

## Chapter 9

# Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance in Vicinity of Municipal Landfills and Sewage Treatment

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### ABSTRACT

*This chapter contains information about application of the electronic nose type instruments to evaluation of ambient air odour quality connected with such sectors of human activity as municipal landfills or sewage treatment plants. The authors present potential sources of emission from these sectors, characterize the chemical compounds responsible for presence of unpleasant odours, describe the influence of those compounds on human health and related discomfort. Legal aspects pertaining to admissible odour concentration levels in selected countries are also presented. The chapter describes instrumental and sensory methods utilized for determination of odour concentration, odour intensity, or hedonic quality. The chemical sensors potentially and currently employed in the electronic nose type devices are also characterized. Moreover, the future prospects of application of the electronic nose instruments to evaluation of ambient air with respect to odour nuisance are discussed.*

## INTRODUCTION

Progress in economic and industrial development significantly contributes to increased emission of pollutants to ambient air. Industrial plants, such as production plants, refineries, meat processing plants, breweries and distilleries, agricultural plants, metallurgical industry, and municipal plants: landfills, sewage treatment plants and solid waste processing plants generate significant amount of environmentally hazardous pollutants characterized by different physical and chemical properties. Such situation occurs despite widespread implementation of modern technologies in the aforementioned plants aimed at limitation of malodorous substances emission to the environment. Negative impact of these compounds can result from both intrinsic properties of individual chemicals as well as synergistic amplification of hazardous properties of various interacting chemical compounds (Byliński, Lewkowska, Gębicki, Dymerski, & Namieśnik, 2016). In some cases individual substances reveal small impact on particular elements of biotic and abiotic environment, nevertheless, their influence can significantly increase upon presence of other, interacting compounds. Among many different chemical compounds the odours (odorous compounds) play a significant role. The odours are volatile chemical organic and inorganic compounds sensed by animals and humans via olfactory receptors at very low concentrations and identified by brain as unpleasant sensations. The compounds characterized by unpleasant odour include:

- **Inorganic Compounds:** Hydrogen sulphide, ammonia, Sulphur dioxide, nitrogen oxide, hydrogen fluoride and hydrogen arsenide,
- **Organic Compounds:** Thiols, sulphides and disulphides, amines, carboxylic acids, aldehydes, ketones, aromatic hydrocarbons.

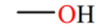
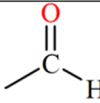
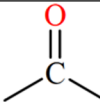
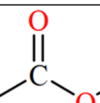
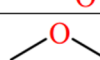
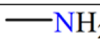



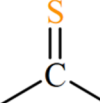

General definition identifies the odour as an individual chemical compound or a mixture of chemical compounds containing osmophoric groups in their structure. Table 1 presents the exemplary osmophoric groups and names of the chemical compounds containing these groups.

Reduction of emission of the odorous compounds becomes a priority for these fields of industry, which are responsible for their emission to ambient air. This reduction can consist in:

- Prevention of odorous compounds emission,
- Implementation of deodorization systems in already existing plants,
- Appropriate design and location of new-built facilities.

Irrespective of applied technology resulting in limitation of odours emission it is necessary to check (monitor) effectiveness of deodorization via measurement of odour intensity or odour concentration at inlet and outlet of an installation. One of the most popular methods of odour measurement, apart from olfactometric techniques, are instrumental techniques including electronic nose method. This technique, similarly to the olfactometric methods, utilizes holistic analysis without a need for identification of particular components contributing to a resultant odour. It belongs to a group of dynamically developing instrumental techniques and is more and more frequently employed to monitoring of unpleasant odours originating from different fields of human activity.

Table 1. Exemplary osmophoric groups

Osmophoric group	Chemical compounds
	Alcohols
	Aldehydes
	Ketones
	Esters
	Ethers
	Amines
	Sulfides
	Disulfides
	Thiols
	Thioketones
	Aromatic heterocyclic compounds

## CHARACTERISTICS OF DEODORIZATION METHODS FOR GASES CONTAINING ODOROUS POLLUTANTS

Odour nuisance in a vicinity of residential areas and increasing social awareness impose a pressure on companies and industrial entities forcing them to undertake more and more efficient steps towards minimization (or elimination) of the effects of their activity connected with emission of malodorous substances. As far as the new-built facilities are concerned the prevention of malodorous substances emission should be taken into account already upon selection of technology and design of process devices. In case of the existing plants all available technological modifications should be employed.

Deodorization of the gases polluted with the odorous compounds can consist in:

- Removal of malodorous pollutants (often present at the trace levels),
- Transformation of malodorous pollutants into odourless chemical compounds or the compounds characterized by high threshold of odour sensing,

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- Introduction of additives changing the character of odour or decreasing its intensity of hedonic quality (masking compounds).

Selection of the most effective deodorization method is difficult and dependent on many factors including: emission intensity, total content of pollutants, odour character of emitted gases. General characteristics of the most popular gas deodorization methods together with the characteristics of their advantages and disadvantages is shown in Table 2.

Most literature data and information concerning the number of complaints on odour quality of ambient air point to the following fields of human activity as the ones having the biggest impact:

- Municipal economy,
- Agriculture,
- Industry.

Table 3 presents a list of municipal and industrial facilities constituting the potential sources of odours (Gebicki, 2016).

The most onerous sectors of human activity with respect to odour emission are: municipal landfills and sewage treatment plants.

*Table 2. Advantages and disadvantages of the most frequently used gas deodorization technologies and mean efficiency of removal of malodorous pollutants using different deodorization techniques*

<b>Deodorization Technologies</b>	<b>Disadvantages</b>	<b>Advantages</b>	<b>Mean Efficiency of Odour Removal</b>
Absorption	<ul style="list-style-type: none"> <li>• problem of absorbent regeneration or disposal remains</li> <li>• possible secondary emissions whose source is used absorbent</li> <li>• high costs of pumping</li> <li>• further stages of gas treatment are often required</li> </ul>	<ul style="list-style-type: none"> <li>• low operating costs</li> <li>• treatment of gases containing high odourant concentrations</li> <li>• possibility of recovery of adsorbed compounds</li> </ul>	50 – 75%
Adsorption	<ul style="list-style-type: none"> <li>• problem of adsorbent regeneration or disposal</li> <li>• necessary to regenerate a deposit using large amounts of gases (subsequent dilution of pollutants)</li> <li>• possible secondary emissions whose source is used adsorbent</li> </ul>	possibility of recovery of adsorbed compounds	> 90%
Thermal neutralization	<ul style="list-style-type: none"> <li>• a high content of inflammable pollutants is required</li> <li>• generation of secondary pollutants</li> <li>• high energy consumption of the process</li> </ul>	<ul style="list-style-type: none"> <li>• ensures high effectiveness of deodorization</li> <li>• waste-free process</li> <li>• simple design and operation of the installation</li> </ul>	> 95%
Biological gas treatment	<ul style="list-style-type: none"> <li>• treated gases must contain biodegradable components</li> <li>• problem with an excessive amount of biomass - installation overgrowth</li> <li>• for biofiltration - a large surface area of the installation</li> </ul>	<ul style="list-style-type: none"> <li>• low operating costs</li> <li>• high effectiveness when biological material is well selected</li> <li>• possible to treat gases with low odourant concentrations</li> </ul>	90%

