nonene-3-one [8]. It is generally accepted that the threshold of the human sense of smell is usually lower than the detection limit of any analytical instrument and, so, organoleptic tests are still held as being the most reliable for determining off-odours.

Odour sensing technologies are essentially three, namely olfactometry, gas chromatography and electronic (or artificial) olfactometry (Fig. 4.2). Other methods use inverse gas chromatography. Odour and taste assessment remain among the most ambiguous tasks in the field of measurement science and are still largely based on human sensory evaluation. The human nose is the qualifying tool for organoleptic analysis. Sensory analysis, a quantitative technique that uses people as the measuring instrument, is widely used in measuring how food interacts with the senses. Where in the US few products reach consumers without detailed sensory testing, in Europe there is a tendency to rely more on instrumental methods.

Various levels of **panel testing** are used. Few expert judges may evaluate a particular product *cq.* flavour/odour. Alternatively, a panel trained to use validated sensory methods [9a], consisting of some 10-30 people, may be selected for their ability to discriminate between particular flavours. Finally, recourse may be taken to the subjects of a consumers panel, which have not been given special training in the use of sensory methods. Quality assurance is forcing industry to make increasing use of trained panels. Odour analysis of industrial products still relies heavily on the human nose. Panels operate at sites manufacturing products with odour specifications. Traditional odour measurements are based on dilution of samples with clean air until a perceptible odour is achieved. This defines a threshold odour number

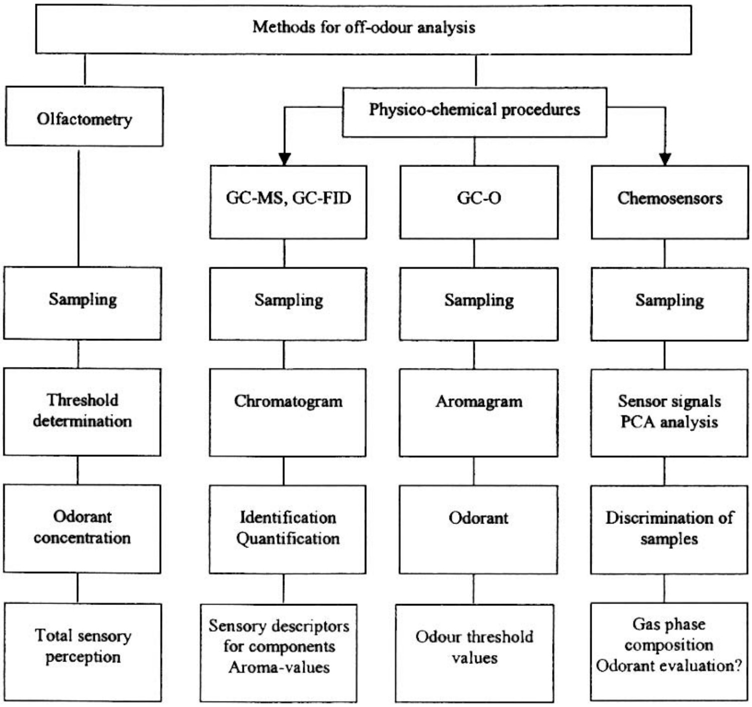

Fig. 4.2 Odour sensing technologies
After Nitz [9].

(TON). For taste panels samples are diluted with water (problem: which water?). Despite having high performances at low concentrations (down to about 10^8 molecules/mL) the use of human panellists for odour and taste characterisation has some severe drawbacks (Table 4.3). It is not easy to obtain a positive "identification" for an odour, even with a trained panel of assessors. The **sensory descriptor** for a particular compound may change with concentration and the medium. Possible chemical compounds related to specific sensory descriptors ("musty", "painty", "plastics", *etc.*) are listed elsewhere [6]. Some examples of compounds that may be associated with "plastics" odour are benzothiazole, methyl(meth)acrylate, trans-2-nonenal, oct-1-en-3-one, *trans*-1,3-pentadiene and styrene. Compounds contributing to the "plastics" odour of HDPE are 1-alkenes, constituting some 50 % of the total volatiles. Odour perception varies with concentration. Typically,

Table 4.3 Drawbacks of panel testing

- Time-consuming; high cost and elaborate methods of sensory analysis
- Sustained training required for each type of product
- Panellists operate for short periods of time and within restricted time windows
- Low degree of reliability
- Highly subjective human sensory evaluation, not suitable for certain types of analysis
- Difficult staffing of odour panels for routine QC testing (potential toxicity of synthetic chemicals)
- Need for standardisation of many experimental conditions
- Vast effort required for standardisation between different production sites
- Difficult intercomparison of panels

4-mercapto-4-methyl-2-pentanone at low concentrations provides the flavour impression of the Sauvignon grape but the off-odour associated with cat urine at high concentrations.

In order to be perceived as a taint, a chemical need not only be positively recognised, but must be characterised as deterioration in flavour quality. Characteristic food taints are often detectable at sub-ppm levels. Some **testing procedures** for odour and taint are as follows: UK standard sensory test method BS 3755: Methods of Test for The Assessment of Odour from Packaging Materials used for Foodstuffs (1964/11971); ASTM Standard E 462-84: Standard Test Method for Odor and Taste Transfer from Packaging Film (1989); ASTM Standard E 619-84: Standard Practice for Evaluating Foreign Odors in Paper Packaging (1989); and DIN Standard 10955: Sensory Analysis. Testing of Container Materials and Container for Food Products (1983). European standards for odour and off-flavour mostly set only the principles of testing. Test methods for the assessment of migration, odour and flavour of plastics piping systems for hot and cold water installation are under preparation. As taste and odour can only be assessed by people making subjective judgements a calibration and validation procedure is needed (and being developed) based on different substances that possess the typical odours or off-flavours of paper and cardboard [10]. Sensory evaluation methodologies of taints and off-flavours were reviewed [5,11,12].

Applications In product development, sensory analysis can be used to determine whether one product is liked more or less than another and to identify the particular characteristics responsible. On the other hand, the use of taste and odour panels is also a common way to determine off-taste *cq.* off-odour. As water is a most sensitive odour and taste medium, the organoleptic properties of **liquid packaging material** need to be outstanding. Odours that can be present with PE and PP and various copolymers are not usually caused by residual monomers. Odours from polyolefin plastics mostly arise from compounds produced by oxidation. It has been found that trace levels of 1-nonene present in LDPE plastics were oxidised to highly odorous 2-nonenal probably by a free-radical mechanism [8]. Plastics in use for mineral water bottles are PVC, PET, PC and HDPE. Storm van Leeuwen *et al.* [13], using both a taste panel and instrumental methods (*cfr.* Chp. 4.2), have tested the hypothesis that very low concentrations of aldehydes, ketones in combination with acids from extrusion coated LDPE gives a “plastic-like” off-taste in water and indicated the concentration range of the off-taste area (*cfr.* Fig. 4.7). Tainting from PET plastics can occur due to acetaldehyde (5-10 ppm), which is formed as a degradation product during the manufacture of the polymer, and processing into the finished packaging. The odour detection limit of acetaldehyde is about 0.2 ppm.

Because the slip additive erucamide is made from a natural raw material it can contain low levels of compounds that are oxidatively unstable. Any breakdown products can potentially contribute to taste and odour. Maltby *et al.* [14] used panel odour testing for the evaluation of various fatty acid amides in HDPE caps of PET bottles. In a special grade of erucamide (Incroslip C, Croda) the problem compounds are removed, resulting in extremely high oxidative stability and hence improved organoleptic properties.

Typical AO systems used in polyolefin hot-water pipes are combinations of hindered phenols, P-based processing stabilisers and S-based co-stabilisers. Because of the possible deterioration of the organoleptic properties that can originate from the oxidation products of thio-stabilisers combinations with HAS are recommended. Hostavin N30, Chimassorb 944 and Tinuvin 783 were tested [15].

A typical multilayer structure in modern packaging consists of paper or board laminated to one or more plastics layers with a foil intermediate. Plastic/board composites are now commonly used for liquid packaging, such as milk. With such **multicomponent packaging**, each layer can contain substances that could be odorous and/or cause tainting in the packaged foods. Odorous and tainting substances can also originate from printing and adhesives. Recently, infant milk (Nestlé - Milupa) in Italy was found contamined by an offset printing ink component (Itx) used for TetraPak containers. In **paper** used for packaging various additives such as sizing agents and fillers can be present, as well as residues of substances used in the manufacturing process, such as defoaming agents and slimicides. Unlike many printed plastics, which usually become less odorous some time after manufacture, some **board materials** have been found to become more odorous on storage. This is attributed to ongoing oxidation reactions, most probably catalysed by metal ion residues, liberating further quantities of aldehydes. Odours that can be present in paper and board materials have been attributed to substances arising from bacteria/moulds, autoxidation of residual resins and degradation of processing chemicals. An odorous oxidation compound identified as 1-hepten-3-one was found to be formed from 2-ethyl-hexanol detected in paper board samples. Surface coatings applied to boards usually consist of a filler such as China clay or calcium carbonate, with a synthetic resins binder. Where the binder is of the styrene/butadiene type, several volatile substances have been identified, including styrene and by-products from the styrene/butadiene polymerisation process such as vinyl cyclohexene, ethyl benzene, styrene, cumene (isopropyl benzene), *n*-propyl benzene, α-methyl styrene, 4-phenyl cyclohexene or other alkyl substituted benzenes [5]. All of these substances are odorous. Plastics coatings on the surface of carton board are a barrier to migration of off-flavour substances from the board [16]; PET is more effective than either LDPE or PP.

