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Synergistic approaches for odor active compounds monitoring and identification: State of the art, integration, limits and potentialities of analytical and sensorial techniques

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ABSTRACT

Odor monitoring has been an issue of concern for a long time and new devices and innovative approaches to recognize and quantify odors, to characterize emission sources and to activate mitigation systems were developed. Chemical characterization of odorants provides useful information about composition and mechanisms of formation but fails in the reconstruction of the final odor perception. Electronic noses remain unmatched devices when the cheapest approach for high temporal resolution monitoring of odorous phenomena is required but their use implies a robust training and is affected by poor reliability. Synergistic approach based on chemical characterization, dynamic olfactometry and electronic noses reveals to be the best way to a) characterize odors; b) evaluate their concentration; c) develop innovative and tailored monitoring systems. Therefore, this review aims to examine the recently advanced in odor detection and monitoring methods highlighting limits and potentialities and proposing the integration of them as a strategic approach.

1. Introduction

Several methodological approaches addressed to odor detection and monitoring have been developed in the past decades with several purposes: a) improving quality of perfumes and food products [1,2]; b) mitigating the impact of odor active compounds emitted from industrial activities on human life and environment [3–5]; c) identifying and replacing unpleasant odors emitted from materials and consumer products [6]. Among the existing sensory-instrumental techniques, dynamic olfactometry, electronic noses and mono/multi-dimensional gas-chromatography/mass spectrometry-olfactometry (mono/MDGC/MS-O) are recognized as the most performing for odor detection and quantification, odor monitoring and chemical characterization associated to sensory evaluation. The present review aims to highlight the main advantages and drawbacks of the aforementioned approaches in odor detection and characterization. Moreover, it aims to demonstrate that for the specific purpose of environmental odor emissions monitoring, none of the methodologies can be self-sufficient to obtain the most complete and exhaustive comprehension of the odor emission phenomenon taking into account the necessary high-time resolution, sensitivity, reliability, and reproducibility. Complementary and integrated approach seems to be the best way to identify odor sources, to elucidate the mechanism of formation, the fate and abatement strategies, and to manage odor annoyance deriving from industrial activities.

2. Characteristics of odor active compounds

Several studies focused on chemical structure/odor perception relationships have been carried out, but the prediction of the odor properties of a novel molecule starting from its chemical structure, remains an hard task [7]. However, in environmental field, some relationship between chemical structure of odor active compounds and emission sources have been found. More specifically, a link between composting plants and both nitrogen and sulfur odor active compounds [8], between landfills and sulfur and aromatic compounds [5] and between gas extraction wells of sludge management site and methyl mercaptan, valeric and iso-valeric acid, carbon disulfide, acetone, 3-pentanone, methanol, trimethylamine, hydrogen sulfide, n-butyl aldehyde, acetic acid, di-methyl sulphide (DMS), di-methyl-disulphide (DMDS), limonene and alpha-pinene [9,10], were found. Nevertheless, the scientific community is still very far from identifying all the substances that determine an olfactory annoyance or fragrance because they are often due to the different interactions among several compounds. Anyway, in order to classify, identify and describe an odor differentiating it from another one of equal intensity, the *Odor perception descriptor* is usually used. All the perception-based classification studies showed results dominated by inter-individual differences in perception, verbal abilities, stimuli characteristics and approaches both in data collection and data analysis [11]. As a result, several classifications of odors exist, whose harmonization is an hard task to achieve and remain a statistical exercise because of the observed variability both in hedonic tone and quality, character or

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odor perception descriptors of the panelists [12]. Amoore in 1964 proposed a classification based on seven primary aroma categories, with example compounds (in parenthesis) as follows: camphoraceous (camphor), ethereal (ethylene dichloride), floral (phenylethyl methyl ethyl carbinol), musky (ω-pentadecalactone), pepperminty (menthone), pungent (formic acid), putrid (butyl mercaptan) [13]. McGinley and McGinley suggested a revised version of the "flavor wheel" proposed by the International Association on Water Pollution Research and Control (IAWPRC), applicable for municipal solid landfill's emissions composed of eight aroma groups with specific descriptors among each group, as reported in Table 1 [14].

Hedonic tone is the measure of the pleasantness or unpleasantness of an odor mixture (pleasant/unpleasant/neutral). It has been demonstrated that a pleasant odor may result annoying or unpleasant to human nose if present at high concentration in a mixture and this evidence suggested that hedonic tone and odor concentration are correlated parameters. *Odor detection threshold (ODT)* also called absolute odor threshold, is the lowest concentration at which 50% of a human panel can detect the presence of an odor without characterizing the stimulus. A positive correlation between chain length of aliphatic compounds and ODTs has been reported by Manuel Zarzo [15]. The *odor recognition threshold* at 50% (ORT 50%) is the lowest concentration at which 50% of a human panel can detect and describe qualitatively the odorant and is, on average, about three up to five times the ODT [16]. *Odor index* (OI) is a dimensionless term linked to ODT and is calculated using vapor pressure (in ppm) and odor recognition threshold (100%) expressed in ppm, by means of the following Formula (1):

$$\mathrm{OI} = \text{vapor pressure}/\mathrm{ORT100\%} \tag{1}$$

The *volatility* at ambient temperature allows the diffusion of molecular odorous gases in the sensory area and it is measured by the vapor pressure (in ppm units by using the gas law). On the basis of volatility, fragrance industry classifies the less volatile and more persistent odorous compounds as the "base notes" and the more volatile ones as the "top notes". The *odor intensity* is the relative strength of the odor above the recognition threshold, logarithmically related to the odorant concentration according to the following equation (Weber-Fechner law):

$$\mathrm{I} = a\ \log(\mathrm{C}) + \mathrm{b} \tag{2}$$

where I is the odor intensity, C is the concentration (mg/m^3) and a and b are specific constants of the odorant. The odor intensity is usually expressed in numerical values on the basis of a description scale related to the odor perception of the panelist (e.g., 1-just perceptible odor, 2-weak odor, 3-clear odor, 4-strong odor or alternatively: 0-no odor, 1-very weak, 2-weak, 3-distinct, 4-strong, 5-very strong, 6-intolerable). Finally, *Odor Concentration (OC)* can be theoretically calculated by Equation (3), summing the odor activity values (OAVs) of each odorous compound (obtainable in turn by dividing chemical concentration of the i-th compounds (Ci) with the odor detection threshold in a mixture:

$$\mathrm{OC} = \sum_{i=1}^{n} (\mathrm{OAVi}) = \sum_{i=1}^{n} \left(\frac{\mathrm{Ci}}{\mathrm{ODTi}}\right) \tag{3}$$

Anyway, although considering errors both in the ODT and concentration values, overestimation or underestimation of OCs were found to be in the range of an unacceptable 50–80% due to synergistic and inhibition cross-effects. To overcome these limits, some authors refer to the Weber-Fechner law (2) and include the sensitivity of individual odor perception in the calculation of OCs. In this way, calculated odor concentrations fit better with observed values [17]. Moreover, the perceived odor is more influenced by ODT than by the compound concentration in headspace [18]. Therefore, chemical analysis by GC/MS is unsuitable for the reconstruction of OC and dynamic olfactometry remain the election technique for the determination of reliable and legally valid OCs.

Table 1
Aroma group and odor descriptors as classified by McGinley and McGinley.

Aroma group	Odor descriptors
earthy aromas	musty, moldy, musk, stale, grassy, herbal, woody
floral aromas	fragrant, flowery, perfume, eucalyptus, lavender
fruity aromas	citrus, orange, lemon, apple, pear, pineapple, strawberry
spicy aromas	cinnamon, mint, peppermint, onion, dill, garlic, pepper, cloves, vanilla, almond, pine
fishy aromas	fishy, prawns, amine
sewage aromas	septic, putrid, rancid, sulfurous, rotten, decayed, cadaverous, foul, sour, pungent, burnt, swampy
medicinal aromas	disinfectant, phenol, camphor, soapy, ammonia, alcohol, ether, anesthetic, menthol
chemical aromas	solvent, aromatic, varnish, turpentine, petroleum, creosote, tar, oily, plastic