*Table 3. List of exemplary economy sectors coupled with potential emission sources and types of emitted odours*

Type of Object or Installation	Emitted Odorous Substances	Potential Source of Odour Emission
animal breeding: animal farms, poultry houses	organic acids, ammonia, phenols, sulphur compounds, toluene	improper management of waste and liquid manure, lack of hermetization and deodorization
chemical and petroleum industry, production of paints, lacquers, solvents, processing of crude oil	hydrocarbons, sulphur compounds, nitrogen compounds, aldehydes	water-waste management, failures of installations, transport and storage
dairies (depending on production magnitude)	ammonia, sulphur compounds	leaks in ammonia cooling installations, improper waste management (high tendency of dairy waste to fast fermentation)
municipal waste management objects: landfills, screening plants and composting plants	ammonia, sulphur compounds	anaerobic processes, lack of appropriate hermetization
processing of meat and fish	ammonia, nitrogen oxides, hydrogen sulphide, phenols, aldehydes	collection and storage of raw material, preparation of raw material, composting, smoking, production of meat-and-bone meal
sewage treatment plants: biological, mechanical	sulphur compounds, nitrogen compounds, aldehydes, ketones	anaerobic operation, preliminary operations, for example collection of sewage, drain points
animal breeding: animal farms, poultry houses	organic acids, ammonia, phenols, sulphur compounds, toluene	improper management of waste and liquid manure, lack of hermetization and deodorization

## CHARACTERISTICS OF MALODOROUS POLLUTANTS EMISSION SOURCES IN MUNICIPAL LANDFILLS AND SEWAGE TREATMENT PLANTS

Landfill is a bioreactor, in which microbiological and biochemical transformations occur due to atmospheric factors and microorganisms activity (Figure 1). Initial decomposition of waste is an aerobic process as just after waste disposal there are air pockets inside the landfill. Soon after the decomposition onset all oxygen is consumed and an anaerobic process starts as fresh oxygen supply to the landfill is impossible. Anaerobic decay of organic waste can be simplified to two fundamental processes, although it must be emphasized that biochemistry of microbe processes is very complicated. In the first stage complex organic substances are biodegraded to simple organic substances including acetic acid ( $\text{CH}_3\text{COOH}$ ), propionic acid ( $\text{C}_2\text{H}_5\text{COOH}$ ), pyropropionic acid ( $\text{CH}_3\text{COCOOH}$ ) or other simple organic acids and alcohols. Bacteria take part in the process and the chemical reactions provide them with the energy necessary for development; certain amount of organic waste is transformed into cellular and extracellular substances. The second stage of anaerobic decay is methanogenesis. Methanogenic bacteria consume the products of the first stage and produce oxygen as well as carbon dioxide. Oxygen, which forms carbon dioxide originates from the organic substrates or from sulphate ions. The methanogenic bacteria prefer neutral pH and they avoid acidic environment. Formation of acids in the first stage reduces pH and if this process continues, activity of the methanogenic bacteria can cease. Municipal landfills are the significant emission sources of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) and for these compounds exceeding of the threshold values defined in the Regulation (EC) No. 166/2006 of the European Parliament and Council



of 18 January 2006 on establishment of a European Pollutant Release and Transfer Register is the most probable. Moreover, there could be emission of smaller amount of non-methane volatile organic compounds (NMVOC), dinitrogen monoxide ( $N_2O$ ), carbon monoxide (CO) ammonia ( $NH_3$ ), Sulphur oxides ( $SO_x$ ) and nitrogen oxides ( $NO_x$ ). Additionally, unloading and planting of waste as well as operation of the machines and vehicles on the landfill constitute sources of dust (PM) emission. It is obvious that odour of the products of aerobic degradation of organic compounds is less onerous than the odour of the products of anaerobic denitrification and desulphurization.

In the case of sewage treatment plants three basic sources of emission can be distinguished depending on the plant type (Figure 2):

- Sewage feed and its mechanical treatment,
- Biological treatment,
- Sludge processing.

Highly onerous anaerobic processes usually occur in the sewage feed and sludge processing zones. Composition and odour of gas mixture mainly depends on biodegradation conditions deciding about the type of bacteria participating in the process. The most important parameter is sewage aeration degree – it is necessary to prevent oxygen shortage and anaerobic bacteria development.

Emission of air pollutants from particular sources of the sewage treatment plants, which can have influence on odour nuisance over the adjacent areas, is presented in Figure 3. Emitted odorous compounds engulf: organic compounds of sulphur, indoles, skatoles, organic acids, aldehydes and ketones.