Tamm [17] has discussed the requirements for film additives in water ink technology in the case of printing of PE film for packaging. Inks require slip additives and must have low- or no-VOC emissions.

Due to their extremely low sensory odour threshold values, chloro- (TCA) and bromoanisoles (TBA) are strong odoriphores. Formation of TCA and TBA from the corresponding halogenated phenols by microorganisms is known and likewise the use of such phenols as wood preservatives (contamination of PE granulate from wood pallets). Trace amounts down to approximately 50 ppt of TCA and TBA can be mass detected in affected packaging [18].

Piringer *et al.* [7] have discussed sensory problems caused by food and packaging interactions. Methods of sensory and tactile evaluation as applied to plastic, rubbers and painted surfaces in automobile interiors, in particular soft touch, were discussed [19,20]. As opposed to sight, touch is a slow sensibility because the procedure of collecting information is long.

4.2 INSTRUMENTAL METHODS IN OFF-ODOUR/OFF-TASTE PROBLEMS

Principles and Characteristics Analysis of off-odours poses a special problem due to several factors (*cfr.* Table 4.2), amongst which the low concentration of the odoriphores. Moreover, some off-odour components are thermally labile, which requires care during their isolation, concentration and analysis. A further complication may arise from the presence of trace components having low sensory detection thresholds; such compounds, even when present in ng/g levels can influence the overall flavour more than other volatiles present in much greater amounts. Steps in **off-odour analysis** are as follows:

(i) qualitative and quantitative global sensory analysis (odour impression and intensity);
(ii) headspace analysis (affinity to test media such as water, fat, *etc.*);
(iii) extraction *cq.* desorption from the packaging sample, enrichment;
(iv) separation and identification (GC, GC-MS, GC-O);
(v) synthesis of odoriphore (validation); and
(vi) identification of cause of off-odour generation.

Replacement of sensory analysis with instrumental techniques is not a trivial matter. This may easily be understood if one considers that the unique mixtures that characterise a particular food (or equally well the smell of old books [21], for that matter) may be composed of hundreds of flavour compounds. To analyse these instrumentally and determine which components are important in human perception is generally considered impossible for all but the simplest cases. Often only a few chemical classes are responsible for the off-odour/off-taste (*cfr.* ref. [13]).

Analytical methods for VOC analysis comprise: *(i)* sensory evaluation; *(ii)* chromatographic techniques and their associated sampling methods, including the “hot-jar” method and dynamic headspace sampling; *(iii)* gas chromatography-olfactory sensing; and *(iv)* artificial olfaction or “electronic nose” technology [22]. **Sampling** is the single most critical step also in odour problem solving as it conditions all the subsequent steps of the investigation. Table 4.4 compares a few of the most commonly used sam-

Table 4.4 Gas analysis sampling techniques

Sampling technique	Sampling volume	Mode	Limit of detection
Headspace autosampler	20 mL	Static	0.1 to 1 ppm[a]
Bag	0.5-100 L	Static	Variable (< 1 ppt)
Purge-and-trap	100 mL - ∞	Dynamic	Variable (< 1 ppt)
SPME	1 mL – 1L	Static or dynamic	Variable (< 1 ppt)

[a] Lower limits attainable by preconcentration methods.

pling techniques for that purpose [23] including sorptive extraction and passive sampling. The "hot-jar" method [24] involves heating a polymer in a sealed chamber and injection of a sample of the headspace gas directly onto a chromatographic column. Polymer pellets may also be kept in contact with mineral water at 40°C or 60°C for days to weeks. Techniques used in odour/flavour investigations include steam distillation-solvent extraction (SDE) [25], SPE, static or dynamic headspace sampling (SHS, DHS), followed by TD analysis [26]. Some of these techniques are more applicable to the less volatile substances. Since in DTD analysis volatiles are thermally sparged directly from the analyte matrix into the GC, errors due to trapping efficiency and volatility are greatly reduced or totally eliminated. However, in this technique artifact production via thermal decomposition reactions is more frequent and high-moisture samples can cause chromatography problems (column plugging). In general, DTD-GC analysis may be applied to (semi)solid samples with moisture contents below 5 % and volatile flavour levels in the 1-100,000 ppm range.

Odour analysis requires a technique that concentrates odour-causing compounds down to ppt concentration. These may be trapping on a Tenax™ trap (followed by thermal desorption) or passing a liquid sample over a column packed with purified Amberlite® XAD-2 (poly(styrene-*co*-divinylbenzene)) resin. Identification of volatile substances from packaging materials at very low levels is often carried out using a concentration procedure, usually DHS, mostly in the DHS-TD-GCO-MS/FID combination [27-29]. DHS-GC-MS is particularly useful in determining the additives which contribute most to the overall odour of plastic products; the sample is heated for a relatively long period of time at a relatively low temperature (*e.g.* 50°C in excess of 30 min), which helps to ensure that additional volatile species are not generated as a result of degradation of the sample. Where reliance as to the true odour profile of a polymeric material is placed on direct headspace sampling or dynamic purge-and-trap headspace analysis concern may be expressed about possible thermal conversion of labile compounds during thermal desorption from Tenax traps; use of $scCO_2$ elution is an alternative. Static headspace-SPME can be put forward as an alternative analytical tool to collect volatile and semi-volatile compounds from polymers [30]. VOC analysis may serve as a fingerprint of polymer type. With HS-SPME the volume of the headspace influences the amount of analyte adsorbed on the SPME fibre. The amount adsorbed decreases with increasing headspace volume, so to obtain higher sensitivity the sample headspace should be kept as small as possible. During sample preparation and analysis, care should be exercised so that the isolate retains the sensory properties of the polymeric materials from which it was isolated.

Thermally generated VOC emissions can be determined quantitatively by means of FID detection and use of a calibration standard [31]. Portable FID monitors for total VOC measurement at concentrations between 1 and 10^5 ppm are ideally suited for emission measurements.

None of these separation methods is ideal for **flavour analysis** because of: *(i)* solvent impurities; *(ii)* loss of volatiles; and *(iii)* thermally induced changes. The analysis of taints and off-flavours is somewhat different from that of volatile compounds contributing positively to flavour [12]. The differences are caused by the fact that, in general, many compounds contribute to the flavour of a product but only a few to taints and off-flavours. Like flavour compounds, off-flavour compounds often occur in very low concentrations and may have extremely low threshold values. Selection and identification is therefore very demanding.

Instrumental techniques frequently employed in odour analysis include GC, GC-MS, and HS-GC, with FID, FPD, ECD, TID or MS detectors, often in combination with advanced statistical techniques. With MSD and AED detectors, only a few chemicals with exceptionally low air odour threshold may require more sensitive sampling methods than regular headspace GC, *i.e.* without the need for time-consuming pre-concentration techniques. However, the resulting chromatograms do not present a true and accurate representation of the odour-active components. The differences in sensitivities of GC detectors to various volatile compounds do not correspond to those of mammalian taste or nose. A chemical compound at very low concentration (possibly below the detection limits) can generate strong odour. Further complications arise from the complexities of naturally occurring odours and the instability of the odour molecules.

SHS-GC-FID can be used to measure solvents in printed packaging [32,33]. Provided the solvents used in printing are known, the solvent residues can be quantified by external calibration. The test may not, however, measure the total concentration of the solvent residue in the packaging, as complete volatilisation into the headspace may not occur. The alternative TD-GC-MS method for determining residual solvents in packaging is relatively quick with a total analysis time of around 20 min. The method is particularly suitable for production monitoring and process control. GC-MS is frequently used for off-odour and flavour analysis. Table 4.5 compares the method to the performance of a sensory panel and e-noses for the same purpose.

Gas chromatography-olfactometry (GC-O) is a unique analytical technique which associates the resolution power of capillary GC with the selectivity and sensitivity of the human nose (*cfr.* Fig. 4.3). GC-O was first rationalised by Acree *et al.* [34], who proposed CHARM (Combined Hedonic And Response Measurement) analysis. This consists of the GC injection of increasing dilutions of the odoriphore extract until no odour is perceived at the sniffing port. Grosch *et al.* [35] have later proposed a similar procedure (AEDA, Aroma Extract Dilution Analysis). These dilution techniques are widely used to determine aroma impact of many foods. In modern GC-O the olfactory detector outlet is designed to take the outlet stream of a GC and transfer it to a nose cone in which it is mixed with humidified air. Special olfactory detector ports enable sensory detection of odours simultaneously with GC detection. This allows the human nose to identify individual components as they elute from the capillary column. It can be combined with MS detection. It is important to maintain similar elution time to both detectors [36]. Recently, odorant quantitation by GC-O on the basis of the detection frequency of odorants by a sensory panel was reported [37]. It appears that GC-O can compete with the most sensitive and selective techniques, such as MS, for determination of extremely intense odorants, because little sample preparation is required and there is no need for synthesis of labelled compounds. Any quantitation requires optimisation of the analytical procedure for the target compound.