3. Sampling and pre-treatment of food and environmental matrices

The choice of an appropriate sample collection and preparation method is crucial to analyze odor compounds. The use of different sample pre-treatment techniques may affect significantly the composition of the sample extract and consequently, the analytical performances [19,20]. In fact, the selection of the proper pre-treatment method is a key step both to obtain an enriched aliquot of sample representative of the matrix, and to prevent decomposition of labile compounds, loss of highly volatile compounds and heat-induced artifact formation. Moreover, it is recommended to choose methods that reflect as closely as possible the release of the odor active volatile compounds from the matrix as this facilitates the correlation with the sensory evaluation data and that whatever the method chosen. As concern liquid-solid matrices such as food, liquid wastes and fragrances, the sample preparation may include mincing, homogenization, centrifugation, steam distillation (SD), solvent extraction (SE), simultaneous distillation-extraction (SDE), solid phase extraction (SPE), supercritical fluid extraction (SFE), Soxhlet extraction, solvent assisted flavor evaporation (SAFE), microwave-assisted hydro-distillation (MAHD), head-space (HS) techniques, solid-phase micro-extraction (SPME), matrix solid-phase dispersion (MSPD), direct thermal desorption (DTD), among others. Conventional distillation and solvent extraction techniques (SE, SD and SDE) combined with chromatography are widely applied to isolate volatile odor active compounds present in food, materials and other complex matrices [21,22]. However, although widely applied, it is well known that these techniques may modify the composition of the extracts and introduce artifacts (mainly heat-induced) [23]. Generally, techniques that imply the use of solvents suffer from contamination and chromatographic masking effect (solvent peak covering early eluting odor-active compounds). Moreover, peaks co-elution may occur making the identification of odor active compounds difficult, in this case fractionation of the extract and re-extraction of single fractions containing acids, bases and carbonyls with solvent is used [24]. SDE is the most rapid and ele-

gant isolation technique able to provide a sample ready to be injected into the GC system. Typical drawbacks are the low recovery of highly volatile odor compounds as well as thermal degradation of labile compounds. Limits induced by thermal degradation may be overcome applying SDE under static vacuum (SDE-SV) that allows extraction at ambient temperature (30–35°C at maximum) and eliminates the concentration step prior to analysis. However, SDE-SV technique revealed to be very time-consuming and requiring a large amount of sample [25]. Heat-induced artifact formation may occur also during the sample introduction procedure; thermal degradation inside the heated GC injector block may be responsible of the total or partial loss of some odor compounds resulting in the formation of new peaks visible in the chromatogram and eventually detectable at odor detection port. A further technique widely applied is SAFE, both after SE techniques and as an individual extraction method, mainly for aqueous samples such as milk, fruit and urine [26]. SAFE extraction is longer, more difficult to conduct and more expensive (liquid nitrogen, distilled solvent, specific materials are needed) but it is more reproducible, furthermore, a SAFE extract can be kept frozen for a long time and used many times for analyses. Static and dynamic HS techniques (SHS and DHS including Purge and Trap) are considered a valuable tool for analysis of odor compounds [27,28]. They are characterized by several advantages: solvent-free procedures (no interferences due to solvent peak), requirements of small sample amounts and no artifact formation. However, Purge and Trap extraction is more influenced by the presence of artifacts and less reproducible. According to the purpose of the investigation and the fraction of volatiles of interest, the analyst can choose to apply static or dynamic technique. Anyway, these techniques required a pre-concentration step on sorption traps with porous polymers such as Tenax® TA or Porapak™ Q and resins such as Lichrolut® EN. The volatile components adsorbed on cartridges are then chemically or thermally desorbed from the trap and analyzed with GC-O. Interesting results were obtained by Machiels and Istasse, 2003 studying the VOCs isolated in a model mouth system by a dynamic headspace sampling technique [29]. This system represents an "artificial mouth" and reproduces both orthonasal and retronasal perception. For the purposes of the present investigation, a standard SPE cartridge filled with 400 mg of LiChrolut EN resins was placed on the top of a bubbler flask containing sample, water, and "synthetic saliva" solution (composed by 0.168 g of $NaHCO_3$, 0.048 g of K_2HPO_4, 0.166 g of KH_2PO_4, and 0.088 g of NaCl per 100 mL). Odor compounds released in the headspace were trapped in the cartridge containing the sorbent and were further eluted with dichloromethane, concentrated under a stream of pure N_2 and finally used in the olfactometry assay. SPME exploits high adsorption power of a fused silica fiber coated with a specific extraction phase selected according to the typology of matrix under investigation [29]. Its application presents some limits as the chemical profile of the collected odor compounds is strictly related to the type, thickness and length of the used fiber as well as to the sampling time and temperature. The efficiency of the technique is dependent on the used fiber coating because the kinetic behavior of the adsorption process differs with the nature of each compound. Moreover, the limited adsorption capacity of the fiber coating material could represent a problem in SPME quantification measurements. For example, SPME with Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber coating is not suitable for the isolation of high molecular-weight compounds or for those with a strong affinity to the matrix [21,22]. Pino et al., 2013, compared four fiber coatings for the extraction of banana volatiles using the same exposure time and temperature conditions: PDMS, PDMS/DVB, DVB/CAR/PDMS, and CAR/PDMS. Results showed that non-polar coating (PDMS) was more sensitive to esters and less sensitive to alcohols than polar coating (PDMS/DVB). However, the best overall extraction efficiency was obtained with DVB/CAR/PDMS [30]. Moreover, the similarity scaling obtained for the three SPME global odors with respect to the reference sample were DVB/CAR/PDMS (2.0 ± 0.1), PDMS/DVB (3.7 ± 0.3), PDMS (6.2 ± 0.4), and CAR/PDMS (8.3 ± 0.5). Therefore, the DVB/CAR/PDMS was chosen as the fiber, which generated the most representative odor. Feng et al., 2015, also showed that CAR/PDMS fiber was able to absorb volatiles from soy sauce more efficiently (higher intensities and widest range of volatiles) than other fibers [31]. Murat et al., 2012 compared three extraction methods, specifically SPME, SAFE and Purge and Trap, and they found extracts of the volatile fraction qualitatively and quantitatively different [32]. The Purge and Trap and SPME extracts were the richest and the poorest in compounds respectively and it included different groups of molecules. SAFE extraction gave a majority of alcohols (55.9% of the total relative amount) and ketones (32%); Purge and Trap extraction gave several alcohols (26%), aldehydes (22.7%) and ketones (20.1%); and finally, the SPME extraction gave 2-methylheptan-3-one (33.9%) and benzene derivates like ethylbenzene (11.8%) and 1,4-dimethylbenzene (11.1%). Purge and Trap resulted less precise and accurate than SPME in detecting off-flavors due to lipid oxidation and better than SPME to extract compounds with a lower molecular weight [33]. Moreover, it has poor recoveries for medium and high-boiling point compounds resulting in less representativeness of the extract. As each extraction technique shows limits and potentialities, a proper combination allows to achieve a more extensive and reliable screening of flavor profile.

With regard to environmental field applications, another key step is the choice of proper sampling method for odor compounds detection in gaseous samples. Air sampling and analysis procedure usually implies that the sample can be collected inside bags made of inert materials such as Nalophan® and Tedlar® or canisters and analyzed with an active air sampling device (e.g. Air Server) connected to a Thermal desorption-GasChromatography/MassSpectrometry-Olfactometry (TD-GC/MS) system or collected on suitable adsorbent materials, thermally desorbed and then analyzed by GC/MS. More specifically, in order to collect air sample inside the bags, the "lung principle" is used. The bag is placed in a rigid container (possibly transparent to control inflation) and the air from the container is removed with a small vacuum pump. Due to the lowering pressure, the bag expands; this prevents sample to pass through sampling pump avoiding volatiles contamination. According to the purpose of the investigation and the fraction of volatiles of interest, the analyst can choose to collect air onto sorption traps with porous polymers such as Tenax® TA or Porapak™ Q and resins such as Lichrolut® EN. In both the aforementioned air sampling procedures, the calibration requires the preparation of standard atmospheres obtained by vaporization of known volumes of the compounds of interest with high purity air. The sampling procedure of the standard atmospheres must be the same of that applied for the real samples. However, for volatile reduced sulfur compounds (i.e. mercaptans and sulfides) emitted from sewages, waste treatment plants and chemical industries and recognized as odor active compounds of high concern due to its very low odor detection thresholds, the most suitable adsorption substrate is a cartridge filled with Tenax® TA [34]. Although sample bags are easy-to-use and low-cost solution for the collection of gaseous odor active compounds, they are not suitable for sampling of reactive sulfur-containing compounds. Losses of sulfur-containing compounds may be attributed to adsorption onto the internal surfaces of the polymeric material as well as to permeation through the surface or reactions with other gases. To minimize losses and avoid a change in gas concentration, internally passivated cylinders (canisters) should be preferred to sample bags [35]. Lower sensitivities were also observed sampling light amines at low concentration because of their poor detection limits by GC–MS [36].