*Figure 1. An example scheme for the construction of a municipal landfill*

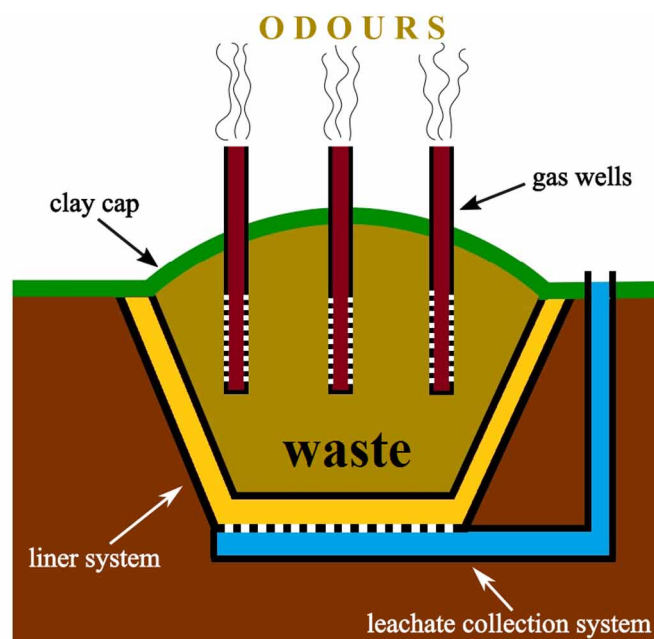


Figure 2. An example scheme for the construction of a wastewater treatment plant

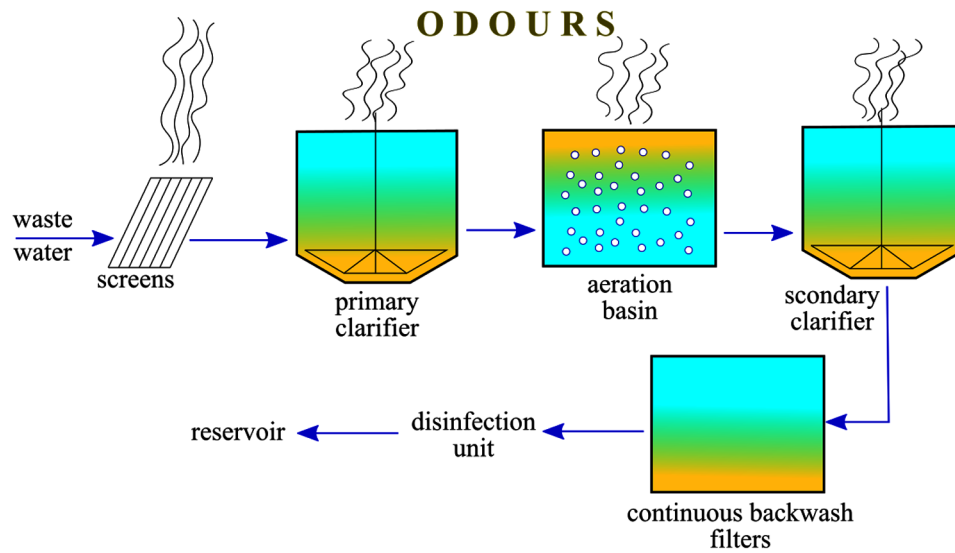
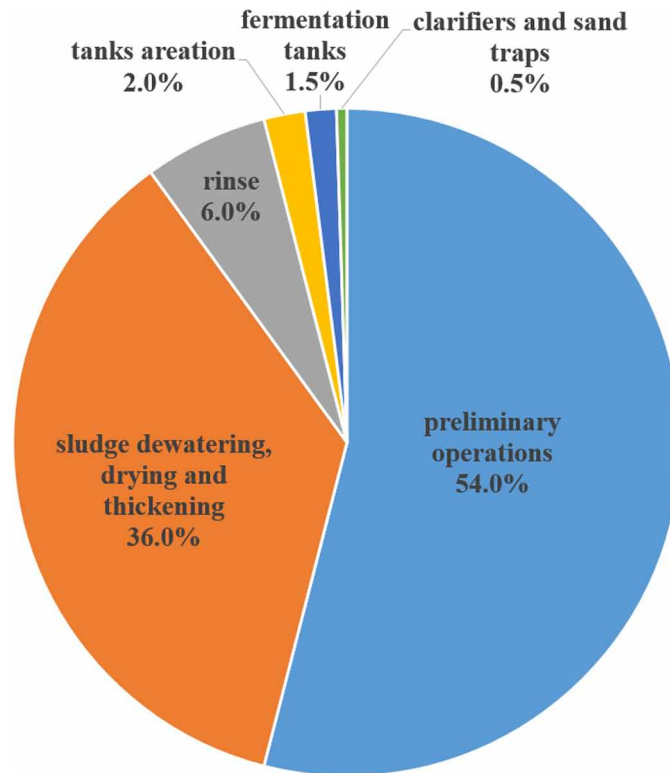


Figure 3. Average percentage distribution of odour emission sources from a sewage treatment plant



## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

In Table 4 collects the information about odour sensing thresholds and smell sensations associated with selected chemical compounds emitted from municipal landfills and sewage treatment plants (Czerny et al., 2008; Fang et al., 2012; Gebicki, 2016; Hansen, Jonassen, & Feilberg, 2014; Lehtinen & Veijanen, 2011; Nagata, 2003; Talaiekhosani, Bagheri, Goli, & Talaei Khoozani, 2016; Wenjing et al., 2015; Zhu, Chen, Wang, Niu, & Xiao, 2017).

Table 4. Odours thresholds and smell sensations for chemical compounds emitted from landfills and sewage treatment plants

Compound	Kind of Fragrance	Odour Threshold [ppm]
acetaldehyde	fresh	$6.0 \times 10^{-3}$ – $1.5 \times 10^{-3}$
acetone	pungent	$4.0 \times 10^{-1}$ – $4.2 \times 10^1$
acetonitrile	ethereal	$1.3 \times 10^1$
acrolein	pungent	$3.6 \times 10^{-3}$
acrylonitrile	suffocating	1.6 - 8.8
ammonia	characteristic	$1.0 - 1.7 \times 10^1$
benzaldehyde	almond	$3.5 \times 10^{-1}$
benzene	characteristic	$4.7 \times 10^{-1} - 2.7$
benzyl mercaptan	garlic	$1.9 \times 10^{-4}$
butanone	pungent, sweet	$1.0 \times 10^1$
butyl acetate	pear	$5.8 \times 10^1$
butyric acid	sweet	$1.9 \times 10^{-4}$
carbon disulfide	sweet, pleasant	$8.1 \times 10^{-3}$ – $2.1 \times 10^{-1}$
carbonyl sulfide	unpleasant	$5.5 \times 10^{-2}$
diacetyl	chloric	$5.0 \times 10^{-5}$
diehylamine	ammonia	$4.8 \times 10^{-2}$
dimethyl sulfide	rotten	$1.0 \times 10^{-4} - 0.5$
dimethyl trisulfide	cabbage	$1.9 \times 10^{-3}$
dimethylamine	fish	$3.4 \times 10^{-1}$
ethanethiol	garlic	$8.7 \times 10^{-6}$ – $1.9 \times 10^{-4}$
ethanol	alcoholic	$5.2 \times 10^{-1}$
ethyl acetate	fruit, pleasant	$8.7 \times 10^{-1}$ – $6.2 \times 10^3$
ethyl formate	fruit	2.7
ethylamine	ammonia	$4.6 \times 10^{-2}$
ethylbenzene	aromatic, sweet	$3.0 \times 10^{-3}$ – $1.7 \times 10^{-1}$
formaldehyde	suffocating	$5.0 \times 10^{-1}$
furan	chloroform	9.9
hexanoic acid	sweet, cheesy	1.8
heptanal	pungent	$1.3 \times 10^{-3}$ – $5.5 \times 10^{-1}$
heptanoic acid	sour	3.0
hexanal	mown grass	$4.5 \times 10^{-3}$ – $6.8 \times 10^{-3}$
hydrogen sulfide	rotten eggs	$4.1 \times 10^{-4}$ – $5.0 \times 10^{-4}$

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## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