Although sniffing the effluent of a GC is a useful means of determining which components of a complex mixture of volatiles are odorous [38], the odour descriptors of the separately

Table 4.5 Comparison of key technologies for off-odour analysis

Feature	GC-MS	Sensory panel	e-nose
Qualitative information	+	-	-
Quantitative information	+	-	-
Comparative screening	-	+	+
Skilled operator	+	+	-
Production control	-	-	+
Aroma profile	-	+	+

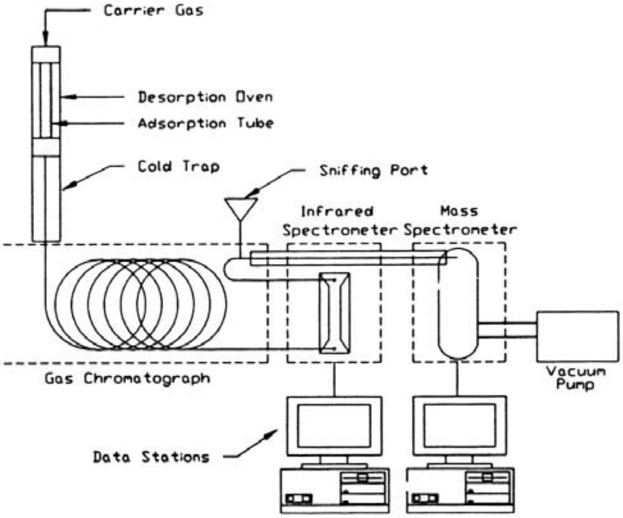

Fig. 4.3 Schematic diagram of a gas chromatograph with thermal desorption unit and dual Fourier transform infrared spectrometer and mass spectrometer detectors, plus odour sniffing port.
After Saxby [6].

eluted compounds are often quite different from the descriptor for a complex mixture of VOCs. This difference makes it difficult to correlate a given SEP evaluation with the corresponding instrumental analysis. It is reasonable expectation that GCxGC will be applied to tackle organoleptic problems. GC analysis with support from a panel enables identification of the problem causing components; no such structural information will be obtained from an e-nose.

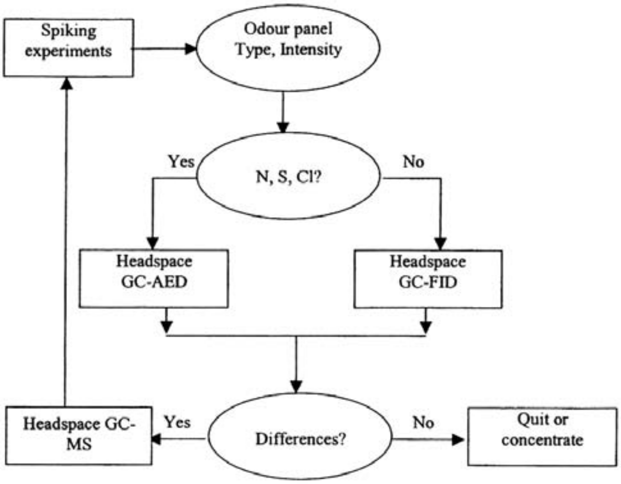

Fig. 4.4 Flow chart for complex odour problem solving.
After Huby. [23].

Huby [23] has developed a **protocol** for complex odour problem solving (Fig. 4.4). The approach of odour analysis depends on whether the analytes are unknown (problem solving) or known (target analysis) compounds. Once an odour panel has categorised a sample as good or bad, GC-AED analysis is focused on N (amine), S (mercaptan, sulphide) or halogen related odours and/or GC-FID examines differences between good/bad samples. At low concentrations reproducibility is a problem. If differences are observed, GC-MS analysis is used to identify the compounds detected by GC-FID. After one or more candidate odour causing compounds are identified and quantified, good samples are spiked with the measured amounts of those compounds and submitted as unknowns to the odour panel to compare them with the actual samples.

Gas chromatography involves high temperatures that may degrade labile compounds. In that case HPLC can be used after trapping the volatile compounds in a liquid. HPLC has not found many applications in off-flavour studies. One of the main reasons is that it is impossible with the usual eluents to evaluate by sensory analysis the contribution of separated compounds/fractions to an off-flavour of a compound. HPLC has been used in the study of less-volatile tainting substances of which the identity is known, *e.g.* chlorophenols [39]. HPLC-MS can be used for identification of tainting and odorous substances but this combination is less well established than GC-MS.

Major problems raised by a chromatographic approach are therefore: *(i)* lack of sensitivity; *(ii)* difficulty to identify the chromatographic peaks of interest; and *(iii)* difficulty to establish the correlation between the perceived odour and observed chromatographic peaks. Moreover, the relationship between the physicochemical properties of odorant molecules and their sensory impact is still unclear [40]. The results may therefore be inconclusive. Selected-ion monitoring mass spectrometry (SIM-MS) is frequently used in off-flavour studies for compounds of known identity. Despite the high sensitivity of APCI-MS systems (*ca.* 10 ppb) a higher level of sensitivity is still needed to detect compounds that have odour thresholds in the ppt range. ToF-SIMS is a very sensitive technique for characterising volatiles emanating from polymer surfaces.

ASTM D 4526-96 describes the determination of volatiles in polymers by SHS-GC [41]. Other relevant standard methods are BS 6455: Monitoring the Levels of Residual Solvents in Flexible Packaging Materials (1984) and ASTM Standard F 151-86: Standard Test Methods for Residual Solvents in Flexible Barrier Materials (1991). Standard testing procedures (ASTM E 595-77/84/90) have been developed to quantify the total mass loss (TML) and collected volatile condensable materials (CVCMs). Automotive materials and systems specifications for odour are available [42,43]. A European standard to determine odour concentration has been developed [44]. Analysis of food volatiles has been reviewed [12,45].

Applications Dynamic headspace sampling has been used as a test procedure for analysing vapours emitted by polymers [46]. In a batch of polyacetol components causing smell and headache complaints trioxane, the cyclic trimer of formaldehyde, was detected using TG-GC-FTIR-FID [47]. Hartman *et al.* [45] have described flavour characterisation using adsorbent trapping-thermal desorption or DTD-GC and DTD-GC-MS.

Many techniques have been used to characterise the organoleptic properties of degraded **PE formulations**, including sensory evaluation [48-50], DHS-GC [49-51], GC-FID [52], GC-MS [48,49,53] and GC-olfactory detection [54]. Sampling techniques include SFE [55], selective volatile extraction [54,56], vacuum distillation [48], and water/steam extraction [57]. Processing polyethylene into packaging materials often takes place between 200 and 370°C. Hoff *et al.* [58] trapped the volatiles produced by PE thermo-oxidative degradation over the temperature range of 264-289°C using GC-MS for identification and GC-FID for quantification. Bravo *et al.* [56] have identified a total of 84 C_5-C_{23} compounds, mainly hydrocarbons, aldehydes, ketones and olefins, produced during thermal oxidation of PE in the presence of excess O_2 at 150-350°C for 5-15 min using DHS-GC-MS and GC-FID. Many of the compounds identified have odour and/or toxicological significance. Although DHS-GC-MS enables very small amounts of VOCs derived from PE to be separated and identified, such an approach does not enable a direct evaluation of the odour level due to each separate VOC. For this purpose GC-olfactory is necessary. Bravo *et al.* [54] have detected 14 and identified 8 odour-active compounds (C_6-C_9 saturated and unsaturated aldehydes and ketones) resulting from the thermal oxidative degradation of PE at 250°C by means of CHARM Analysis [59]. In most cases, these compounds occurred at concentrations that did not produce measurable peaks in the GC-MS total ion current plots and so would not have been normally detected. A review of VOCs originating from PE by thermal oxidation, irradiation, storage, handling and package-product interactions has appeared [22]. The source of undesirable VOCs is not always related to the polymer, but may also be associated with additives, contamination from repeat-use containers, cross-contamination from storage silos, *etc.* Thermal decomposition of metal stearate additives to produce stearic acid, which can undergo further reaction to produce carbonyl species, is a source of off-odour generated during PE processing. A rancid odour may be produced during PE processing due to the thermo-oxidation of the slip agents erucamide and oleamide [60].

Off-odour compounds formed during extrusion coating of (unstabilised) **LDPE** at 285°C and 315°C were analysed by Tenax desorption, TD and DHS-GC-MS analysis with simultaneous sniffing [61,62]. The most odorous compounds were identified as carboxylic acids while most of the volatile compounds were hydrocarbons. The main VOCs derived from irradiated LDPE were identified by GC-MS to be aliphatic hydrocarbons, C_2 to C_5 aldehydes, C_4 to C_8 ketones, and C_2 to C_5 carboxylic acids [63].

In HDPE/(Vitamin E, glycerol, PEG-400, GMC) extrusion glyceryl monocaprylate/caprate (GMC) greatly contributed to off-odour (sensory panel and GC-MS analysis), and Vitamin E to yellow colour formation [64]. Odour and taste problems in HDPE (granules and water) were analysed by P&T techniques in combination with GC-MS-SNIFF and GC-FTIR-SNIFF [65]. Off-flavour compounds in **HDPE water pipes** were identified mainly as carbonyl compounds.

In an attempt to identify the chemical origin of undesirable odour of coffee cups, extraction of volatile compounds from PP sheets by hot water (steam distillation-extraction according to Likens *et al.* [25]) was carried out to assess the organoleptic consequences of the temperature of sheets injection [66]. Minor volatiles with strong odours that could be extracted from **PP pellets** include aliphatic aldehydes, 2-methylketones, quinones, disubstituted phenols and aliphatic alcohols and aids. The odorous compounds were selected by means of GC-SNIFF, identified by GC-MS and quantified with an internal standard method. PP can be considered as organoleptic packaging when processed at low temperatures. In PP films manufacture from virgin and recycled resin feedstock over 100 volatile organic compounds were detected by TD-GC-MS [45], with a cluster of some 25 peaks in the low boiling region in case of the recycled resin (Fig. 4.5). These peaks were identified as a mixture of C_7 to C_9 aliphatic and olefinic hydrocarbons with branched, linear, cyclic, and oxidised (aldehydes) species present. Sensory evaluation confirmed these components to be the cause of off-odour complaints.