Taking into account the aforementioned analytical procedure, the environmental burdens should be mitigated by means of green approaches in extraction techniques [37–39]. During the last decades, the need of detecting trace and ultra-trace levels compounds in complex matrices determined a relevant consumption of solvents for isolation and or enrichment of investigated analytes. Therefore, to minimize the amount of chemical wastes and to limit the negative impact of analytical procedures on both environment and laboratory employees, solvent-free and safe not toxic sampling and pretreatment procedures should be preferred, guarantying at the same time, an adequate level of data quality. At this regard, an appropriate level of quality control can be guaranteed following specific good practices. More specifically, sorbent tubes used for air sampling should be conditioned prior to each use, even if already cleaned, to ensure any trace of organic volatiles possibly trapped onto the sorbent material have efficiently been removed. In case sorbent tubes are not used immediately after conditioning procedure, good practice is to store them in an emission-free container at room temperature and use them within at maximum four weeks. Moreover, if a measurement environmental campaign is carried out, good practice is to analyze about 10% of blanks samples subjected to the same handling procedure in the field as the sample tubes, except for the actual air sampling. Finally, potential analyte losses during the sampling procedure, especially for volatile compounds, are avoided using back-up tubes; this practice ensures that 'safe sampling volume' for the analyte of interest is collected and the breakthrough volume is not exceeded [40]. Regarding air sampling inside polymeric bags, the sample should be transferred to the laboratory and analyzed as soon as possible after the sampling in order to avoid 'sink effects' (i.e. adsorption of less volatile compounds onto the inner material surfaces, condensation and dissolution in condensed humidity) and/or diffusion of volatile compounds through the polymeric material.

4. Sensory-instrumental approaches for odors characterization

The main purpose of odor detection is to identify the odor active compounds and to relate them to human perception. Instrumental approaches based on Gas Chromatography coupled with Mass Spectrometry (GC/MS) are the most used ones to characterize and quantify odor active compounds in an environmental, food and/or fragrance sample. However, the main limitation of this technique is related to its low sensitivity in odor detection because of the concentration of many odor compounds are often lower than the instrumental detection limit. Moreover, the information about the relationship between human perception and odor compound is not provided.

Therefore, in the last years, the development of more sensitive analytical techniques (e.g. Multi- Dimensional GC/MS) and their integration with sensorial ones (Olfactometry), allowed to deepen odor characterization and to investigate the correlation between a quantified compounds and an olfactory stimulus.

4.1. Gas Chromatography/Mass Spectrometry (GC/MS) and Multi-Dimensional Gas Chromatography (MDGC)

Gas Chromatography coupled with Mass Spectrometry (GC/MS) is the standard technique for the determination of a wide range of odor active volatiles such as sulfur compounds, esters, amines and mercaptans. In the field of air quality assessment and odor nuisance monitoring, thermal desorption (TD) coupled with GC/MS (TD-GC/MS) is considered the gold standard methodology to obtain accurate and reliable data from different matrices. From the analytical point of view, the choice of the proper chromatographic conditions such as oven temperature program, injection mode and stationary phase of the column is a strategic step in a GC/MS analysis and is strictly related to the matrix under investigation and to the odor active compounds of interest [22]. With regards to columns, non-polar stationary phases allow odor active compounds to elute at the lowest possible temperature but its use results in poor peak shapes for very polar molecules such as fatty acids. Polar stationary phases generally show good selectivity and separation efficiency although both parameters depend upon the complexity of the composition of the matrix [20]. When odor active compounds investigated were isomers, the expected selectivity and resolution can be gained using a chiral stationary phase. TD-GC/MS, over the years, has been successfully applied for the chemical characterization of odor active VOCs. In Ribes et al., 2007, for instance, analytical performances of the TD-GC/MS methodology have been improved to reach, for selected chemical classes, the following Limit of Detection (LOD) ranges: 0.02–0.5 ng for esters, 0.002–0.1 ng for ketones, 0.01–0.53 ng for terpenes, 0.001–0.1 ng for aromatics, 0.03–14 ng for aldehydes, 0.003–7 ng for alcohols, 14–97 ng for amides and 0.2–10 ng for isocyanates [41]. However, at this point of the discussion, it is important to underline that when the matrix composition is characterized by a high level of complexity, mono-dimensional gas chromatography may be inadequate to assure the desired separation capacity. Therefore, in all the cases the matrix complexity results in multiple peak overlaps, an enhanced chromatographic separation can be obtained by applying Multidimensional Gas Chromatography techniques (MDGC) [24,42]. MDGC has been widely applied for detection of odor active compounds and nowadays represents an innovative methodological approach to improve both chromatographic resolution and identification capability. The operational principle of MDGC techniques is the employment of two sequentially connected capillary columns characterized by different selectivity towards chemical compounds present in the sample mixture. Although the choice of the column combination is strictly related to the matrix composition and the purpose of the investigation, the first column (first dimension, ^{1}D) is typically non polar and separates mainly by volatility, while the second column (second dimension, ^{2}D) is polar and separates by polarity [43]. Unresolved sample fractions eluting from the first column are transferred to the second one via a device operating an effective heart-cut or a modulation process. Today, there are two kinds of MDGC: conventional or 'heart-cutting' MDGC and 'comprehensive' two-dimensional gas chromatography (GCxGC). Heart-cutting MDGC technique is based on the transfer of one or more unresolved fractions of sample mixture eluting from the first column, generally non polar and with a length of 30 up to 60 m, to the second column with higher polarity and with a length of 30 m. The transfer of the sample fraction can occur immediately after the separation from the first dimension or, alternatively, can be postponed after a cryogenic refocusing step. Moreover, in order to gain higher analytical responses, many heart-cuts of the same analyte coming from sequential injections may be collected in the trap and, only after this enrichment step, separated on the second dimension. Comprehensive two-dimensional gas chromatography (GCxGC) differs from heart-cut MDGC as the components of the entire sample mixture, not only of a specific fraction, are separated on the second dimensions [44]. Capillary columns employed in GCxGC facilities are shorter, typically 15 up to 30 m for ^{1}D and 1 up to 5 m for ^{2}D, enabling very fast separations. The core of GC × GC systems is the modulator whose function is to accumulate, refocus and rapidly inject fractions eluting from ^{1}D-column to ^{2}D-column, guarantying the injection of effluent in narrow chromatographic bands. The short ^{2}D column length, moreover, guarantees that the separation in the second dimension is completed before a successive modulator injection. The Injections are run in fixed time frame and fast enough to preserve the original separation on the first dimension. The modulator can be a thermal (mainly cryogenic) or flow-based system. Cryogenic modulation is the most used approach

although the flow modulation is characterized by lower operational costs. Due to the fast separation, very fast detection systems are therefore required such as FID (flam ionization detector), micro-ECD (electron capture detector) and TOF-MS (time-of flight mass spectrometer). Although the conventional columns configuration (^{1}D: non polar; ^{2}D: polar) has been widely applied over the years, an 'inverted column configuration' revealed to be useful where an increased separation capacity was required, as demonstrated in the study carried out by Adahchour et al., 2004 regarding the identification and quantification of polar odor active compounds such as aliphatic acids and alcohols [45]. The inverted column configuration has been also successfully used by Chin et al., 2011 for identification of odorants and in particular sulfur compounds, in wine and brewed coffee samples [46]. MDGC-O methodologies combining multidimensional separation MDGC and simultaneous olfactive characterization have been developed over the years with the aim to identify individual odor active compounds in complex matrices and to assess their contribution to the overall odor perceived [24]. The application of integrated MDGC systems with simultaneous MS and olfactometry detection (MDGC-O/MS), for instance, has been reported as a successful approach to identify compounds responsible of odor annoyance in air samples taken in environmental sites of interest (e.g. livestock environments, beef cattle feedyard etc.) [47]. In fact, the application of MDGC-O technique revealed to be useful to derive a more complete odor profile of the air near a beef cattle feedyard respect to previous investigations (e.g. identification of trimethylamine, p-cresol, 2-aminoacetophenone, isovaleric acid and p-ethylphenol, indole and skatole). Heart-cut MDGC-O technique is the most used methodological approach although the first attempt of hyphenation of GCxGC to olfactometry was reported in 2007 by D'Acampora Zellner et al. [48]. Although the attempt was successful, GCxGC-O technique remains technically demanding due to the difficulty to couple very narrow chromatographic peaks (e.g. 100–400 ms), created during the modulation process, and the breathing cycle of humans (typically 3–4 s).

Taking into account the complexity of the analytical techniques usually used for odor compounds identification and the high number of variables affecting the quality of analytical data, specific practices can be employed in order to guarantee an appropriate level of quality control in each step of analysis, from desorption to chromatographic separation. More specifically: a) a representative number of conditioned sorbent tubes should be analyzed to guarantee that the blank value is acceptable (no greater than 10% of the typical areas of chromatographic peaks of the analytes of interest) and therefore, can be neglected in deriving quantitative results; b) desorption efficiency of VOCs and odor compounds from adsorbent materials should be controlled using internal standards; c) response factors of selected and representative compounds should be monitored inserting standard mixtures in the analytical sequence; d) the repeatability of the analytical method should be evaluated collecting and analyzing samples in triplicate (standard deviation not exceeding 15%); e) the recovery of analytes should be 95%.