Table 4. Continued

Compound	Kind of Fragrance	Odour Threshold [ppm]
indole	smell of feces	$3.0 \times 10^{-4}$
isopropyl alcohol	alcoholic	1.0
isopropylamine	ammonia	$2.5 \times 10^{-2}$
limonene	citrus	$1.8 \times 10^{-3}$ – $3.8 \times 10^{-2}$
m-cresol	unpleasant, pungent	$1.0 \times 10^{-4}$
methanethiol	rotten cabbage	$7.0 \times 10^{-5}$ – $1.1 \times 10^{-3}$
methanol	alcoholic	$3.3 \times 10^1$ – $1.0 \times 10^2$
methyl formate	pleasant	$1.3 \times 10^2$
methyl methacrylate	fruit	$2.1 \times 10^{-1}$
methylamine	fish	$3.5 \times 10^{-2}$ –4.7
m-xylene	pleasant	$4.1 \times 10^{-2}$
naphthalene	characteristic	$2.7 \times 10^{-2}$ – $3.8 \times 10^{-2}$
n-butane	solvent	$3.8 \times 10^{-2}$
n-heptane alcohol	characteristic	$4.8 \times 10^{-3}$
n-hexane alcohol	fruit	$6.0 \times 10^{-3}$
n-octane alcohol	unpleasant	$2.7 \times 10^{-3}$
n-pentane alcohol	fruit	$1.0 \times 10^{-1}$
o-cresol	unpleasant, pungent	$2.8 \times 10^{-4}$
octanal	citrus	0.1–1.2
octanoic acid	sweet, cheesy	1.9
o-xylene	pleasant	$8.1 \times 10^{-2}$ – $3.8 \times 10^{-1}$
p-cresol	unpleasant, pungent	$5.4 \times 10^{-5}$
phenol	characteristic	$5.6 \times 10^{-3}$
propanethiol	cabbage	$1.5 \times 10^{-5}$
propionaldehyde	pungent	$8.1 \times 10^1$
propionic acid	pungent, unpleasant	$5.7 \times 10^{-3}$
propyl acetate	pear	$2.4 \times 10^{-1}$
propyl foramate	rum-plum	$9.6 \times 10^{-1}$
p-xylene	pleasant	$5.8 \times 10^{-2}$ – $8.1 \times 10^{-2}$
pyridine	characteristic	$6.3 \times 10^{-2}$
skatole	smell of feces	$5.6 \times 10^{-6}$
styrene	unpleasant	$3.5 \times 10^{-2}$ – $4.7 \times 10^{-2}$
sulphur dioxide	suffocating	$9.0 \times 10^{-3}$ – 2.7
toluene	pleasant, intense	$2.1 \times 10^{-2}$ – 2.8
triethylamine	fish	$5.4 \times 10^{-3}$
trimethylamine	characteristic	$3.2 \times 10^{-5}$
valeric acid	honey	$3.7 \times 10^{-5}$
$\alpha$ -pinene	fir	$2.9 \times 10^{-3}$ – $9.0 \times 10^{-1}$
$\beta$ -pinene	pine	$3.3 \times 10^{-2}$

## **INFLUENCE OF ODOROUS COMPOUNDS ON HUMAN HEALTH AND ENVIRONMENT**

Negative impact of odours is most frequently a derivative of their subjective perception and their action consist in destructive influence on human psyche. This can result in appearance or intensification of somatic system malfunction. Hence, while speaking about odour nuisance one should discriminate between toxic effects and the effects caused by odour properties. Biological effects, resulting exclusively from odour nuisance, will trigger physiological changes at most, but without fatal implications, which can be caused by toxic substances.

Odours can induce a number of negative effects including (Nicell, 2009):

- Deterioration of natural environment quality,
- Damages to properties, fauna and flora,
- Discomfort,
- Deterioration of life safety and quality,
- Loss of normal ability to utilize real estate,
- Disturbances in normal business activity.

Odours can trigger a number of unwanted reactions in humans, from aggravation to documented health problems. In the societies exposed to odours emission the health problems connected with odour impact may not be evident immediately, however there can be morbidities or physical as well as mental handicap. Moreover, long-term exposure to odour can result in undesirable emotional reactions such as anxiety, feeling of discomfort, depression as well as physical symptoms including irritation, headache, respiratory track problems, nausea, vomiting . Exposure to unwanted odours can also lead to mental tension and caused such symptoms as insomnia, lack of appetite and irrational behaviour. High levels of odorants can be a source of acute toxicological symptoms and they can trigger the mechanisms connected with reaction of the organism to odour. These mechanisms can include intrinsic reluctance with respect to odour, heightening of fundamental conditions connected with odour perception (hypersensitivity), stress-induced diseases or even psychogenic diseases . Other identified odour influence of on human engulf: difficulties breathing, frustration, stress, increased tendency to cry, reduction of appetite and/or difficulties with consumption and preparation of meals, feeling of discomfort at night (difficulties with falling asleep, restless sleep) (Capelli, Sironi, Del Rosso, & Centola, 2009; Trincavelli, Coradeschi, & Loutfi, 2009). High complexity of odour nuisance problem is evidenced by numerous complaints of the residents from the regions located in direct vicinity of the main emitters of air pollutants. Every year the number of complaints on malodorous compounds presence in ambient air increases (for instance in Poland the number of complaints doubled during the period of 5 years). The number of complaints connected with odour nuisance in highly developed or developing countries also rises. The most important elements deciding about a degree of nuisance are: odour concentration, odour hedonic quality, frequency of unpleasant smell sensation occurrence and perceived odour intensity. Combination of those four properties of odour creates a complete image associated with presence of odour in ambient air. Each of these elements plays a significant role in perception of the entire phenomenon. An increase in odour concentration is connected with stronger smell sensations occurring upon presence in a vicinity of an emission source; odour hedonic quality influences on connotations related to perception of particular substance (most often a gas mixture of odorous compounds); frequency of unpleasant smell sensation

occurrence determines frequency of increased odours emission situation; odour intensity described 'strength of perceived odour'.

## **LEGAL REGULATIONS AND LIMIT VALUES OF ODOUR CONCENTRATION IN SELECTED COUNTRIES**

Due to odour impact of industrial, agricultural or municipal facilities and nuisance connected with odours emission the legislative bodies of highly developed countries face the problem of admissible emission of odorous pollutants within the frame of health and environmental protection programmes. So far suitable legal acts have been established in industry and agriculture as well as in other branches of economy in Germany, France, the Netherlands, the Great Britain, Japan, the USA and Canada. Introduction of universal measurement method in Europe according to the standard PN-EN 13725:2007 makes it necessary to define odour concentration and odour unit. Odour concentration is defined as the concentration, for which given person is able to sense single odorous substance – it is called individual (for particular person) detection threshold for given substance. Hence, the detection threshold of odour must be averaged value representative for a population (population detection threshold). The detection threshold is such concentration of the odorant, which causes smell sensation in half of the population (or representative group) exposed to odour impact. For individual substances the odour concentration will be equal to a quotient of odorant concentration and threshold concentration. In the case of odorous substances mixtures it is not possible to define odour concentration in a similar way because it is impossible to determine the detection threshold. Then the odour concentration cod can be defined as multiplicity of dilution of investigated sample (with clean, odourless air) necessary to achieve the detection threshold. In Table 5 presents the examples of admissible odour concentration accepted in different countries (Hung, Wang, & Shamma, 2012; Mahin, 2001; Naddeo, Zarra, Giuliani, & Belgiorno, 2012; Nicell, 2009; Ritvay & Kovács, 2006).

## **INSTRUMENTAL AND SENSORY METHODS UTILIZED FOR DETERMINATION OF ODOUR CONCENTRATION, ODOUR INTENSITY AND HEDONIC QUALITY**

General classification of the techniques employed for ambient air quality evaluation with respect to odour distinguishes two fundamental approaches:

- Analytical (instrumental techniques),
- Sensory.