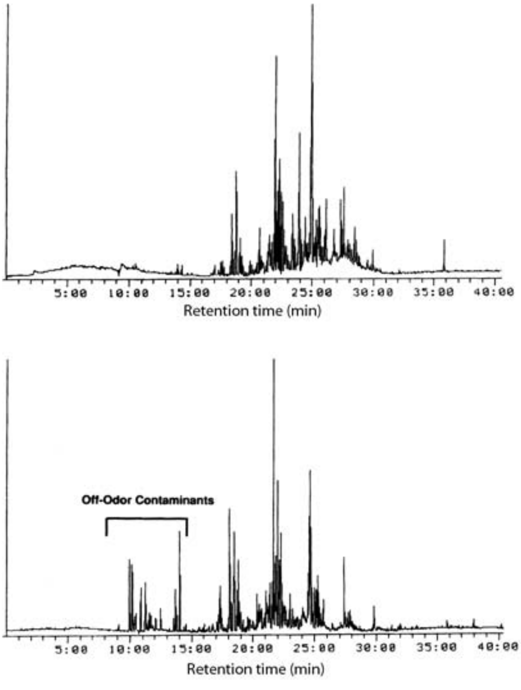

Fig. 4.5 TD-GC-MS analysis of PP films manufactured from virgin (upper trace) and recycled (lower trace) resin feedstocks. Off-odour components are evident in the recycled film.

After Hartman *et al.* [45].

Sensory changes and migration caused by **radiolysis products** were discussed only in a few papers [29,63,67-70a]. Irradiation results in formation of volatile products (aldehydes, ketones and carboxylic acids from PE and PP) and additive related decomposition products. Many radiolysis products are well known, such as 1,3-di-*t*-butylbenzene and 2,4-di-*t*-butylphenol (both ex Irgafos 168). Although the volatile radiolysis products go undetected by overall migration studies (in conformity with EU regulations), their formation is quite evident from HS-GC (*cfr.* Fig. 4.6).

Where monomers have a strong odour or taste monomer residues may be responsible for pronounced odour, *e.g.* methacrylic acid, ethylacrylate or styrene. In particular the latter monomer is well known for its odour (odour threshold of 50 ppb). The free styrene monomer levels in **polystyrene** plastics can be relatively high (300-400 ppm); the quantities found in food products due to migration are usually in the low ppb range [71]. Tice [5] has given examples of food tainting due to free styrene monomer (GC-MS analysis). Residual styrene in PS containers for milk packaging has been quantified by HS-GC-MS. Trace amounts of acetaldehyde (with a very low odour threshold: 20 to 40 µg/L in water) can form during processing of **PET** due to the decomposition of chain ends. Using GC-O cyclic acetals and ethers were identified as odour bodies in **PU foams** [72]. PU odour has been related to the catalysts, surfactants, antioxidants, polyols and isocyanates used in its manufacture. Also a hydrolysis conversion product of the plasticiser dioctylphthalate, 2-ethylhexanoic acid, may be responsible for undesirable odour of PUs. Good agreement between HS-GC, HS-EN and human sensory panel tests in outgassing and odour intensity measurements of ABS has been mentioned [73] (*cfr.* Chp. 4.3).

Incorporation of fillers can lead to considerable odour generation in compounds, although fillers are generally odourless. The reason for this effect is interaction of active sites and/or heavy metal traces of the filler with the polymer or the stabilising system. Testing and rating can be done by olfactometry, or inverse gas chromatography.

Packaging receiving particular attention includes plastic bottles for water, paperboard/plastic multilayer containers, *etc.* It is well known that (semi)volatile components in **packaging**

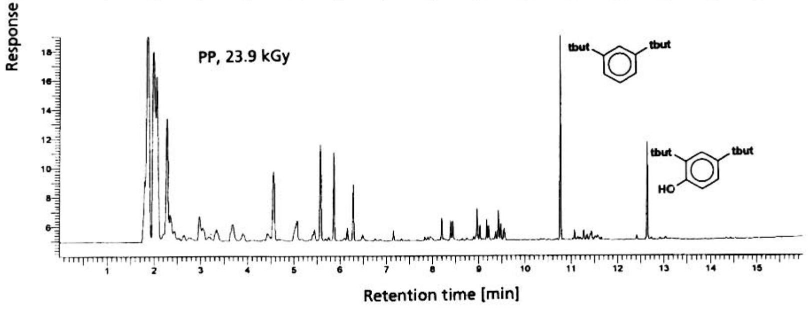

Fig. 4.6 Headspace gas chromatogram of non-irradiated and e-beam irradiated polypropylene yoghurt caps. After Welle *et al.* [67].

materials can migrate into foods stored therein, often imparting off-odours/flavours to the products [74]. It is also established that flavours from foods or beverages can be absorbed into polymeric matrices causing flavour loss in the products [75]. The problem of food contamination with packaging-borne migrants has recently been exacerbated by the increased use of polymers in microwave cooking applications. The transfer of organoleptically active VOCs from LDPE to packaged foodstuffs is well known. Bigger *et al.* [53] produced an odour map of 87 LDPE/(1000 ppm erucamide, 1000 ppm SiO_2) and LDPE/(1000 ppm erucamide, 1000 ppm SiO_2, 500 ppm Irganox 1076) film-grade formulations for food packaging applications by means of DHS-GC-MS and DHS-Tenax-GCO using both sniffing port analysis by a sensory evaluation panel (SEP panel) and an odour meter/SnO_2 semiconductor device. Packaging materials have been analysed for off-odours using the DTD technique [76]. DHS-GC-MS with trapping on Tenax has also been used for the study of VOCs in LDPE packaging materials [77]. Quantitative analysis of chloroanisoles in packaging materials has been carried out by means of SIM-MS [78].

Food packaging materials are subject to increasingly strict quality requirements. Therefore, packaging materials are being developed with improved organoleptic properties. These properties are generally determined by three types of interaction between packaging material and foodstuff, namely: *(i)* absorption of components that determine taste and odour of the foodstuff by the packaging material (flavour scalping); *(ii)* migration of components out of the packaging material into the foodstuff, resulting in deterioration of odour and taste (flavour sorption); and *(iii)* permeation of components through the packaging material from or to the external environment (flavour permeation). For HDPE blow moulding and LDPE extrusion coating applications in which food (milk, water, orange juice) is in direct contact with PE the organoleptic properties of the PE types are important. In particular, migration of aldehydes and ketones, which are formed during processing, play a role. Alcohols, carboxylic acids and other components, which are also formed during processing, exhibit much higher threshold values and have less influence. Kolnaar [79] has reported cold multiple extractions of cryogenically milled HDPE bottles to remove selectively first the additives by diethylether and next PE wax fractions with hexane and heptane. Oxidised compounds, which may influence flavour and taste, were only found in the hexane extract, which is a good indicator for the organoleptic product quality of HDPE. Using GC-MS Yam *et al.* [80] identified more than 60 volatile compounds which were released from HDPE bottles, namely C_5 to C_{10} *n*-alkanes, 1-alkenes, aldehydes, ketones and olefins. The oxygen-containing volatile compounds, which cause off-taste problems, are mainly produced during melt processing of the resin. Ho *et al.* [81] examined the volatiles generated during thermal and mechanical oxidation of blow-moulded HDPE bottles.

Hybrid sensory-instrumental analysis systems, such as GC sniffing techniques, have been used, *e.g.* for the characterisation of flavour changes arising from migration from packaging materials into mineral water [82]. Alkane traces coming from PE are a source for unsaturated carbonyl compounds in PE-containing packaging material. Through a combination of selective enrichment, GC-MS analysis and sensory analysis, the presence of 1-heptene-3-one and 2-nonenal could be identified in several PE-containing packaging materials [7]. Storm van Leeuwen *et al.* [13,83] have examined the organoleptics of extrusion coating LDPE for aseptic liquid packaging applications (*cfr.* also Chp. 7.3.1.2 of ref. [83a]). Volatile compounds that can migrate out of LDPE are formed during extrusion of the polymer. At high shear and temperatures in the extruder, mechanical degradation, thermal oxidation and chain scission reactions occur whereby low-MW, oxidative degradation products are formed such as acids, alcohols, aldehydes, ketones, alkanes and alkenes [84,85]. In a package containing a polar medium, *e.g.* water, lemonade or fruit juice, polar low-MW molecules will have a strong tendency to migrate from the packaging material towards this medium. The cause of **off-taste in packed water** was determined using samples of water in which LDPE film specimens had been incubated ("film samples") and synthetic water samples [13]. DHS-CT-GC-FID/MS analysis was used to identify and quantify aldehydes and ketones in water samples at a detection limit of 1 ppt; carboxylic acids were determined using precolumn derivatisation with 2-nitrophenylhydrazine

(NPH) and RPLC. According to a taste panel the "plastic-like" off-taste of film samples was similar to that of synthetic water samples containing aldehydes and ketones (1.5 ppb) together with acids (100-200 ppb). Despite the fact that these concentrations are below the threshold levels, in combination an off-taste is produced. On the basis of the results of GC and LC analysis and the taste panel the **off-taste concentration region** containing aldehydes, ketones and acids could be defined (Fig. 4.7). This off-taste region enables to express organoleptic quality of LDPE packaging material in measurable and reproducible terms by means of GC analysis. This allows faster quality control.