4.2. Gas Chromatography-Olfactometry (GC-O)

The GC-O couples traditional gas chromatographic analysis with olfactometric detection providing qualitative and quantitative information on volatile odor-active compounds in complex matrices. Its introduction in the last years in aroma research represented a breakthrough enabling the identification of odor-active compounds present in their relative concentrations in the extract from the investigated raw matrix, through the association of the analytical data with the human perception [19,20,22,31,32]. The GC-O technique revealed to be a useful tool for investigations in food industry for the detection of the key odorants contributing to "aroma profile" of food and beverages and for studying the odor changes in food processing (i.e. fermentation, cooking, preservatives and flavorings additions) [2]. In the perfume industry has been used to improve quality and pleasantness of natural and synthetic odorous compounds [32,49,50]. In environmental studies has been used to study the impact of odors on the quality of human life and environment and to evaluate efficiency of malodor abatement systems [3,51]. In commodity science is being used for the detection and identification of odor active compounds responsible for off-flavors coming from a wide range of materials and consumer products, from building products to wood plastic composites made from landfill-derived plastic and sawdust [52]. GC-O works under the principle that once separated and eluted by the chromatographic column, each odor active compound able to generate an olfactory stimulus can be detected by a single or a team of properly trained human assessors by means of a specifically designed olfactometric detection (sniffing) port (ODP) connected in parallel to conventional detectors, such as flame-ionization (FID) or mass spectrometer (MS) [20]. Precision and accuracy of data collected is ensured by a careful selection and training of the assessors involved in the sensory evaluation. The simultaneous comparison of the signals is obtained splitting the GC effluent into two streams towards each detector, with fixed split ratio obtained by flow splitters equipped with appropriate restrictions towards the two outlets. Due to the dependence of flow resistance with temperature, the use of a special dome splitter with five capillaries has been also developed to obtain variable split ratios over the whole temperature range of a GC run [53]. The simultaneous sensory evaluation allows to establish if a specific compound is odor active (at a given concentration in the sample extract higher than the threshold of sensory detection). Human assessors are asked to indicate the duration of the odor activity (start to end), to describe the hedonic tone using suitable and standardized descriptors and to quantify the intensity using an odor intensity scale [2,19,20]. The thresholds of human perception of odor active compounds may differ by many order of magnitude and it frequently occurs that only a small portion of volatiles present in the matrix can really contribute to the overall perceived odor. Moreover, odor active compounds do not contribute at the same extent to the odor profile of a blends and, due to the odor intensity/concentration relationship, a large peak area in GC do not necessarily corresponds to high odor intensity, in other words GC/MS results were not comparable with GC-O. Over the past years, the design of the GC/MS-O systems have been improved to avoid some technical drawbacks. A T-piece with capillary restrictors (with appropriate length and diameter) has been inserted before the mass spectrometer to increase the pressure drop between the interface and the flow splitter to overcome the time delay between the mass spectrometer and the ODP detection due to the different pressure conditions (vacuum in the first case and atmospheric pressure in the second one). An uncoated and heated transfer line (deactivated silica capillary) has been inserted between the column and the ODP, to allow the quantitatively transferring of odorous compounds avoiding condensation of high boiling molecules. Careful should to be paid on carriers as gas flow must be carefully selected as well as the auxiliary gas (moist air), the latter added to the GC eluate to prevent the drying of the assessors' nose mucous membranes and to ensure comfort during the analysis [54]. This basic experimental apparatus over the years has also been modified leading to a multi-assessment of odor detection in eight ways gas chromatography olfactometry (8W-GC-O) [55]. This innovative device consists of a gas chromatograph coupled with a divider that synchronously distributes the volatile compounds to eight transfer lines connected to eight separated sniffing ports. Flow rates can be adjusted to ensure the optimal conditions and obtain the best compromise between chromatographic resolution and sensory sensitivity at the sniffing ports. As previously mentioned in section 4.1, olfactometric evaluation has been coupled also to MDGC

for quantitative analysis of the marker odorants from livestock odor based on thermal desorption coupled with a multidimensional GC/MS-O system used for simultaneous chemical and odor analysis [56]. The system was equipped with a non-polar pre-column (5% phenyl-methyl-polysiloxane stationary phase) and a polar column (fused silica capillary column coated with polyethylene glycol) connected in series by means of a Dean's switch showing higher identification and quantification of polar and non-polar key odor active compounds of the matrix under investigation (detection limits ranged from 40 pg for skatole to 3590 pg for acetic acid). Higher limits of detections were only observed for sulfur compounds due to limitations of Tenax sorbent. Key odor active compounds may be present in the matrix at trace level and co-elution of compounds may easily occur making the correlation between the chromatographic peaks and the perceived aroma difficult to assess. Moreover, the role of the key odor active compounds may be difficult to evaluate also considering the low sensitivity of analytical instruments with respect to human nose [2,6,19]. The higher sensitivity of the human olfactory system is well documented and the theoretical odor detection limit hypothesized is 10^{-19} mol [57]. For example, 1 pg of β-damascenone, a key-odor compound in rose essential oils, is detectable by sensible individuals at 50–500 fg [58]. Another important aspect of the GC-O to underline is that volatile compounds are assessed separately and behavior of compounds in the mixture and the role played by the single compound on the overall perceived smell cannot be elucidated [59]. No information can be obtained regarding the unpredictable extent of interaction occurring among volatile compounds in the real matrix, more specifically the phenomena of hypo-additivity (masking effect) or hyper-additivity (synergistic effect) making the integration of GC/MS data with sensory characterization of the overall aroma necessary to understand the olfactometric phenomenon. Recognized limits of GC-O are directly related to the use of human assessors as a detector as the performance of the sensory evaluation may be affected by a bias in the odor detection. First of all, olfactory capacity and odor thresholds may vary significantly both within and between people and cases of specific anosmia may occur, when a member of the sensory panel may be too highly or too little sensitive to certain classes of compounds [20]. Secondly, assessors are asked to sensory evaluate (qualitatively and quantitatively) many different odors appearing at ODP for a few seconds at undefined intervals over the period of a chromatographic analysis (30 min or more) and could miss the opportunity to perceive the stimulus and to describe it due to several reasons such as a lack of concentration, the breathing cycle, the health status and the natural variation of the olfactory response over the time [20,22]. Typical bias is an anticipation error occurring when the same sample is presented repeatedly or individual samples, not significantly different in composition, were analyzed sequentially. This limit can be overcome by randomizing the sequence of samples presented and/or by randomly adding blanks or unknown samples. As a consequence, one of the major concern to take into account in a GC-O analysis is the number of assessors that should be used in order to preserve the reliability of the results. In addition, the type of detection method used may also affect the quality and expressiveness of GC-O data. At this regard, over the years, many methods have been developed and they may be classified into four categories; dilution to threshold methods, such as combined hedonic response measurement (CHARM) and aroma extraction dilution analysis (AEDA), detection frequency methods, direct intensity methods such as posterior intensity evaluation methods and OSME [19]. In order to guarantee an adequate level of quality control, all the good practices mentioned for GC/MS (mono e multi-dimensional) in section 4.1 should be adopted. In addition, representativeness of sensory evaluation data can be guaranteed by a significant and proper number of panelists sniffing at the olfactometric port.

5. Dynamic olfactometry

Another approach for odor detection is the dynamic olfactometry. This technique allows to evaluate the odor perception of human considering that the most sensitive and broader range odor detector is undoubtedly the mammalian olfactory system. Therefore, great attention has been paid over the last years on the use of human nose in performing odor measurements with scientific soundness. In fact, sensory evaluation of smells by means of panels of sensory trained evaluators it is revealed an useful tool for odor assessment and quantification in the trade industry (i.e., food, beverages, perfumes, etc.) and in environmental field. More specifically, with regard to environmental applications, the methodology of dynamic olfactometry has been deeply developed and standardized in order to determine odor concentrations of emissions coming from industrial activities [60]. In particular, olfactometric data are principally used to: a) verify the compliance of odor emissions with limit values defined in regulatory provisions; b) to calculate odor emission rates used, as input data, in atmospheric dispersion models to predict odor impact areas; c) to evaluate the efficiency of odor abatement technologies. The methodology employs human noses as detectors, relating directly to the properties of odors as experienced by humans, providing measurements of odor concentration expressed in odor units per cubic meter (ouE/m^3), numerically equal to the dilution factor needed to reach the odor threshold. According to the European Standard, 1 ouE/m^3 is defined as the amount of odorant that, when evaporated into 1 m^3 of gaseous air at standard conditions, causes a physiological response from a panel (detection threshold) equivalent to that of n-butanol (reference gas - 40 ppb v/v) evaporated into 1 m^3 of neutral gas [61]. Dynamic olfactometry is based on a gas-dilution apparatus, the olfactometer, which presents the collected air samples diluted with odor-free air according to precise ratios, to a panel of human assessors. The panel is previously selected according to a standardized procedure, by using reference gases. To provide objective results and overcome the subjectivity associated with olfactory perception, dynamic olfactometry is regulated according to technical standards explaining the requirements an olfactometric laboratory have to fulfill, including sampling procedure and analysis. Specific provisions have to be respected taking into account all the variables that could affect the measurements described in detail in the following subsections (5.1–5.4).