The sensory techniques, including most frequently applied dynamic olfactometry and field olfactometry, allow determination of summary concentration of the odorous substances present in an investigated sample, odour intensity and its hedonic quality. In case of these techniques human nose plays the role of 'measurement sensor'. Dynamic olfactometry is one of the most common solutions in the field of sensory techniques, which makes it possible to determine odour concentration expressed in European odour units per cubic meter ( $ou_e/m^3$ ) (Figure 4). Concentration expressed in this way describes a degree of dilution of gaseous odorous sample with a stream of odourless air, which is necessary to achieve so-called detection

*Table 5. Examples of acceptable odours values accepted in different countries*

Country	Acceptable Odour Value (ou <sub>e</sub> /m <sup>3</sup> )	Averaging Time (min.)
Germany	1	60
France	5	60
Italy	1-5	60
Denmark	5-10	60
Netherlands	0.5-3.5	60
Hungary	3-5	60
Great Britain	5	1
Ireland	3-6	60
Norway	5-10	60
Australia	2-10	3-60
United States of America	1-20	< 5
China	5	5 s
Japan	< 5	no data
Korea	< 2	no data
New Zealand	2	60
Taiwan	50	no data
Tasmania	1	3

threshold. Detailed information about the methodology of determination of odour concentration with dynamic olfactometry technique are provided in the European standard EN 13725:2003: 'Air quality. Determination of odour concentration by dynamic olfactometry'. This document constitutes the only example of unified legal regulation concerning the methodology of air quality investigation with respect to odour properties. Nowadays the technique of dynamic olfactometry is commonly used for identification of odorous compounds emission sources and assessment of emission level.

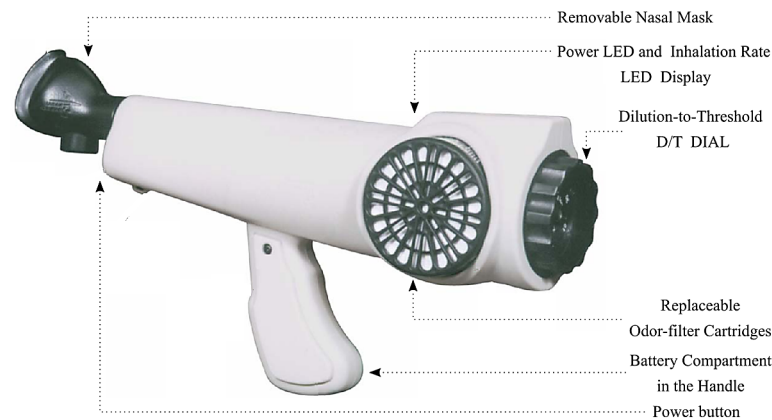
However, in some cases this solution does not provide satisfactory results, for example in the case of low concentrations. Another limitation of dynamic olfactometry technique is a necessity of samples collection and their transport to laboratory, which increases the time of single analysis and has a negative impact on the results due to a risk of partial loss of analytes that can undergo adsorption processes inside a bag. It is difficult to determine odour concentration, especially in case of variability of emission over particular area. Then more convenient solution seems field olfactometry technique. Such approach allows characterization of properties of the odorants present in ambient air as a result of dilution of investigated air stream with odourless gas (typically air purified on carbon filters). The most popular device used in olfactometric measurements is a field olfactometer Nasal Ranger (St. Croix Sensory, USA), the scheme of which is presented in Figure 5.

This instrument is comprised of two replaceable filters made of active carbon, a valve adjusting flow rate of non-purified air (thus containing odorous compounds), replaceable mask for air inhalation via the olfactometer and a sensor allowing control over the flow rate of gas stream passing through the device, the value of which should be less than 20 dm<sup>3</sup>/ml. The adjusting valve offers selection of one of six available levels of dilution of inhaled air: 60, 30, 15, 7, 4, 2. There is a possibility to take advantage of an

Figure 4. Example of a dynamic olfactometer



Figure 5. Scheme of Nasal Ranger field olfactometer



additional valve for higher concentration of odorants in air, which enables to obtain higher dilution. This valve provides the following values of dilution: 600, 500, 400, 300, 200, 100. Moreover, each available valve possesses 'blank' position (air passes only through the filters so the air inhaled by an assessor is purified and free from pollutants, thus also from odorous compounds). Accuracy and repeatability of the field olfactometer are  $\pm 10\%$  and  $\pm 5\%$ , respectively (Kośmider & Krajewska, 2007).

Application of the field olfactometers allows identification of the point sources of odours emission, which reveal the highest sensory nuisance over the regions neighbouring with the most important emitters of odorous air pollutants. The olfactometers can be used as both the measurement devices as well as the instruments for verification of the complaints about the odour nuisance over the areas in a vicinity of potential emitters of odorous compounds. In olfactometric measurements the assessors are expected to determine the ratio of purified air passed through the filters to non-purified air by-passing the filters

(D/T – Dilution to Threshold), which corresponds to the first moment when the odour of diluted air is sensed. Based on the D/T values it is possible to calculate individual odour concentration using the following formulas:

$$Z_{yes} = \left( \frac{D}{T} \right)_{yes} + 1$$

where:

$Z_{yes}$  = dilution ratio, at which the odour became perceptible,

$(D/T)_{yes}$  = dilution ratio corresponding to the moment when the odour became perceptible for the first time,

$$Z_{no} = \left( \frac{D}{T} \right)_{no} + 1$$

where:

$Z_{no}$  = dilution ratio, at which the odour was imperceptible,

$(D/T)_{no}$  = dilution ratio corresponding to the moment when the odour was imperceptible just before the dilution  $(D/T)_{yes}$

$$Z_{ITE} = \sqrt{Z_{yes} \times Z_{no}}$$

where:

$Z_{ITE}$  = individual odour threshold estimate.

Values of odour concentration are calculated as geometric mean from n-element set of all individual estimates for particular measurement point using the formula:

$$c_{od} = \sqrt[n]{\sum_{i=1}^n Z_{ITE,i}}$$

where:

$c_{od}$  = value of odour concentration [ou/m<sup>3</sup>],

n = number of all individual estimates.

Application of field olfactometry technique allows direct control over emission of odorous compounds released from different types of industrial and municipal facilities. Such investigations can contribute to verification of correct operation of production plants as far as amount of odours emitted during a single production cycles is concerned. Field olfactometry exhibits many advantages including relatively

low cost of equipment (much cheaper than dynamic olfactometers), simple operation and possibility to determine odour intensity upon imission. The most significant drawbacks of this technique engulf lack of legal regulation, which would clearly define the conditions pertaining to assessors selection for the investigation, the way of measurements execution and the interpretation of obtained results. There are two dominant approaches in instrumental analysis of odorous samples. The first one consists in identification of volatile odorous compounds contained in the sample using gas chromatography (GC) couple with a suitable detector, the second one is based on 'holistic' analysis of an odorous mixture without separation into individual components, which employs the electronic nose instruments (Bai & Shi, 2007; Gallego, Perales, Roca, & Guardino, 2014; Harynuk & Górecki, 2004). The chromatographic techniques, including gas chromatography mass spectrometry (GC-MS), are one of the most common solutions utilized for identification and quantitative measurement of main ambient air pollutants, including odorous compounds. The information about chemical composition of the ambient air samples taking into account sampling and analysis procedures (analyte derivatization, conditions of separation process) enable preliminary estimation of emission level of atmospheric air pollutants over the investigated region. This information can be valuable at the stage of elaboration of efficient solutions for deodorization of odorous substances. Numerical values of concentration of particular chemical compounds present in the ambient air samples make it possible to determine odour activity value (OAV). This parameter is calculated as a sum of the ratios of concentration of particular chemical compounds present in ambient air to their individual odour detection threshold following the formula:

$$OAV = \sum_{i=1}^n \frac{c_i}{OT_i}$$

OAV = Odour Activity Value [ou/m<sup>3</sup>],

c<sub>i</sub> = concentration of compound i [mg/m<sup>3</sup>],

OT<sub>i</sub> = Odour Threshold value of compound i [mg/ou].