The effects of vitamin E in extrusion coating LDPE formulations were studied by storage of water in aseptic liquid packaging [86]. Formation of low-MW oxidation products of LDPE during processing and ageing was suppressed, as evaluated by both a taste panel and Tenax trapping with DHS-GC-FID/MS analysis (LOD, 1 ppt). The presence of vitamin E enhances the quality of film *and* water.

In a case of **failure analysis**, the unusual taint of water contained in HDPE spring-water bottles could be ascribed to trace levels of benzophenone, originating from a photoinitiator present in the printing ink from the bottle labels [3]. McGorrin *et al.* [87] have reported identification of the musty component 4,4,6-trimethyl-1,3-dioxane ($C_7H_{14}O_2$) from an off-odour printed packaging film using SHS-GC-FID, organoleptic evaluation, GC-MS (EI and CI) and GC-MS/MS. The compound is an interaction product of 2-methyl-2,4-pentanediol, used as a solvent coating for ink adherence, and formaldehyde (from an unknown source). In another example, the observed "catty" off-odour in cook-in-the-bag ham products was ascribed to the mesityloxide-hydrogen sulphide adduct 4-methyl-4-mercaptopentan-2-one resulting from a complex sequence of interactions between a residual red printing solvent, components of the packaging materials (diacetone alcohol in polyamide-ethylene ionomer laminate, identified by HS-GC, GC-sniffing, GC-FID and GD-MS) and food ingredients [88,89]. Piringer *et al.* [8] have reported the identification of off-odours in packaging materials (collection, concentration, separation by GC and identification by MS). 5-Methyl-4-hepten-3-one was identified as the source of off-odour in a printed plastic film; its origin was the reaction of TiO_2 in the dye with MeCOEt formed from a polyvinylbutyral adhesive by aldol condensation with a basic catalyst. Piringer *et al.* [7] have also described several case studies of sensory problems caused by **food and packaging interactions**, such as off-odour from styrene-butadiene coatings, off-odour from printing, unsaturated carbonyl compounds, off-odours caused by halogenated phenols and anisols, and methylmercaptopentane as an interaction product between packaging and food. Paraffins in food contact materials that do not contain polyolefin oligomers were identified by means of LC-GC-FID and LC-FTIR and quantified by LC-ELSD [90].

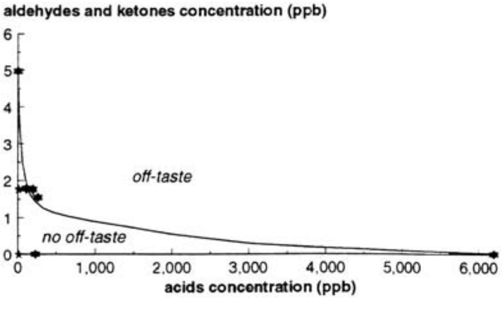

Fig. 4.7 Off-taste region in water containing aldehydes, ketones and acids.
After Storm van Leeuwen and Wullms [13].

Volatiles from an EVA/EVOH **laminate** were analysed by ToF-SIMS, with phenyl stearate being detected, which was the result of a reaction between stearic acid (lubricant) and phenol (from the cross-linking agent 4,4'-methylene bis(phenyl isocyanate)) [91].

Off-odour from styrene-butadiene **coated paper** was attributed to 4-phenyl-cyclohexane, as identified by GC-MS [92]. In another off-odour complaint related to methoxy-propanol from printing of a film it was assessed that 5-methyl-4-heptene-3-on had been formed [8].

There are a number of specific tests that automotive companies insist that rubber components have to pass. An example of such a test is the VW emission test which involves placing the component in a cell of given dimensions and heating the cell for a given time at a specified temperature. Rather than carry out a detailed analysis of the components liberated from the rubber component, the result is expressed in terms of ppm of total organic compounds as determined by an organic vapour analyser (OVA). Limits are given as to the permissible concentrations allowed. Gaseous emission (VOCs) and condensable emissions (fogging) from materials for **automotive interiors** are routinely determined by TD-GC-MS for quality control purposes [43]. HS-GC-FID is often used for collecting and analysing volatiles evolved from plastics used in car interiors [93,93a]. The emissions are expressed as the total area of all the species peaks obtained and are quantified against a single species calibration curve. Work has been carried out to determine the additives which contribute most to the overall odour of car products such as car mats and other odour prone products. For this purpose DHS-GC-MS is often used.

Emissions from automotive materials are usually broken down as follows: *(i)* low to medium volatile compounds, causing fogging; *(ii)* highly volatile organics (gaseous); *(iii)* formaldehyde; and *(iv)* strong odoriphores. Fogging is usually caused by additives such as plasticisers, stabilisers and flame retardants, *i.e.* typically phthalates, dibenzoates, adipates, phosphoric acid esters and alkanes, with low vapour pressure which condense on colder parts of the car interior. The two main polymers which contribute to this effect are PVC and PU (flexible foams). In PU foams the volatile compounds have been related to the type of polyol, antioxidant package, type of amine catalyst, type of flame retardant additive and the presence of plasticisers contained in the pigments [94]. An analytical procedure is available [95]. Highly volatile organics are rest monomers, solvents, amines (catalysts for polyurethane foams), and low-MW additives. An analytical procedure based on SHS-GC technology (5 h at 120°C) has been described [96]. Formaldehyde emission is determined as water soluble formaldehyde after heating of the sample at 60°C for 3 hrs [97]. Off-odour is evaluated according to VDA-270 [98]. In addition to certain plasticisers and process aids, odours can be associated with cure system breakdown products or additives such as pine tar or reclaim rubber. SERS was used for the analysis of low ppb traces of methyl mercaptane at the surface of **vulcanised rubber** after contact with the fumigant methyl bromide [99].

Volatile organic compounds from fitted carpets for office use have recently caused a major problem for indoor air quality (IAQ). Analysis was carried out by collecting air samples on a Tenax tube, followed by thermal desorption to release the trapped organic compounds into a cryogenically precooled PTV for GC-MS analysis [100]. As it turns out, the high-boiling component phenoxypropanol from the water-based adhesive was hydrolysed in service conditions to phenol, which reacts with inorganic bromide (from the latex back of the textile covering) forming bromophenol. Emission of this compound was the major cause of the reported air pollution. Due to the use of high-boiling and polar compounds, the impact of the problem has thus been shifted from the installation process to the tenant of the office. DHS-GC-MS has been used to monitor outgassing of clean-room construction materials [101].

Taste and odour issues related to food packaging interactions have been reviewed [102].

4.3 ARTIFICIAL OLFACTION

Principles and Characteristics Although chromatographic techniques enable the separation and identification of individual VOCs released from polymers, they are incapable of characterising the overall odour due to a particular volatile substance or group of substances. The analytical signals measured do not necessarily reflect the odour perceived by a human. Recently, electronic odour sensing or “artificial olfaction” techniques have been developed in an attempt to address this problem. Chemical multisensor systems (“electronic noses” or electronic olfactometers) are nowadays a viable tool complementing traditional analytical techniques and human sensory evaluation. An **electronic nose** (e-nose or EN) is defined as an instrument that comprises an array of electronic chemical sensors with *partial* specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours [103]. This **definition** intentionally restricts the term “**electronic nose**” to those types of gas array sensors that are

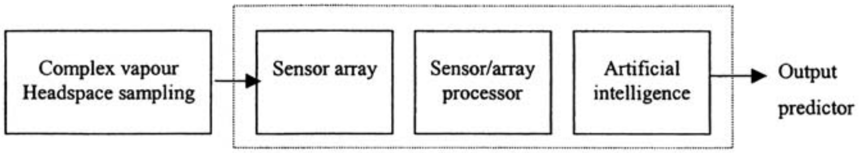

Fig. 4.8 Electronic nose block design

specifically used to sense odour molecules. The concept of an e-nose combined with a pattern recognition technique dates from 1982 [104], and the first commercial instrument was introduced to the market in 1993. E-noses are not conventional analytical chemical instruments. While analytical chemistry is generally used to precisely identify and quantify concentrations of chemicals, e-noses are generally used to produce qualitative results indicating presence of a substance or quality of a product.

Electronic noses or volatile sensors can detect changes in the nature and concentration of compounds present in a gas in an instrumental approach that mimics the mammalian olfactory systems [105]. The three basic building blocks of an e-nose are shown in Fig. 4.8. E-noses are the integration of multiple gas sensors and artificial intelligence. As the vapour will normally exist as the headspace above a liquid or solid sample, all sensors are usually combined with a headspace-sampling unit. SPME sampling allows better sensitivity (sub-ppm LOD). The system needs to be able to analyse a complex vapour as it exists without affecting it in any way. Analysing a complex vapour cannot be achieved by using discrete sensors. Analysis with discrete sensors requires the exact composition to be known. A discrete sensor system would be analogous to GC-MS analysis. The sensors to be used must be non-selective, *i.e.* they must respond to many different individual and complex compounds. In the e-nose the aroma is analysed as a complex vapour using an array of sensors. The system generally gives comparative rather than quantitative or qualitative information and therefore is ideally suited for quick QA/QC control. The exact composition of the vapour is not the result. Among the components of the e-nose, the chemical interactive material plays a fundamental role in defining the sensitivity of the instrument and, finally, the range of possible applications. The requirement for the sensors in an e-nose is that they have a partial sensitivity, *i.e.* that they can respond broadly to a range or class of gases rather than to a specific one. This is the opposite of the ideal gas sensor, which should respond to one gas only, *e.g.*, methane, and provide a unique output (for example ISE, GC). Most e-noses are different implementations of the same working principle. For odour source analysis the sensor signals serve as input to feature extraction using statistical pattern recognition methods, multicomponent analysis, cluster analysis and artificial neural networks with reduction to learned data and comparison to a database. Electronic noses equipped with appropriate data evaluation software allow establishing various correlations in terms of emissions:

(i) Fingerprinting (“equal” or “different”) to verify constant quality of supply.
(ii) Comparison to (acceptable) standards.
(iii) Cluster analysis to discriminate incoming goods.
(iv) Analysis of unknown samples (comparison with data set).