5.1. Design of devices used for sampling and analysis

The critical issues of dynamic olfactometry are adsorption/desorption phenomenon and contamination of sample during both sampling and analysis steps. In fact, all materials used for sampling and analysis and constituting the olfactometer should be tailored to avoid them [62]. Low-absorbency materials such as Teflon, Tedlar® and glass are preferred. Moreover, use of stainless steel materials has to be accurately considered since recent scientific studies showed a remarkable loss effect up to 50%–60% of hydrogen sulphide after the passage of the sample through a steel dilution system and/or other components of the same material [63]. The European technical norm on the issue (EN 13725/2003) is currently under review to overcome some limitations encountered during the first applications of the methodology. To minimize risks of adsorption or contamination, internal surfaces of the devices used for sampling and analysis must be minimized and cleaned with neutral air during odor presentation to panelists. Innovative design of 3D-printed nasal mask inlet for common sleep laboratory masks for lateral divided stimulus presentation have been also proposed in order to increase performances in odor detection [64].

5.2. Procedure of analysis

Two standardized methods for the presentation of odor sample to the panel are commonly applied: forced choice and yes/no method [61,65]. In the forced choice method, two or more sniffing ports are used; the sample is presented at one port, and neutral air at the other port(s). In this case, the examiners have to compare the different presentations and choice the port from which odor exits. In the yes/no method each examiner sniffs from a single port and communicates if an odor is detected or not. Odorous sample diluted with neutral air according to fix ratios or only neutral air can exit from the sniffing port. It is commonly preferred to present odor sample in concentration-ascending order, whereby the weakest odorous samples (highest dilution) are presented before stronger odorous samples (lower dilution) to avoid olfactory adaptation in panelists. The volume of diluent is decreased by a predetermined and constant factor, in subsequent presentations, creating a geometric progression of dilutions useful to describe the logarithmic relation between odor intensity and concentration. The process continues until each panelist positively detects an odor in the diluted mixture; at this stage the panelist has reached the detection threshold for that odor, calculated as the geometric mean between the dilution of the last negative answer and the dilution of the first positive answer. The geometric mean is preferred to others in order take into account the logarithmic relation between odor intensity and concentration An odor active sample should be analyzed considering different measurement cycles and the final result is calculated as the geometric mean of the values obtained for single series. The concentration is expressed as:

$$C = \frac{V_0 + V_f}{V_0} \tag{4}$$

where C is the odor concentration, V_0 the volume of the sample and V_f the volume of odor-free air required to reach the threshold.

For a dynamic olfactometer the concentration is given by:

$$C = \frac{Q_0 + Q_f}{Q_0} \tag{5}$$

where Q_0 is the flow of odorous sample and Q_f the flow of odor-free air required to reach the threshold.

As described by the preceding equations , odor concentrations result dimensionless and may be expressed as threshold odor numbers (TON) or dilution to threshold (D/T) ratios, although it is common to consider them as physical entities and expressed as odor units per cubic meter (ou/m^3).

5.3. Selection of the panel

Human assessors have to fulfill specific requirements and accurately trained to become adequate sensors for odor measurements. For this reason, it is compulsory to follow a standardized procedure to choose a representative sample of human population with average olfactive sensitivity. The procedure suggests training the assessors using reference gases (e.g., n–butanol). The panel of assessors must comply with the following repeatability and accuracy criteria:

- average n-butanol odor threshold in a range of 20–80 ppb v/v (40 ppb v/v represents the accepted odor threshold for n-butanol);
- antilog standard deviation of individual responses less than 2.3.

Moreover, panelists have to be continuously screened and trained and must observe a simple behavior code in order to preserve the reliability of the measure and to comply with the selection criteria independently from the individual olfactory perception. Pre-selection tests are necessary to improve in the range 30%–46% the efficiency of jury approvals and to restrict the number of certifiable candidates [66].

5.4. Olfactometric data quality

To ensure high quality performance, an olfactometric laboratory has to be compliant with quality criteria, particularly the coherence of panel responses. For the first quality criterion, a laboratory performance is defined through the measure of accuracy and precision, calculated for both the standard (n-butanol) and all the other odors. For example, the European standardization reported the following criteria for laboratory performance [61]:

$A_{od} \leq 0.217$, where A_{od} indicates the laboratory accuracy;

$r \leq 0.477$ or $10^r \leq 3.0$, where r indicates the laboratory precision, meaning that the result from two consecutive measurements must not be higher than 3.0 for 95% of the time.

Moreover, the laboratory must evaluate the coherence of panel results during each measurement cycle, according to a validation procedure aimed to exclude panel members giving invalid responses. An example of this type of procedure is represented by the *retrospective screening*, based on the valuation of ΔZ parameter, calculated for each individual panel response, as the ratio between the individual threshold value Z_{ITE} and the geometric mean of all individual threshold values $\bar{Z}_{ITE}$ obtained during a measurement sequence:

$$\text{If } Z_{ITE} \geq \bar{Z}_{ITE} \text{ then } \Delta Z = Z_{ITE}/\bar{Z}_{ITE} \tag{6}$$

$$\text{If } Z_{ITE} < \bar{Z}_{ITE} \text{ then } \Delta Z = -\bar{Z}_{ITE}/Z_{ITE} \tag{7}$$

This parameter must satisfy the following relation:

$$-5 \leq \Delta Z \leq 5 \tag{8}$$

If the result of a panel member does not satisfy this criterion, all responses given by the same panel member must be eliminated from the ultimate results; the procedure is repeated until all data provided by panel member are consistent with the criterion. Moreover, each panel member must not commit mistakes more than 20% for the detection of neutral air during the administration of the measurement sequences, otherwise the measurement is considered not valid. Odor measures can be affected by odor background from sampling bags and interaction of odors with materials: these issue can be particularly critical at lower concentrations when the dilution with free-air is higher [67]. Laboratory, panel and panel sessions are components of variance that significantly differ between n-butanol and other odorants and the transferability of performance characteristics from n-butanol to other odorants is questionable [68]. In order to improve data quality, it can be advantageous that laboratories develop more detailed and restrictive internal procedures to perform panel training and selection and analytical sessions. In a recent study, Hove et al., 2017 have examined the influence of panelist's performance level, panel size and number of rounds per sample on the precision of an odor laboratory for n-butanol and a pig odor [69]. The authors put in

evidence that all the tested variables affected the precision and that the incidence of increasing panel size was the highest. So, the increase of panel size represents a good method to improve precision; moreover, the authors noted that the precision determined for pig odor was higher than that of n-butanol, suggesting that the use of n-butanol, as unique reference for panel selection, could be debatable. The objective measurement of odor concentrations directly related to human perception represents the main advantage of dynamic olfactometry. On the other hand, the methodology is not able to discriminate the single chemical compounds and their contribution to the overall odor concentration. Dynamic olfactometry, moreover, provides punctual odor concentration data but does not allow to perform continuous measurements useful to monitor industrial processes causing malodors. Attempts to use chemosensors instead of panelists gave poor calibration results [70]. Odor samples are difficult to store, because of their instability, and require rapid time of analysis; the methodology is time-consuming and quite expensive and moreover frequency and duration of analysis are limited. Odor measurements would ideally be carried out directly at the odorous site allowing continuous odor sampling without the need for storage. Unfortunately, this approach involves the need to isolate the panel of assessors from the surrounding environment and to maintain them in an odor-free environment to prevent olfactory adaptation or fatigue. Usually in-situ measurements can be performed using mobile laboratories even if their provision is much expensive. Instead of direct olfactometry, it is preferred collecting odor samples in situ and transferring them to an off-site odor laboratory for the assessment.

5.5. Field olfactometric measurements

In order to overcome the drawbacks related to sample storage and to valuate even low odor concentrations in ambient air, specific devices to assess odor on site, called "field olfactometers", were developed over time [71,72]. These devices allow to produce dilutions by mixing the odorous ambient air with odor-free air, provided by a portable gas cylinder or made on-site by forcing ambient air through a carbon filter. The application of field olfactometer is particularly widespread in USA and Canada, where several states fixed limits at the receptor sites or at the boundary of industrial plants [62] whereas in Europe, field olfactometers are not standardized. Its use can show some concerns, related to the objectivity of examiners, that could be affected by the direct view of sources of odor emissions, and their difficulty to isolate themselves by environmental odors. Moreover, the accuracy of field olfactometers to dilute odor sample has not been sufficiently investigated. Some studies focused on the comparison of odor concentrations observed by using different field olfactometers, revealed significant differences between them [63]. In a recent study, the performance of two commercially available field olfactometers (Nasal Ranger by St Croix Sensory and Scentroid SM110C by Ides Canada Inc.) were investigated to verify the accuracy in dilution-ratio production, showing, for both instruments, some discrepancies between the set and observed dilution ratios and suggesting improvements for its control [62].