Determination of odour activity value allows visualization of odour nuisance degree over the investigated region via calculation of odour activity values for the ambient air samples collected from different locations in given time. Correlation of the odour activity values with chemical composition of the ambient air samples (types of compounds and their concentrations) makes it possible to identify these compounds, which have the biggest contribution to strength of perceived odour. Such approach is characterized by relatively high repeatability and reproducibility of results as compared to the olfactometric techniques. However, the main drawback of this approach is a lack of possibility of holistic characterization of many important properties of odorous mixtures – odour intensity and hedonic quality, which are important from the point of view of odour nuisance. Determination of OAV parameter seems to be good complement of the results obtained with the olfactometric techniques.

The electronic nose is defined as an analytical instrument intended for the rapid detection and distinction of mixtures of odorous substances as a result of imitating the principles of operation of the human sense of smell. In the case of electronic nose, the recognition of the composition of the gaseous mixture is possible, thanks to the stimulation of all sensors making up the electronic nose. This stimulation (signal sensor) occurs in each sensor to a varying degree. As a result of such stimulation, a characteristic

collection of signals is created from single sensors, which is called the response vector. Analysis of the obtained response vector allows for classifying a given gaseous sample into the collection of previously known response vectors (during the electronic nose training process). The brains fulfil this role in a person as it compares nervous impulses obtained from the olfactory bulb to the database of odours that a person gets to know over their life. In the case of the electronic nose, the obtained response vector is assigned to the sets found in the computer database from the appropriate mathematical and statistical algorithms. Electronic noses are most often used for qualitative analysis tools; it is also possible to use electronic noses for quantitative analysis. To obtain information about quantitative nature, the following tools are used amongst other things:

- Multiple linear regression using selected features,

$$c_{od} = a_0 + \sum_{n=1}^{\infty} (a_n X_{i,t})$$

where  $X$  is the value of the  $i$ -th signal at a given measuring moment during exposure of the sensor matrix to the tested gaseous mixtures,  $a_n$  - coefficients of the model,

- Multiple linear regression using extracted features,

$$c_{od} = a_0 + \sum_{n=1}^{\infty} (a_n PC_n)$$

where  $PC_n$  is the  $n$ -th main component selected as a result of transformation of the feature vector that is the development of the entire matrix of features,

- One-dimension of non-linear regression with the use of selected features,

$$c_{od} = ab^X$$

where  $a$  and  $b$  are coefficients of the model,

- One-dimension of non-linear regression with the use of extracted features,

$$c_{od} = ab^{PC1}$$

where  $PC1$  is the first main component,  $a$  and  $b$  are coefficients of the model.

These are the simplest and the least required methods for solving the problem of determining the olfactory concentration using the electronic nose; however, the most frequent olfactory concentration is determined experimentally according to the following principle:



## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

- Signals from sensors are normalized and averaged according to methods specified in Table 6.
- Normalized and averaged signal is calibrated according to the reference substance (n-butanol) at various levels of concentration,
- The correctness of calibration with the use of olfactometric techniques.

At present the e-nose instruments constitute only complementary solution with respect to sensory analysis of ambient air. However, in many cases subjectivity of the assessors participating in olfactory evaluations creates many doubts. The olfactometric techniques call for an experienced team of assessors, the smell sensitivity of who can significantly change upon numerous external factors. Special laboratory equipment utilized for olfactometric evaluations significantly elevates the cost of such analysis. These problems could be eliminated by application of the devices enabling fast and cheap analysis of odorous compounds. Looking at the potential and development pace of the e-nose instruments one can expect that their role in ambient air monitoring is going to increase continuously and current reference techniques for odour concentration determination will be supplemented with the electronic nose technique. Table 7 presents comparison of the olfactometric techniques (dynamic and field olfactometry) with the electronic nose technique with respect to selected aspects of discussed solutions.

## CHARACTERISTICS OF CHEMICAL SENSORS USED FOR THE CONSTRUCTION OF THE ELECTRONIC NOSE

The level of odourant concentration in the air determines the selection of chemical sensors for their measurement. The application of single chemical sensors for air monitoring is limited due to very low odourant levels that usually occur at concentration levels of 0.1 ppb-0.1 ppm. For emission measurements or measurements similar to emissions (i.e. at a close distance from the source of emissions), the level of odourant concentrations may exceed the value of 1 ppm v/v; then we can talk about the possibility of

Table 6. Basic methods of sensor signal normalization

Method	Formula	Comments
Differential	$X(t) = x_t - x_{0,t}$	Reduction of the drift signal with an additive character
Quotient	$X(t) = \frac{x_t}{x_{0,t}}$	Reduction of the drift signal with a multiplicative character
Fractional	$X(t) = \frac{x_t - x_{0,t}}{x_{0,t}}$	Reduction of the drift signal with a multiplicative and additive character
Logarithmic	$X(t) = \log \frac{x_t}{x_{0,t}}$	Reduction beneficial in the case of a large range of concentrations

where:  $X(t)$  - the value of the sensor signal at time  $t$  after the application of normalization,  $x_t$  - the value of the detection signal at time  $t$  before normalization,  $x_{0,t}$  - the value of the sensor signal corresponding to the reference gas (clean gas).

## **Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance**

*Table 7. Comparison of electronic nose and olfactometry techniques*

<b>Properties</b>	<b>Olfactometry Techniques</b>	<b>Electronic Nose</b>
legally regulated methodology	dynamic olfactometry – yes field olfactometry - no	no
element for odour measurement	human nose	sensor matrix
team of trained assessors	necessary for investigation	no need for training of the personnel participating in investigation
repeatability of obtained results	low	high
time of single analysis	short	short
mathematical algorithm	simple	complicated
possibility to conduct field measurements	yes (as an element of portable laboratory in case of dynamic olfactory)	yes
allows measurement of low concentrations of odorous compounds	dynamic olfactometry – no field olfactometry - yes	depending on applied sensor matrix
objectiveness of obtained results	low	high
limitation of the number of performed investigations	dependent on condition of the assessors (determining factor – smell adaptation)	no significant limitations
identification of odours	lack	a need to teach e-nose to identify and discriminate particular odours
a need of samples collection	dynamic olfactometry – yes (exception – mobile laboratories); field olfactometry - no	no need of samples collection in case of utilization of continuous monitoring devices
a need of samples preparation prior to analysis	lack	lack

practical use of chemical sensors in the electronic nose design. The selection of an appropriate chemical sensor/sensors for the construction of an electronic nose, of course, depends on the ingredients that are to be detected, the expected range of concentrations, whether the presence of other ingredients of the gaseous mixture should be identified (selectivity), which could influence the reading or the possibility of damage to the sensor. If a single sensor is used, requirements for these sensors are based on the best selective detection of a specific odourant, so that it can be detected and determined quantitatively at the lowest level of concentrations. Electronic noses, which are intended for distinguishing odourant mixtures with a complex composition, can contain chemical sensors in their design that are characterized by limited selectivity, which is, of course, a flaw for single sensors that should be characterized by high selectivity. For electronic noses, this feature of chemical sensors often becomes an advantage due to the integral element of the design of these devices - i.e. a reference recognition block, which is used for analysing signals from individual sensors. As a result, the universality of electronic nose devices increases. An additional advantage of electronic noses is the possibility of performing field analyses in an on-line system around odourant emission sources, as they do not exhibit olfactory adaptation, as opposed to the human nose. It is also possible to record short-term episodes of high odourant concentrations in a given area, which may not be recorded using dynamic or field olfactometry technique. Such a situation

## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

is related to the arrival time and the time when samples are collected by qualified personnel (for field olfactometry). Table 8 and Figure 6 presents the basic and most frequent chemical sensors used in the design of electronic nose devices. Their detection range — as well as advantages and disadvantages of each type of sensor — are described.