The human and artificial olfactory approaches are compared in Fig. 4.9. The human nose, the best instrument for odour measurement (and always available), is equipped with far more sensors (some $20x10^6$ reception cells) than artificial arrays (up to 32 sensing elements). An e-nose can be exploited commercially provided adequate steps are taken [106]: *(i)* a gas analysis of the molecules associated with the odour of interest with the key molecules being identified by the human nose; *(ii)* a choice of non-specific sensors capable of responding electrically to the key molecules; *(iii)* removal of interferants (*e.g.* water vapour); *(iv)* compensation of electrical data for systematic variations (temperature changes, humidity, sensor drift); *(v)* an adequate

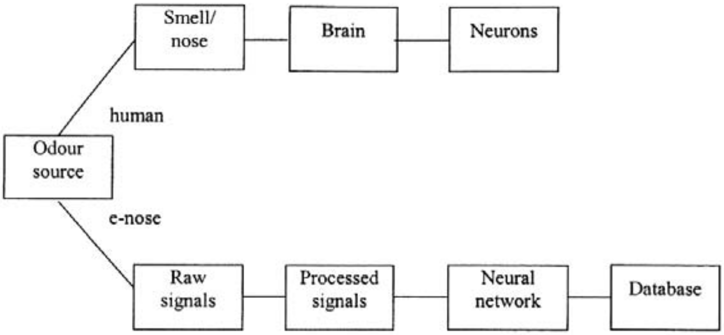

Fig. 4.9 Human and artificial olfaction

training set; and *(vi)* powerful pattern recognition algorithms capable of discriminating and characterising smells with a high success rate (*e.g.* artificial neural or fuzzy techniques). Aimed at mimicking the human olfactory system, the e-nose is an analyser which can recognise, classify and quantify gaseous emissions and odours. Although an objective aroma profile is obtained within minutes, the e-nose detects both odorous and non-odorous compounds and in this sense should not be thought of as an electronic equivalent to the human nose. However, a careful choice of the sensors used in the e-nose may enable the instrument to be tuned to respond to aroma molecules in a manner similar to the human nose. Each sensor possesses individual odour characteristics while at the same time being sensitive to a broad spectrum of gases. Due to their non-specificity, a small number of sensors can be used to monitor vapours from a large number of compounds.

A large variety of sensors and transducer principles is available nowadays [107]. In order to mimic human sense common e-noses employ metal oxide (MOX) semiconductor gas sensors [104], quartz crystal microbalance (QMB) arrays with sorption films deposited on the electrodes [108], piezoelectric sensors, surface acoustic wave devices (SAW) [109], electrochemical cells, opto-electronic sensors [110,111], organic conducting polymers (OCP) [112] or hybrid sensor systems which comprise different **sensor principles** [113], *e.g.* QMB and MOX modules [114]. The main differences concern the choice of the kind of sensors which are mostly either mass transducers (such as QMB and SAW) or chemoresistors (metal oxides or conducting polymers). The particular choice of sensors depends on the individual application. Table 4.6 lists the main characteristics of e-noses.

In **metal oxide semiconductor arrays** the response depends on changes in conductivity

Table 4.6 Main types of commercial gas array sensors used in e-noses

Array type	No. of sensing channels	Array type	No. of sensing channels
Sintered metal-oxide chemoresistors	6, 8, 12, 18	Organic polymers on chemoresistors	12, 20
Lipid layers piezoelectric/SAW	6, 8	Electrochemical	2-18
		Pd-gate MOSFET	10
Phthalocyanine chemoresistors	5	Optical FET camera	324 pixels

of each element when a volatile species is adsorbed in the sensor surface. The response of the most commonly used sensor is based on a two-part electrochemical reaction. In the first step chemisorption of oxygen onto the surface results in ionisation by electron transfer from the semiconductor to the oxygen molecule. The second step involves sorption of the analyte onto the semiconductor and subsequent reaction of the analyte and ionised oxygen on the surface. Metal oxide sensors have a very good sensitivity (ppm-ppb level) for a very broad range of chemical compounds. Only the use of arrays leads to an induced selectivity. Devices can be selected from a range of more than 40 different elements. A metal oxide e-nose is usually equipped with a number (*e.g.* 18) of different sensors. Among a related series of pure chemicals, the intensity of the signal for each sensor is highly correlated to the vapour pressure of the analyte. The reactivity of the analyte with a given sensor affects the response of the sensor to the analyte. Figure 4.10 shows an example of two analytes responding to an eight-element MOX semiconductor sensor array composed of 1. ZnO/SnO_2; 2. $Pd/ZnO/SnO_2$; 3. SnO_2; 4. Pd/SnO_2; 5. $Pd/WO_3/SnO_2$; 6. WO_3/SnO_2; 7. TiO_2/SnO_2; 8. $Pd/TiO_2/SnO_2$. Multivariate statistical techniques can be used to identify sensors having particularly high affinities for certain classes of chemicals. Miller *et al.* [115] have reported a study on the fundamental response and discriminative power of MOX sensors exposed to pure chemical samples. Literature reports the advantages of the MOX sensors [116] in comparison with polymer sensors [117]. Despite a somewhat smaller detection range, MOX sensors are less sensitive to humidity variations. In addition, they are more rubust, with a lifetime up to 3 years, and are much cheaper to replace. However, they lack time-resolution.

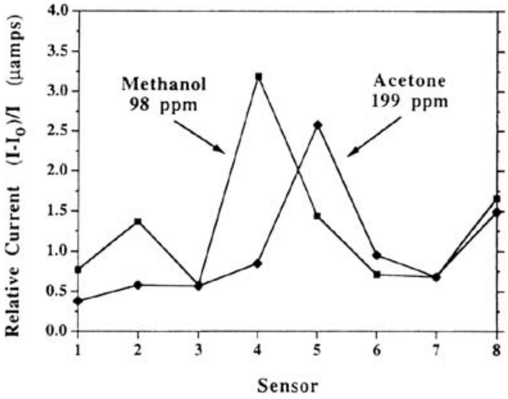

Fig. 4.10 Response patterns of acetone and methanol from an eight-element integrated metal oxide semiconductor array. See text for elements of the array. After Carey [118].

The **quartz microbalance chemosensory (QMB or QCM) system** consists of combined headspace and chemosensory technology [73]. Several sensor elements are integrated on a common quartz substrate. These sensors are coated with different gas-sensitive materials that react differently to the gases and vapours to be analysed. The adsorption of volatiles on the gas sensitive coatings of a sensor element results in a frequency change or sensor signal of the oscillator. The sensor elements of a quartz microbalance can thus detect a change of mass accurately via resonance frequency shifts. QCM gas sensors have stable responses and a simple fabrication process can easily produce sensors with a variety of characteristics. Plasma-organic-film coated QCM sensors are suited for odorant detection at 500-800 ppb concentrations [119]. **Conducting polymers** (CPs) based on (hetero)aromatic compounds, such as polypyrrole, polyaniline or polythiophene, are sensitive to many odorants and a reversible change in electrical conductance is observed [120]. Several characteristics of these materials make them attractive for use as odour sensors. There are few problems due to poisoning, rapid reversibility, use at room temperature, rapid response absorption/desorption within seconds to most volatile chemicals, allowance for time resolution, and a long sensor lifetime (several years). On the other hand, competition for binding on the surface causes poor sensitivity to odour molecules at high humidity levels [112]. Understanding of the electrical conduction mechanisms and the physico-chemical interactions between the volatile chemical and the conducting polymer is still restricted.

An **opto-electronic nose** is based on variation of spectral absorbance, induced by chemical adsorption by volatile organic compounds [110]. The optimal features of metalloporphyrins make these molecules particularly appealing for optical sensing purposes.

Sensor array systems differ in the number of sensing channels (arrays of 6 to 18 sensors), pixels (in optical FET cameras) or mass values. It has been pointed out [103] that it is attractive to consider using **mixed arrays** comprising different types of sensors such as metal oxides, conducting polymers, surface acoustic wave devices and MOSFETs in a single array, or the alternative approach of using multidimensional measurements from the same sensor (*e.g.* conductivity, mass increments, transient responses and multifrequency measurements).