6. Electronic noses

In order to assess in real time the odor emission from different samples as food or environmental ones is useful to use smart device as well as the electronic nose. The term "electronic nose" was introduced for the first time in the late 1980's and since then specifically used in conferences. An exhaustive definition, however, is still needed. A definition useful for the purposes of this review should be the following: "an instrument composed of an array of chemical sensors with partial specificity and a pattern recognition system able to recognize odors also in complex mixture" [73]. In the attempt of reproducing an analytical device capable to mimic human sense, researchers were addressed towards a design inspired by the human apparatus. The electronic nose may be composed of a sampling system (pumps), a matrix of sensors and a pattern recognition system mimicking the neuronal elaboration of the signals into an odor sensation. About the sensor array, the first gas sensor transducer was introduced at the beginning of the 1960s, using ZnO thin films as a sensing layer in a chemo-resistive device [74]. Soon after, in 1961, the patent of Taguchi opened the way to the development of industrial gas sensor devices for practical applications using SnO_2. This typology of sensors, the so called "Taguchi sensors", have been rendered increasingly selective to families of volatiles by adding a small amount of catalytically active dopants (Pd, Pt, ZnO, CuO, Cd) [75]. The realization of the first array of sensors traces back to 1982 when it was demonstrated that useful discrimination capabilities could be achieved without the use of highly specific receptors like those working in the human nose [76]. Electronic noses are divided into passive and active devices depending upon the presence of a pumping system: in the first case, odorous substances are passively detected by the sensor array by free diffusion and the device is commonly placed close to the odor source, in the second one a pumping system actively load the sampled air into the array chamber. A three-way valve serves as purging system when clean air is conveyed in the array's chamber, or sampling system when inlet (from the odor source) is conveyed (Fig. 1). During purging, sensors are reported to the baseline signal after one sample assay. Electronic nose can perform the analysis by sampling the air collected in suitable polymeric bags (Nalophan or Tedlar), inside canisters or directly from the effluent of a chromatographic column, acting in latter case as a detector. One advantage of the electronic nose is the ability to detect odorless compounds not perceived by the human nose, expanding its discrimination capabilities among volatile organic compounds (VOCs) [77]. In Fig. 1 a scheme of an electronic nose with active sampling is reported.

Odor detection represents a subclass of gas sensing technology, as not all VOCs are odor active molecules, and efforts of the gas sensor industry are directed towards the realization of devices useful for odor discrimination and quantification. The term discrimination should be used instead of recognition as the electronic nose is not able to perform a qualitative analysis like GC/MS but to discriminate among various volatile profiles, upon the adequate training. In Table 2 some of the commercially available electronic noses specifically designed or used for odor detection are reported, with indications on manufacturers, models and sensors technology.

The main applications of electronic noses are found both in food and environmental research fields. The application of electronic

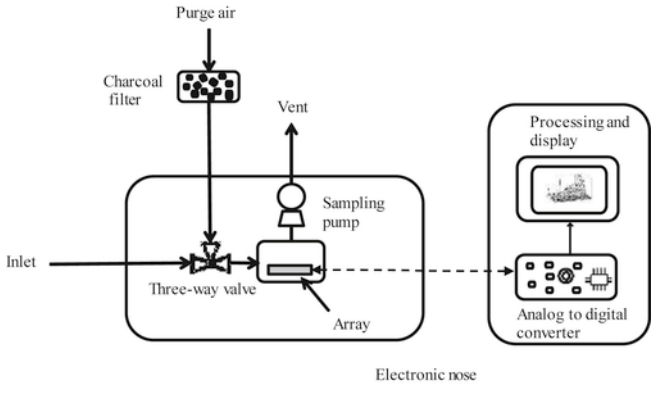

Fig. 1. Scheme of an electronic nose with active sampling. Charcoal filter may be replaced by a zero-air generator.

Table 2
Commercially available electronic noses used for odor detection.

Manufacturer	Model	Technology
Airsense GmbH	PEN3, PEN2	MOS
Alpha MOS	FOX 2000, 3000, 4000, 5000	MOS
Applied Sensor	iAQ-Core C, iAQ-Core P, iAM	MOS
Aromascan plc UK	Aromascan	polypirrole conducting polymer
Gerstel GmbH	QCS	MOS
Neotronics Scientifics Ltd	Neotronics NOSE (model D)	polypirrole conducting polymer
Olfosense	Airsense GmbH and PCA Technologies	1 PID, 1 EC, 4 MOS
Osmetech Plc	Aromascan A32S	Conducting polymer
RST Rostock System-Technik GmbH	FF2	MOS
S.a.c.m.i scarl (Imola, Italy)	EOS507	MOS
Scensive Technologies Ltd.	Bloodhound ST214	Conducting polymer
Sensigent	Cyranose 320	Polymer/black carbon/NCA
Sysca AG	Artinose	MOS

NCA = Nano Composite Array, MOS = Metal Oxide Semiconductors, PID = Photo Ionization Detector, EC = Electrochemical Cell.

noses in the food research field is well documented in scientific papers and reviews and is mainly addressed to discrimination among food matrices such as samples of milk, wine, tea, coffee, fish and meat [78] in developing new sensor array with different technologies (electrochemical sensors) and chemometric approaches aimed at fostering discrimination capabilities [79] and in detection of contamination and defects in foodstuffs [80]. Environmental monitoring and control are emerging issues in electronic nose science although some limitations due to complexity of use and lack of specific regulations for standardization [81]. Odor quantification by means of electronic noses suffers from some limitations as the literature suggests. Electronic nose is: a) site specific; b) dependent on a multivariate statistical or a specific and tailored neural network approach chosen and tested depending on the specific application; c) climatic conditions influenced (i.e., humidity, temperature). In more details, the data quality provided by electronic nose depends on the used statistical data elaboration approach. Moreover, drift effects may occur due to sensors degradation and due to relative humidity (RH) and temperature changes during sampling. RH and temperature in fact, may vary qualitatively the composition of the volatile profile. In order to reduce the sensor drift due to RH, the use of a water scrubber is suggested. In those cases, in which water vapors cannot not be completely removed from the sampling volume, some e-noses integrates an automatic compensation system to adjust sample air to a pre-set of RH values. Another strategy to mitigate drift effects due to RH changes consists in heating the sensor array to temperature above boiling point of water. This strategy limits also temperature drift as the array is maintained at a constant fixed temperature. Some e-noses contains RH and temperature sensors which are the inputs of a correction algorithm [82]. Moreover, sensor drift limitations may be also overcome by periodic instrument calibration or by training sessions repeated over the time. The mitigation of drift effect is important to guarantee the repeatability of analysis especially in environmental applications. Some custom devices with selected sensors have been developed tailored for specific applications (environmental monitoring, process monitoring, abatement system alert devices) and integrated with forecasting dispersion models. Whatever is the application, the definition of minimum performance requirements and standardization procedure are needed and specific *ad-hoc* groups are working to implement new European standard in instrumental odor monitoring [83]. Summarizing, electronic noses are cheap devices suitable for in-field monitoring, allowing to monitor odorous phenomena with high time resolution. Although other reliable and on-line devices such as Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS) exist, they are quite expensive and require well trained technicians, and thus electronic noses are preferred.

Finally, electronic noses are not reliable for odor impact assessment when the complaining population exposed require scientific results with legal validity. About QA/QC issues the members of CEN TC264 "Air Quality" have established in 2015 the working group CEN/TC 264/WG 41 composed of experts working on "Instrumental sensors for odorant monitoring" [84]. The standard is expected to set benchmarks for the application of a wide range of e-nose technology in continuous odorant monitoring, and probably will be launched within 2019. The focus of the panel is on definitions of an e-nose, criteria for developing and validating mathematical models linking instrument metrics to odor measurements and validation of measurement results benchmarked to odor measurement. A parallel working group WG42 is focused on low cost air quality sensors. The electronic nose should detect the presence or absence of odor above a given threshold, identify and classify relevant odors at different concentrations and quantify the odor magnitude giving stable responses with varying temperature and relative humidity. The relevant EN standards for monitoring are: EN 14181 (Stationary source emissions - Quality assurance of automated measuring systems) and EN 15267 (Air quality - Certification of automated measuring systems - Performance criteria and test procedures for automated measuring systems for periodic measurements of emissions from stationary sources). The relevant performances to be satisfied in outdoor and indoor air are [84]:

- Detection of odor (presence or absence): 0.1–10 ou/m^3
- Identification/classification of odors: 1–100 ou/m^3
- Quantification of odor magnitude: 1–200 ou/m^3

7. Critical comparison and evaluation of existing approaches known from the literature

An overview of strengths and weaknesses of the odor detection techniques is reported in Table 3.