Table 9 summarizes basic information about types of sensors available on the market and their metrological parameters and intended for measuring odorous gases such as: hydrogen sulphide, ammonia, total volatile organic compounds. The table presents only chemical sensors that are characterized by the limit of quantification below 1 ppm v/v.

### THE USE OF ELECTRONIC NOSE DEVICES FOR THE ASSESSMENT OF AIR QUALITY AROUND MUNICIPAL LANDFILLS AND SEWAGE TREATMENT PLANTS

A lot of methods for determining malodorous substances are considered to be too expensive to create commonly available measuring instruments or developed environmental monitoring systems. High hopes for the development of such systems are placed on electronic nose devices. Literature data show that odour analyses are performed more and more frequently with the use of electronic nose devices. Despite the low applicability of these devices for the monitoring of air pollution as compared with olfactometric techniques, their application is growing. The process of the appropriate selection of chemical sensors

Table 8. Comparison of chemical sensors used for the construction of electronic nose devices

Type of Sensor	Advantages	Disadvantages	Limit of Detection
Amperometric (EC)	high sensitivity, relatively good dynamic properties. Time constant of achieving 90% of response magnitude to a step change of measured gas concentration is typically shorter than 60 seconds, low energy consumption	medium selectivity, dependence of signal on operation temperature, relatively big dimensions	> 0.1 ppb
Semiconductor MOS-type	high sensitivity, low influence of temperature on sensor signal, low dependency of signal on humidity, short response time, fast regeneration, long lifetime, small, dimensions, low price	low selectivity, high operation temperature, high energy consumption, sensitivity to sulphur compounds and alcohols	> 0.1 ppm
Semiconductor CP-type	high sensitivity, short response time, high reproducibility, resistance to poisoning, relatively high selectivity, operation at ambient temperature	sensitivity to temperature and humidity changes, slow regeneration, short lifetime, signal drift, time-consuming process of controlling of this type of sensors	0.1 ppm
PID-type	limit of detection at ppb level, small size, mainly VOC detection	low selectivity, ionization only certain volatile chemical compounds, short lifetime of the lamp ionizing	1 ppb
Surface acoustic wave sensors (SAW)	low limit of detection, high sensitivity, high selectivity, good response time, diverse sensor coatings, small, inexpensive, sensitive to virtually all gases	complex circuitry, temperature sensitive, poor signal-to-noise ratio, specificity to analyte groups affected by polymeric film sensor coating	1 ppb
Quartz crystal microbalance sensor (QCM)	high selectivity, good precision, diverse range of sensor coatings, high sensitivity, short response time	complex circuitry, poor signal-to noise ratio, temperature sensitive, complicated production process precluding sensor reproducibility	> 0.1 ppm

## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

Figure 6. Chemical sensors used for the construction of electronic nose devices

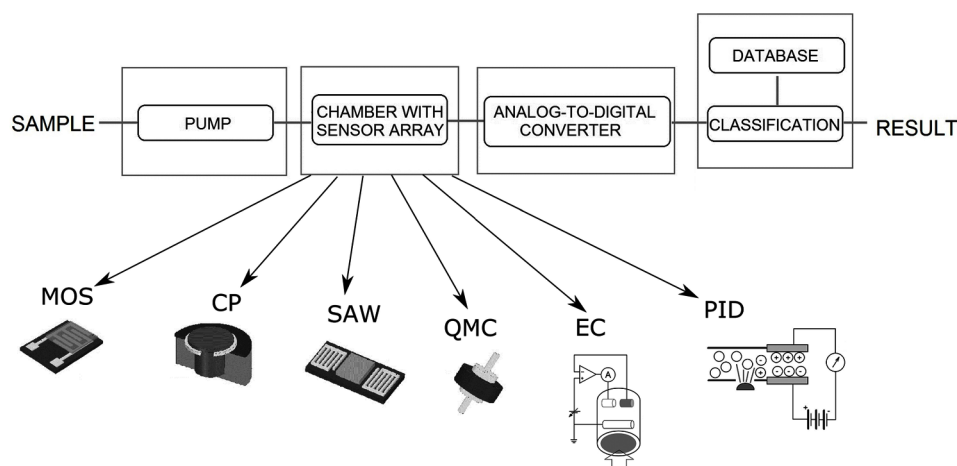


Table 9. Chemical sensors available on the market that are intended for determining odorous gases and are characterized by the limit of quantification below 1 ppm v/v

Gas	Manufacturer	Model	Sensor Type	LOD
H <sub>2</sub> S	Alphasense	H2S-B4	EC	40 ppb
H <sub>2</sub> S	Aeroqual	EHS / EHS2	MOS	40 ppb
NH <sub>3</sub>	Aeroqual	ENG	MOS	0.2 ppm
NH <sub>3</sub>	Alphasense	NH3-A1	EC	0.3 ppm
VOC	Aeroqual	VOC Sensor Head	MOS	0.1 ppm
VOC	Alphasense	PID-AH2	PID	1 ppb
VOC	Cambridge CMOS Sensors	CCS801	MOS	10 ppm
VOC	Environmental Sesnors CO	Formaldehyde Monitor Z-300	EC	0.1 ppm
VOC	ION Science	MiniPID	PID	5 ppb
VOC	Mocon Baseline Series	10.6, 10.0, 9.6 eV Photoionization Sensor	PID	1-250 ppb
VOC	Unietc SRL	SENS-IT (TF-MOS)	MOS	0.1 ppm
VOC	Unietc SRL	SENS-IT (EC)	EC	0.6 ppb

and the data analysis method allows for using electronic noses for tests of the quality of air polluted with odorous compounds of various origins. One of the main advantages of these devices is the possibility of skipping the first stage of preparing samples for the analysis and the possibility of their field use as a portable unit to monitor emission sources in real time. Table 10 contains information using exemplary applications of electronic nose devices for controlling and assessing air quality about odour emission sources such as landfills and sewage treatment plants. This table presents information about the type of electronic nose used, the chemical sensors it contains and the data analysis method used.