Recently, **mass spectrometers** have surfaced as sensor arrays for e-noses and as competitors to the "traditional" multi-sensor systems [121]. Such MS sensors are essentially HS-MS systems: the sensing principle is based on direct injection of a complex sample headspace into a mass spectrometer, creating a mass spectrometric pattern of the unresolved gaseous mixture. The instrument works on the basis where for the purpose of data analysis each individual (*m/z*) ratio is treated as the equivalent of a sensor response from the conventional electronic noses. This means that there are potentially several hundred sensors. By selecting a set of particular fragment ions the sensor array used for sensor analysis is defined. The size and type of the optimum "sensor array", *i.e.* the optimum set of fragment ions (and the corresponding scan-time/ion), can be tailored towards the particular application. The sensor output of a measurement, a reduced mass spectrometric pattern, is used to create a database of known, characterised reference samples - employing principal components analysis or an artificial neural network. Patterns of unknown samples are compared to those of the reference samples. Once an array is defined for a definite application, results obtained with different types of MS-instruments (but equal ionisation mode) are directly comparable. In case further quantitative or qualitative analysis is needed, the system can be used as a fully operational HS-GC-MS.

It cannot be taken for granted that an odour can actually be measured or analysed. The response of EN is not species-specific, as a single chemical will give a graded response over several individual elements. A strong response to a volatile does not necessarily imply that the volatile will have a strong odour response. Consequently, the use of "noses" requires careful calibration against human response using formal sensory analysis techniques.

Method development involves the following considerations: *(i)* sampling mode; *(ii)* purging and equilibration time for sensor head and sample vessel; *(iii)* temperature for development of headspace volatiles; *(iv)* corroborative data needed to characterise the samples; and *(v)* transferability from R&D laboratory to production shop floor for QC. It is important in the analysis to include only those sensors that are contributing useful information. Removal of non-discriminating sensors leads to better signal-to-noise ratio. Factors affecting reproducibility are temperature, humidity, concentration of odoriphores in the headspace, and any carryover of analytes from one measurement to the next. Changing headspace concentration will affect the sensor response characteristics. The state of knowledge on method development with the e-nose is similar to that of GC some 30 years ago. There are problems as to the best choice of sensors for particular tasks. Stoll [1] has argued that the quest for an "ideal" odour sensor system is futile. The quality and suitability of a sensor system must be evaluated in the context of a specific application, *e.g.* rubber smell. Evaluation of the e-nose should then concentrate on five issues:

- Instrument stability under standard working conditions.
- Repeatability of the responses from the sensors.
- Medium and long-term reproducibility of the odour assessment.
- Discriminative power of the model over production batches.
- Relevance of the sensor response to the human olfactory perception.

For the product life cycle the stability and validity of the database needs also to be secured. Some important experimental issues relate to interference from fluctuations in temperature and the adverse influence of humidity. Transferability of results is an important issue when different sensor principles and technologies are used. The key criteria for transferability of EN to be successful are: *(i)* interchanging ability of the sensors; *(ii)* sensor-to-sensor reproducibility; *(iii)* sample-to-sample reproducibility; *(iv)* reproducibility over time; and *(v)* system-to-system reproducibility. Sensors can be used to monitor a process, but variations in a process necessitate recalibration/optimisation of sensors.

It is quite essential to understand the sensory characteristics for the design of a sensor array for target odorants. Nakamoto *et al.* [108] have used computational chemistry for the prediction of QCM gas sensor responses. Enhancement of both sensitivity and selectivity of organic vapour sensors is the key factor for further breakthroughs.

Table 4.7 lists the **main characteristics** of e-noses. Advantages of non-specific chemical sensor arrays are the provision for rapid odour analysis (total analysis time *ca.* 20 min), potentially at low cost. Samples can quickly be run with operators that are lower skilled than those necessary to run HS-GC. They allow discrimination among samples based on their volatile compounds contents, but only within their operating range of concentration. As long-term monitoring devices, e-noses assess total odour *objectively* by predicting human sensory response from physical measurements. The electronic nose has the potential to minimise the total reliance on panel tests in routine evaluation and enables to support the oleochemical business by a systematic odour control of raw material or finished products. In addition, EN is a valuable tool in the shelf-life study of these products. Using multivariate or neural network software e-noses can detect changes in volatile patterns, which can potentially be related to changes occurring on storage. Many applications in product quality control and process or environmental monitoring can be envisaged. However, as shown in Table 4.7, there are quite a few conceptual and practical limitations to application. All commercialised systems are designed to be broadly non-specific or semi-specific. Electronic noses are not diagnostic, are much less selective than the human nose and also less sensitive for most of the chemical compounds; e-noses show partial selectivity only. The e-nose can never fully substitute a panel. At present there is still little fundamental knowledge to explain their response characteristics. E-noses require training (method development) and are limited in quantification of odour intensity. Problems are related to reproducibility and ruggedness. Sensitivity decreases with time. Sensor arrays (rather than mass spectroscopy) as electronic noses often show unsatisfactory performance [122]. The e-nose can only be used under carefully controlled conditions. Practical limitations for objective quality control comprise sensor drift, adverse affection by atmospheric conditions (p_{H_2O}, T), no system-to-system matching, *etc.* For successful analysis of polymers with chemical sensor systems moisture management is important [123]. Moreover, e-noses are not capable of identifying the chemicals responsible for the odour of a multicomponent sample. Consequently, the currently commercially available instruments are not a total solution for many emission problems and do not even solve very specific industrial chemicals odour problems (not being specific gas sensors).

Table 4.7 Main characteristics of multi-array electronic sensors

Advantages:

- Rapid and objective assessment, low cost alternative to VOC analysis
- Evaluation of *total* volatile fraction
- Removes potential risks for human olfactory system
- At-line measurement of product consistency (QA, QC) by low-skilled operators

Disadvantages:

- Limited operating range
- Non- or semi-specific (classification rather than identification)
- Not diagnostic
- Low to partial selectivity
- Less sensitive than human and dog's noses
- Restricted fundamental knowledge
- Method development required (need for training set)
- Calibration against human response required
- No quantitative sensor-odour relationship
- Questionable (medium and long-term) reproducibility and ruggedness (sensor drift)
- Carefully controlled conditions needed
- Limited service life
- No mature technology
- Poor transferability
- Limited applicability

Neither the GC nor the EN sensor technology is capable of indicating which of the sample components is relevant to the odour. Since odours are not related to relative peak sizes of different components, certain compounds may exhibit very strong odours even if their responses are small. No information can be deduced from concentration data unless the odour-concentration relationship is known for all the components measured. The use of EN as a GC detector has been advanced for the purpose of determining quantitative sensor-odour relationships [124]. GC-EN must be seen as an aid in EN development rather than a replacement of GC-O. The interested reader is referred to specialised texts and reviews [103,125-127] for further consultation.

Applications E-noses (and e-tongues) are primarily used for qualitative sensory applications, which include the determination of the origin and quality of raw materials, consistency of finished products, and taint-free products. Other applications of the technologies include shelf-life measurements and the evaluation of any interactions between packaging and the product. Semiquantitative applications include sensory score correlation and the measurement of the concentration of flavours or fragrances within a food or cosmetic product. The following examples illustrate typical applications of the techniques.

Sensory analysis techniques are particularly appropriate for any consumer products that rely on sensory response for their appeal (*e.g.* personal care, food and beverage products) but have wider significance. Apart from the cosmetics (perfume) and aroma industries other fields of applications of e-noses are environmental and chemical (measuring paper odours, solvents from paint or plastics materials and surfactants in household products), and can be found in the polymer industry (assessing the organoleptic quality of polymer formulations, penetrability of aroma through packaging). In the chemical industry, the use of sensory systems is being driven by the statutory need to ensure quality. Areas of application are **quality control** of raw and manufactured goods, usually as part of a quality assurance programme such as ISO 9000 or Total Quality Management. Sensory analysis can be used to classify products into grades of different qualities. It can also reduce the risk of consumers receiving tainted foods, particularly from chemical contaminants that have taste thresholds well below ppt level. At these levels, the human senses can be considerably more sensitive than sophisticated instrumental methods. Conditions for the use of e-noses as QC tools are: *(i)* sensitivity; *(ii)* long-term stability and reproducibility; and *(iii)* control on the influence of humidity and temperature on the sensor signals. Different moisture contents of polymer samples influence the headspace composition of the samples and change the sensor discrimination. HDPE and PET can be analysed directly in the presence of unknown moisture contents after a calibration; PA requires a sample treatment prior to analysis [123]. The multi-sensor systems can also be used to take measurements in the environment (*e.g.* to detect harmful substances). A trend is apparent towards combined sensory and instrumental methods. For example, simultaneous time-intensity and mass spectrometry systems are used to measure volatile (flavour/odour) release.

Industrial applications include detection of off-odours related to synthetic polymers and polymer outgassing [23]. Various e-nose devices have been used to assess the odour level in PE formulations [53,128]. Thirty LDPE pellets from the same manufacturer have been analysed by a sensory panel, GC analysis and e-nose technology (3 min volatile headspace sampling, 6 different sensors for polar, apolar, aminated and sulphur compounds, aldehydes and compounds emitted during cooking) [129]. Statistical analysis such as cluster analysis, PCA and discriminant analysis were used to determine the groups within the samples, to obtain the olfactory territory of a sample series and to study product evolution during the process. Classical PCA discriminated the samples by odour intensity.

Due to their simplicity, rapidity and objectivity, e-noses have started to be extensively used by **industrial packaging** companies. Knowledge of the range of odoriphores derived from packaging-grade polymers and an understanding of the phenomenon of odour is important with regard to: *(i)* determining the suitability of polymeric materials for the containment of sensitive produce; and *(ii)* the development of advanced techniques that measure and control odour. Without needing any prior fractionation, e-noses can determine the fingerprint of a complex volatile or dissolved compound mixture by an array of semi-specific sensors coupled to a pattern recognition system. E-noses are a complementary tool to GC or to sensory panels to assess extremely rapidly (less than 60 sec) the quality of various types of packaging films or the kind of contamination. Although SEP assessment is still regarded as the most important technique for the analysis of odoriphores that originate from PE, a combined approach using a variety of analytical techniques is recommended in order to acquire full understanding of the nature of the VOCs. It has been reported that a 12-element conducting polymer sensor array is useful in assessing taint in HDPE used for food packaging applications [130].