Several methodological approaches can be applied to characterize odor mixtures in terms of odorants concentration and composition [85]. Gas Chromatography coupled with Mass Spectrometry (GC/MS) is considered a precise and powerful analytical tool for the separation and identification of volatile organic compounds and odor active compounds thanks to the combination of enhanced peak resolution provided by capillary columns and the low detection limits achieved by mass spectrometer detector (MSD). Multidimensional gas chromatography mass spectrometry (MDGC/MS) improves the chromatographic resolution and identification capability of volatile compounds decreasing the analytical problems associated with peak coelution and expanding the range of chemicals simultaneously detectable (both polar and not-polar compounds) [42,44,45]. Gas Chromatography-Olfactometry (GC-O) is among the aforementioned gas chromatographic techniques, the only one ensuring the integration of analytical information with olfaction evaluation data. This strategic approach allows to accurately identify the odor active compounds inside complex mixtures providing also useful information on the chemical nature of compounds responsible of odor annoyance. However, due to odor thresholds lower than detection limits, not all odor active compounds detectable by the human nose can be identified [86]. Nevertheless, the aforementioned techniques are limited by the following aspects: difficulties in the preparation of multi-component

Table 3
Comparison among mono/multi-dimensional gas-chromatography/mass spectrometry-olfactometry, dynamic olfactometry and electronic noses in terms of strengths and weaknesses.

Analytical technique	Strengths	Weaknesses
Mono/multi-dimensional gas-chromatography/mass spectrometry-olfactometry	GC-MS/MDGC-MS/GC-O: complete characterization of chemicals in odor mixtures. MDGC-MS: improvement of resolution for co-eluting chemicals and simultaneous detection of compounds with different polarity. GC-O: integration of sensory evaluation data (description, intensity and duration of odor stimulus) with chromatographic output.	High costs and time analysis. Off line measurements. Overall odor concentration and synergistic and antagonistic effects cannot be assessed. Thermal degradation of labile compounds.
Dynamic olfactometry	Objective measurements of odor concentrations. Quantitative measurements of odor concentration. Standardized methodology. Direct relation to human perception.	Not able to discriminate single chemical compounds. Limited temporal representativity (punctual monitoring and not in continuous). Difficulty to store samples. Time-consuming and expensive. Limited frequency and duration of analysis.
Electronic noses	Cheap. High time resolution coverage. Suitable for in-field monitoring.	Lower sensitivity with respect to gas-chromatography. Affected by weather conditions. Low specificity. Needs robust training. Not targeted odors cannot be detected. Not reliable for odor impact assessment.

gaseous substance standards, thermal degradation of unstable volatiles compounds, in particular sulfur compounds, ascribable to high operating temperature both in thermal desorption units and injectors, water interferences to be eliminated by purging or using suitable scrubbers, high costs, time of analysis and highly qualified operators requirements, low time resolution not allowing a real time source identification and odor impact assessment [85]. The complexity of the olfactory phenomenon leads generally to prefer an integrated approach in monitoring, since the several methods of investigation are able to provide different information, often complementary. Dynamic olfactometry is the only standardized methodology able to relate directly to human perception and to quantify the concentration of an odor mixture. In this sense, it does not discriminate the chemical compounds in the mixture. However, as sensorial methodology, it is affected by some limitations due to the restricted frequency and time of analysis. Moreover, it provides punctual data, representative of the moment of sampling; therefore, related to high variability industrial processes, it does not enable to follow the emission trends, as continuous monitoring methods [19,50,67].

Electronic noses are cheaper than both analytical instrumentations and olfactometers, as prices ranges usually from about 25,000 Euros for a MOS-based sensor array as bench device for laboratory use to about 10,000–15,000 Euros for a hand-held conductive polymer-based one (with high variability depending upon market conditions). The resolution coverage depends on the sampling time, but usually do not exceed few minutes for active sampling and few seconds for passive sampling. The application of commercial devices in on-field applications or customized solutions for specific industrial applications are numerous and sometimes reported in literature as promising instruments to monitor the transient odor plumes emitted from the source, or to serve as inputs of dispersion models aimed to forecast odor concentrations at sensible urbanized sites taking into account orography [87]. Electronic noses have been used to differentiate and quantify main gases emitted from municipal solid waste facility, to respond to sewage odors [88] or in a combination with GC-MS and dynamic olfactometry [89]. In all these cases the recognition of odors and its classification rely on a robust training of the monitoring system (often based on more than two devices) and is critically affected by weather conditions (temperature, humidity, wind direction and speed). For these reasons not-targeted odors can be detected thus making the system of low specificity so dynamic olfactometry, which is based on human panel assessors, is the unique reliable and legally valid system for quantification of odor concentration in ambient air. Despite the initial enthusiasm towards human olfaction mimicking, the electronic noses revealed standardization issues in practical application that vary according to the application: fruit ripening and human cancer diagnosis by breath analysis, need different classification uncertainty. To solve the issues, the European Committee of Normalization on Air Quality, CEN TC/264, has recently composed a working group for drafting an European Standard on instrumental odor monitoring. For environmental odor monitoring at receptors, an accurate and reliable test was made by Eusebio et al., who computed the Accuracy Index (the ratio between the number of measurements of odorants that were correctly classified and the number of total measurements) of a MOS-based electronic nose to five odorants (acetone, ethanol, limonene, hydrogen sulphide and trimethyl-amine), revealing the "confusion" between acetone and ethanol, so acetone samples at low T and RH were erroneously recognized as ethanol, and the other way around [83]. This behavior was attributed to the structure similarity, and the instrumental detection limit of the electronic nose towards the target compounds ranged in the interval 15–25 ou/m^3. About percent of correct classifications, it depended on the substance considered as better results were obtained for ethanol, limonene, and H_2S (100%), with respect to acetone and trimethyl amine (90%), which gives an overall mean of 96%. By considering all the results obtained the minimum requirements are: the electronic nose repeatability (response's invariability to atmospheric conditions that should be fixed as two minimum accuracy index values, one related to tests in which RH is variable and T fixed and vice-versa, minimum 70%); the instrumental detection limit (should be fixed testing electronic nose capability to recognize samples with, as an example, accuracy index > 70% above 5 ou/m^3 and accuracy index > 95% above 20 ou/m^3) and accuracy in classification of odors (an accuracy index of 80–90% should be sufficient in classification of odors provided we trained the device with a predefined standard set of odorants, specific for the application).

8. Synergistic approaches in odor monitoring

As discussed in previous sections, GC/MS-O (with mono- or multi-dimensional separation), dynamic olfactometry and electronic noses were recognized among instrumental and sensory-instrumental techniques as useful tools to detect, study and manage odors, but only recently the effectiveness of an integrated approach was recognized as strategic to study odors both in food aroma science and environmental management. At the state of the art, none of the described

techniques can be self-sufficient as none has the required high-time resolution, sensitivity, reliability, reproducibility if compared with the human nose. The integration of data, instead, obtained from all or at least two of the aforementioned techniques, may provide an exhaustive comprehension of odorous phenomena. Several authors recently reported useful examples of the application of such an integrated and synergistic approach. One of the first attempts to investigate the relationship between electronic nose and odor concentration was attributable to Misselbrook et al., that used two different electronic noses, the Odormapper (a self-developed one equipped with 20 polyindole sensors) and the Aromascan (commercially available equipped with 32 polypirrole sensors) in measuring the signals of the arrays, during application of cattle-slurry to a grassland in different locations and with different relative humidity. A linear regression of average responses of all sensors versus odor concentration measured by dynamic olfactometry revealed a good fitting but with a large variance around 59% and 62% [76]. The Aromascan A32S has been used by Sohn et al., for the quantification of odors emitted in a piggery effluent ponds by using a two layer back-propagation neural networks, with a tan-sigmoid transfer function in the hidden layers and a linear transfer function in the output layer obtaining $R^2 = 0.894$ but with a large variance. Therefore, the same authors suggested that R^2 values could not represent the correlation between the measures and predicted odor concentrations. Moreover, the authors noted that the performance of the network was improved by using an early stopping technique to avoid overfitting and by using just 20 hidden neurons, with R^2 raising to 0.98 [90]. To reach odor quantification at lower ranges Micone et al. used a sensor array consisting of 16 different unspecific commercial SnO_2 sensors (Taguchi and FIS, Japan) contained in a stainless-steel chamber of 1 L. Odor concentrations were presented to the sensor array by dilutions ranging between 1 and 200 ou/m^3, most of them in the low concentration range. The samples were collected in a waste landfill plant (landfill gas mainly composed of methane, carbon dioxide and Sulfur odorants at very low concentrations) and a multilayer perceptron neural network and a radial basis function networks were used. The Rs/R_0 ratio (ratio between resistance during sampling and background, respectively) decreased as the odor concentrations increased, until a plateau was reached thus revealing sensor saturation at higher OCs. Moreover, at very low OCs and at Rs/R_0 ratios close to 1, signal noise reached a level that impeded the reliable measure of odor concentration. Values of the ratio Rs/R_0 above unity were due to the presence of oxidizing molecules that increased the sensor resistance above the background level. The concentration of odors where saturation occurred was around 150 ou/m^3 [91]. An in-depth testing procedure for the definition of the minimum requirements of electronic nose performances for applications in environmental odor monitoring has been done by Eusebio et al. [83]. Three main aspects were highlighted: 1) invariability of response with respect to weather conditions (temperature and RH); 2) calculation of instrumental detection limits; 3) odor classification accuracy towards five selected compounds, representative of five classes of odors (ethanol, acetone, limonene, H_2S and trimethylamine). The detection limits obtained at 20°C and 65% RH were in the range 15–25 ou/m^3. However, temperature T and relative humidity RH strongly affected sensor's response depending upon the target molecule: limonene, H_2S and trimethylamine were correctly classified by the electronic nose at every T ad RH, whereas ethanol and acetone were misclassified especially at lower T and RH. The authors attributed this behavior to the chemical similarities existing between the two oxygenated compounds and this evidence pointed out the necessity to accurately choose the training molecules according to a reliable classification scheme. Poultry farm and livestock odors were monitored by means of an intelligent portable system called "odor expert" to assist farmers in odor management during operations [92]. Four sensors were chosen: one MOS ammonia sensor, an H_2S hybrid sensor, a SnO_2 butane specific sensor and a tungsten oxide sensor specific for amine compounds. Sensors measuring T and RH were inserted in a customized solution. OC downwind the farm operations was measured as dilution-to-threshold (D/T) ratio using a portable Nasal Ranger Field Olfactometer (St. Croix Sensory, Inc, Lake Elmo, MN, USA) while the customized electronic nose monitored at the same time. Accuracy prediction of OC was confirmed by $R = 0.932$. Anyway, it was pointed out that the electronic nose was able to only evaluate punctual odor events without providing an overall odor mapping around the facilities and it was suggested the integration of an electronic nose network placed along the perimeter of farm facilities with an air dispersion models in order to predict the downwind odor nuisance on the basis of odor emission rates, topography and meteorological data. Regarding odor quantification using customized electronic noses, Naddeo et al. used an array of 12 not-specific MOS gas sensors (TGS, Figaro), two specific and two ambient sensors (humidity and temperature) in a patented (SeedOA) solution using linear discriminant analysis and partial least square regression. E-nose measurements were perfectly correlated with dynamic olfactometry with $R^2 = 0.987$ [93]. Stuetz et al., compared the response of a polypirrole based sensor array to odor concentration (Neotronics nose model D) in a sewage treatment plant, in order to linearly correlate a reduced set of sensor's responses to the odor concentration in sampled bags. The best correlation was achieved at OCs below 4000 ou/m^3 indicating a tendency of the polypirrole sensors to saturate at higher concentrations but again with high variances. Moreover the correlations were found to be strongly site-specific, therefore not universally applicable to all the sewage works as correlations were better in each plant separately and in concentration ranges between 125 and 781,066 ou/m^3 [94]. Bundy et al., used dynamic dilution triangular forced-choice olfactometry, an AromaScan A32S electronic Nose (composed of thirty-two semi-conducting polypyrrole sensors) and SPME-GC/MS to identify and quantify odorous compounds in air samples collected in Tedlar bags from two environmentally controlled, mechanically ventilated feeding rooms in which six pigs were housed [95]. The following VOCs were detected: Acetic acid, 3-methylphenol, Propionic acid, 4-ethylphenol, Isobutyric acid, 3-ethylphenol, Butyric acid, 2,6-bis (1,1-dimethylethyl phenol), Isovaleric acid, Indole, Valeric acid, 3-methylindole, Phenol, 2-methylindole, 4-methylphenol, 4-methylindole. Correlation between odor concentration measured by olfactometry and VOC concentrations was poor, although panelists with the greatest standard error were removed (the best correlations were 3-methylphenol ($r = 0.23$), 2,6-bis (1,1-dimethylethyl) phenol ($r = 0.14$), 4-methylphenol ($r = 0.12$), and indole ($r = 0.11$)). This evidence means that the selected VOCs were not sufficient and additional analytes were needed or that GC-O was more appropriate. The electronic noses classification capabilities revealed a lack of clustering on the PCA biplot among air samples taken from the rooms of housing pigs fed with three different diets. The electronic nose regression capabilities were poor as the first principal component for the response of the 32 electronic nose sensors was correlated to the olfactometry with $r = 0.18$. Deshmukh et al. used a customized electronic nose composed of seven MOS not-specific sensors and one CO dedicated sensor for quantitative determination of sulfur volatiles emitted by pulp and paper facilities [96]. The sensor's signals were used to predict odor concentration by using a singular value decomposition-based technique to generate an overall index of the sensor's response, the "e-nose index", to reduce dimensionality of the system and noise. The same concentrations were exposed to panelists to evaluate odor intensity using the ASTM Standard E-544 odor intensity referring scale (expressed in terms of methyl mercaptan equivalents). The output of the panelists correlated well with the "e-nose index" and followed the Weber-Fechner law

(2). Samples from industrial sites were chemically analyzed using gas chromatography with flame photometry detection (GC-FPD) to evaluate the concentration of four selected sulfur volatiles (methyl mercaptan, H_2S, dimethyl-sulphide, dimethyl-disulphide) and with a response surface methodology. Four different second order polynomial empirical models were obtained to predict odor concentration from 8 sensor's signals, with R^2 above 0.97 and $p < 0.0001$. Another synergistic approach has been applied in a waste landfill plant. GC/MS-O was used with the purpose to identify odors emitted during the handling of wastes with soil, dynamic olfactometry to estimate emission rates of the sources and electronic noses with different technologies (MOS and polymer/black carbon nano-composite array) to compare the most used sensors available in the market. The two different technologies employed in each nose, the MOS and the polymer/black carbon Nano-composite array, may reach better discrimination capabilities when used together. This suggests that the future construction of more heterogeneous array using different sensors based on different technologies will provide higher performances in odor discrimination and quantification [5]. Capelli et al. demonstrated that there was no correlation between the chemical composition of the air samples collected on a landfill site and the correspondent dynamic olfactometry odor concentration, but chemical analyses revealed its usefulness in evaluating odor composition towards the design of intervention and abatement strategies; moreover, electronic noses placed in three strategical sites allowed to quantify the percentage of time in which the presence of odors is perceived at the landfill boundaries and at a receptor located 2 km far apart from the landfill, also in the case the legal limits were not exceeded [89].

9. Conclusions

Over the last decades, the growing interest of scientific community in odor research field has been addressed to: a) develop advanced and innovative methodological approaches for the monitoring and detection of odors active compounds in several matrices; b) identify the chemical compound responsible of olfactive stimulus; c) identify the finger print of different odor emission sources (landfills, composting plants, urban wastewater treatment plants, fragrance, food); d) evaluate the odor impact on the quality of human life and environment; e) evaluate of efficiency of malodor abatement systems and f) improve for marketing purposes, the aroma profile of food and beverage and the odor profile of perfumes. Combined sensory-instrumental methodologies such as Gas Chromatography/Mass Spectrometry- Olfactometry (GC/MS-O) and Multi-Dimensional Gas Chromatography/Mass Spectrometry-Olfactometry (MDGC/MS-O), are recognized as useful tools to identify the odor active compounds and combine the instrumental information with human sensory perception. Although many efforts have been made in order to evaluate the contribution of individual odor active compound in complex mixtures to the overall odor perception, further research and technological development are needed. Dynamic olfactometry is the standardized methodology based on human assessors to obtain measurements of odor concentrations of gaseous complex matrices but the discrimination of each odor active compound and the evaluation of relative contributions to the overall odor concentration are not allowed. All the aforementioned analytical and sensory techniques are time-consuming and quite expensive, therefore, especially when high temporal resolution and in situ monitoring of odors is required, the application of a cheapest approach with low cost devices (e.g. electronic noses) is to be preferred with respect to chemical and olfactometric analysis. Summarizing, an exhaustive and overall evaluation of perception and chemical characterization of odor active compounds is possible only by the integration of different analytical and sensorial methodological approaches. Such synergistic approach is with no doubt the best way to identify odors for food quality purposes, to manage malodor emissions in industrial plants and eventually to develop a cheap and reliable monitoring system.

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