Bazzo *et al.* [131] have optimised a MOX sensor array (consisting initially of 18 sensors) for QC packaging in a plant environment. Good discrimination was obtained for (four) different qualities of HDPE from several manufacturers. With headspace generation parameters set at 20 min at 80°C, and an injection volume of 2500 μL for a 2 g sample, an optimisation process was used to validate the important instrumental parameters, which comprised:

(i) discrimination of different qualities for several manufacturers;
(ii) validation of discrimination over several production batches;
(iii) optimisation of sensor set to obtain the most discriminating sensors;
(iv) use of dynamic cleaning to ensure good sample throughput for quick routine analysis;
(v) choice of chemical standards (heptanoic acid, heptadecane and capric acid); and
(vi) demonstration of transferability of one database over several sensor sets, MOX systems and autosamplers.

The different odour levels of HDPE were used to build a PLS model to predict odour level. High correlation (0.99) was obtained between a sensory panel and EN analysis using PLS. The development of a turnkey EN instrument (with 6 selected sensors) has been shown for both qualitative and quantitative prediction for HDPE. Electronic nose technologies can thus provide sensory panel and/or analytical chemical expertise to be transferred to the production shop floor for routine analysis. E-noses are not only used for control of product and package quality but also the solve package/product interaction problems. PE manufacturing of drinking water bottles is now routinely controlled by EN analysis [132], including screen caps.

Modern industrial requirements comprise the olfactory stability *cq.* conformity of a raw material or product. Emission problems for multicomponent materials are usually complex with low detection levels (often ppt). Industrial smell or odour problems may be solved at various levels (short time *vs.* long term), namely by:

(i) changes in raw materials supply or process(ing) parameters (*e.g.* extruder temperature);
(ii) harmonisation of raw materials; and
(iii) analytics: identification of the odorant.

For comparison of materials verification of smell test conditions is crucial. In smell design no masking agents are allowed.

With an average of 182 kg of plastics in an average vehicle (US, 2002) [133] the **automotive industry** is an important consumer. There are a number of – car manufacturer specific – tests that automotive companies insist that plastics components manufactured by suppliers have to pass, essentially all based on total emission, *cfr.* Chp. 4.2. In the VW emissions test no detailed analysis of the components liberated is attempted. In other cases alternative odour tests are being applied to incoming materials (ranging from the human sensory method to DHS-TD-GC-MS, HS-FID/5 h at 120°C, or the use of sealed jars, in water), often simulating worst case conditions. The matter is complicated by the fact that for comparison of materials a constant time between production and analysis is needed. Just-in-time delivery of raw materials used in modern manufacturing processes allows little time in reaching olfactory conformity of the finished products by mere outgassing. Use of e-noses for QC of automotive supplies benefits from extensive testing and optimisation to set international standards and worldwide test methods. Subsequent rejection of off-spec deliveries then leads to the need for identification of the origin of the emission problem, either the raw material supply or processing. Also in this stage the use of e-noses is called for. Figure 4.11 strongly advocates the benefits of interdisciplinary method co-development.

Bullert [134] has used a hybrid modular sensor system composed of 8 QMB and 8 semiconductor (SnO_2) sensors for the detection of off-odours of automotive parts of various polymers (PP, PPO/PS, EPDM, PA, PP/PE, SMA, PVC).

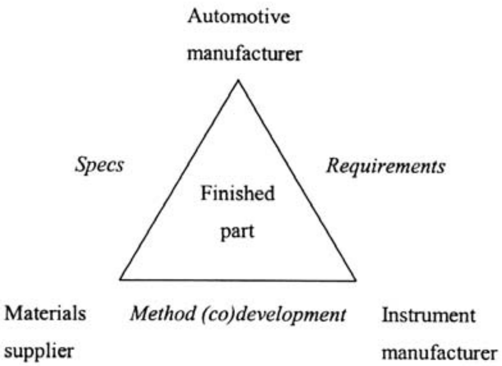

Fig. 4.11 Quality triangle

QMB sensors are generally more sensitive to higher-molecular-weight compounds, and SnO_2 sensors to small, oxidisable components [135]. Sassmannshausen [136] has reported multivariate data analysis of off-odours of incoming high UV resistant **ABS grades** using a CP sensor. Also a HS-QMB chemosensory system has been used for the analysis of ABS polymers [73] and three methods of polymerisation were compared: bulk polymerisation, emulsion and emulsion plus additives. The volatile components of the different ABS polymers interacted with the different coatings of six sensors, resulting in characteristic signal patterns (Fig. 4.12). The signal patterns formed classes related to the polymerisation method. The results with the HS-QMB chemosensory system were obtained more rapidly than by the more time consuming HS-GC analysis sensory panel tests. Table 4.8 shows satisfactory correlation between the three evaluation techniques.

Olfactory testing of cars was once left to the user. The high degree of customer complaints concerning aliphatic amines and phenolic bonded materials first, and “rubber-like” smell more recently, has increased the awareness of car manufacturers to emission problems. For a perfect finished product, perfect raw materials and perfect process manufacturing parameters are needed. Gas emissions inside cars, caused by the release of VOCs from the **interior trim materials**, such as leather or plastics, contribute greatly to the internal air pollution. Existing methods of analysing such emissions are a DIN standard 75-201 fogging test [137] and tests for total VOCs (TVOC) using GC-FID and GC-MS. However, these give inconsistent readings, are time-consuming and in the DIN test only one material at

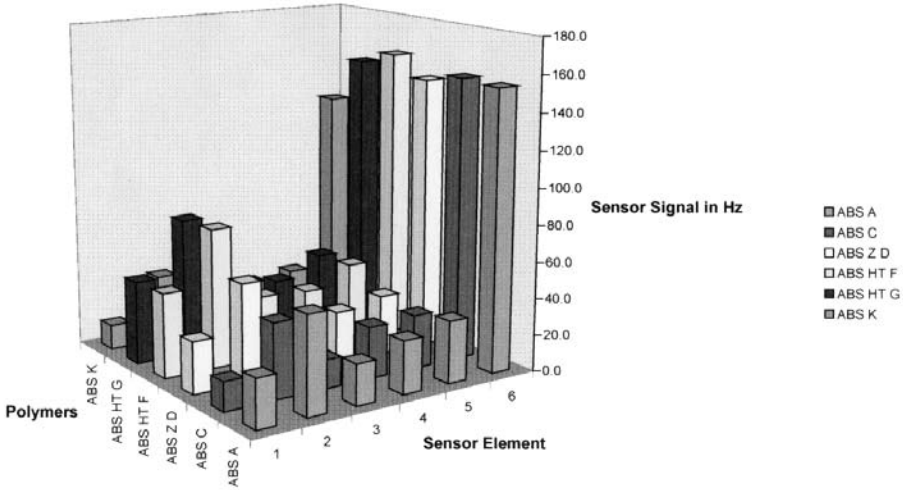

Fig. 4.12 QMB signal patterns for ABS polymers.
Courtesy of Perkin Elmer.

Table 4.8 Outgassing and odour intensity[a]

Polymer	HS-GC (relative area counts)	HS-QMB (average sensor signals)	Olfactometry (odour units)
Bulk Polymer:			
- Sample C	5.3	47	–
- Sample K	4.8	40	32
Emulsion Polymer:			
- Sample A	15.0	53	50
- Sample D	15.6	53	56
Emulsion Polymers + additives:			
- Sample F	28.5	66	120
- Sample G	27.8	64	95

[a] Sensor signals not normalised.

After ref. [73].

a time can be measured. These methods are also rather expensive, require skilled personnel and are thus not suited for process monitoring or on-line product control. There is a need to develop methods for characterising mixtures of VOCs in materials and indoor air. Kalman *et al.* [138] have classified complex gas emissions from automotive leather (known for its particularly high gas emission) using a hybrid e-nose composed of a gas sensor array of 10 MOSFETs with gates of thin Pt, Ir and Pd of different thicknesses and combinations, and 5 semiconducting MOXs. An e-nose has also been developed for the detection and measurement of odours in PUR foams (MultiSampler-PU). The emission quality of rubbers is targeted next for e-noses.

E-noses have also been applied to evaluate clay-coated newsback **paperboard** with distinctive aromas; control of relative humidity was important [139]. A sensory panel and e-nose evaluated samples of laminates from different processes. E-noses (MOX type) were also employed to distinguish latices used as paper whiteners and to investigate the impact of inks on paper [140].

Sadik *et al.* [124] have used GC-EN to relate sensor structures and activities for **low vapour odorants**, including polyaromatic hydrocarbons, industrial solvents and polychlorinated phenols. Results agree with FID with errors in the 0.5-3.0 % range. An example was reported of the detection of tainted corks using HS-MS technology, as an alternative to GC-MS [141].

The examples reported are in line with the trend that e-noses are not expected to replace but to reduce recourse to odour panels. Since they cannot identify compounds, they are of restricted use in many odour problems. They are expected to have a great potential for process and environmental monitoring in the chemical industry [23].

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