*Table 10. Examples of the use of electronic nose devices for the assessment of air quality around municipal landfills and sewage treatment plants*

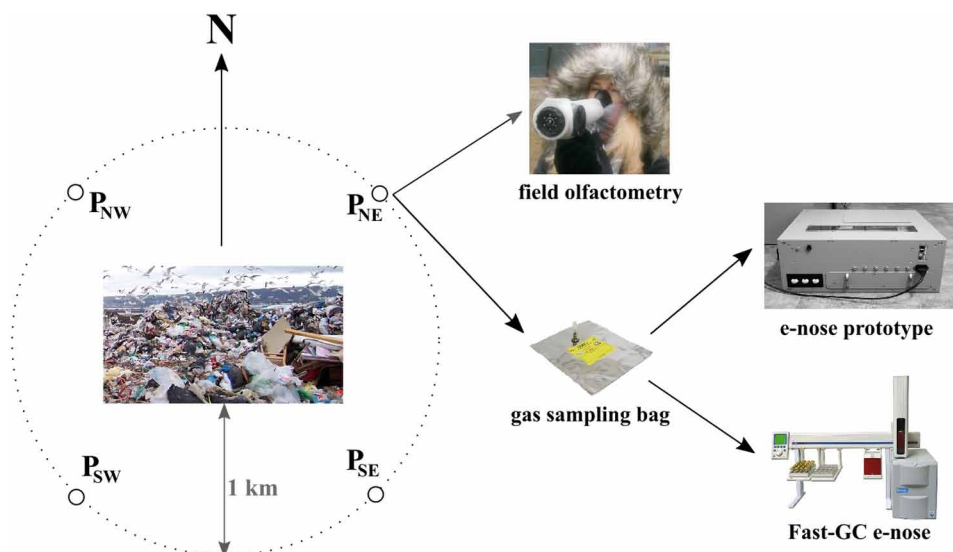
Source of Malodours	Type of Sensors/ Name of Electronic Nose	Reference
Landfill	16 tin oxide	Micone & Guy, 2007
Landfil site	3xEOS835	Capelli, Sironi, Del Rosso, Centola, & Il Grande, 2008
Waste disposal, landfill areas	6 to 8 tin oxide sensors	Romain, Delva, & Nicolas, 2008
Wastewater treatment plant	FOX3000	Dewettinck, van Hege, & Verstraete, 2001
	eNOSE 5000	Bourgeois & Stuetz, 2002
	Neutronics Scientific Ltd. model D;	Onkal-Engin, Demir & Engin, 2005; Stuetz, Fenner, & Engin, 1999
	Pen-2	Nake, Dubreuil, Raynaud, & Talou, 2005; Littarru, 2007
	5x e-nose; 6 MOS	Nicolas, Cerisier & Delva, 2012
	EOS25, EOS28, EOS35	Capelli, Sironi, Centola, del Rosso, & Il Grande, 2008
Landfil	MOS	Gębicki, Dymerski, & Namieśnik, 2016

## **EXAMPLE OF THE USE OF ELECTRONIC NOSE FOR THE ASSESSMENT OF AIR QUALITY AROUND A MUNICIPAL LANDFILL**

The study compares the discriminatory possibilities of two types of electronic noses in the distinction and classification of air samples collected around a municipal landfill (Gębicki, Dymerski & Namieśnik, 2017). One of the noses consists of four commercial solid-state sensors from the FIGARO company (TGS 832, TGS 2600, TGS 2602, TGS 2603), one photo-ionizing sensor of the PID type (PPB MiniPID) and two electrochemical sensors from the Figaro company (FECS44, FECS50) - self-assembled. The other one is based on the ultra-fast gas chromatography technology and it was bought from the Alpha MOS company. This device combines the advantages of gas chromatography with the advantages of electronic noses. Additionally, using Nasal Ranger field olfactometers, odour concentrations in the air were estimated at places where samples were collected for analysis using both types of electronic noses. Figure 7 presents a diagram of the place where the research is performed and samples are collected for the assessment of its quality as regards the odour. This research was conducted in the spring and winter period, and in the spring. The kNN classifier (where k=3) was used as a method of data analysis. On the basis of air sample classification around the municipal landfill, it was observed that the largest number of correctly classified samples came from checkpoints with the highest odour nuisance. The research conducted using a field olfactometer showed that the average odour concentrations at these points ranged from 14.5 to 32.2 [ou/m<sup>3</sup>] depending on the season. The correctness of the classification of samples collected at those places was at the level of 100%, regardless of the type of electronic nose used for measurements or the season. At other measuring points, where odour concentrations were low (at the level of detection of a filed olfactometer where this level is 1.7 ou/m<sup>3</sup>), the correctness of the classification was at a much lower level. The example of the use of electronic nose devices presented above show universality and a significant practical aspect in the use of electronic nose devices for the assessment of air quality around such sectors of human activity such as a municipal landfill.



Figure 7. Example of the use of electronic nose for the assessment of air quality around a municipal landfill



## SUMMARY

Electronic nose devices are not commonly used for assessments of air quality with regard to odours due to numerous limitations:

- Variable sensitivity and drift of sensor signals in time,
- Variability of sensor signal depending on ambient atmospheric conditions,
- The influence of temperature and humidity on sensor signals,
- The lack or limitation of legal regulations allowing for the use of this type of device for routines measurements of air quality with regard to odours.

At present, electronic noses are only solutions that supplement sensory analysis methods as regards sensory assessment of atmospheric air. However, in many cases, the subjectivity of panellists who take part in olfactometric assessments may raise doubts. Moreover, the use of olfactometric techniques requires an experienced team whose olfactory sensitivity needs to be controlled on a regular basis, which makes olfactometric analyses labour- and time-consuming.

Potentialities and limitations of particular techniques suggest that the most advantageous solution seems to be combination of a few mutually supplementary approaches. In this way it is possible to obtain full picture of odour nuisance phenomenon, starting from odour generation in different industrial or municipal plants, through emission and imission processes, to evaluation of individual or population hazard due to exposure to malodorous compounds in particular area. Table 11 gathers selected examples of the papers, in which the minimum of 2 techniques were employed for evaluation of odorous properties of the gaseous mixtures originating from different fields of human activity.

## Application of Electronic Nose to Ambient Air Quality Evaluation With Respect to Odour Nuisance

Table 11. Examples of the ambient air investigation, in which the minimum of 2 measurement techniques were employed for characterization of odorous compounds

Techniques	Source of Emission	Results: Identified Compounds/Groups of Compounds/ Other Comments	Reference
DO & FO	WWTP	a discrepancy was revealed between the odour concentrations obtained via dynamic and field olfactometry	Barczak, Kulig, & Szyłak-Szydłowski, 2012
GC-MS & DO & E-NOS	Landfill	poor correlation between the odour concentrations obtained with olfactometric technique and the ones determined using concentration of particular compounds and detection threshold; significant potentialities associated with application of electronic nose instruments to identification of odorous compounds presence in air, for example due to installation failure	Capelli, Sironi, Del Rosso, Centola, & Il Grande, 2008
	Landfill	it was revealed that due to limitation of applied methods, only combination of many techniques allowed precise determination which odorous compounds have the biggest impact on environment	Romain, Delva, & Nicolas, 2008
GC-MS & DO	Landfill site	correlation was revealed between odour concentrations and total concentrations of volatile organic compounds in the investigated gas samples; it was shown that such groups of compounds as aldehydes, ketones and esters were the best indicators of elevated odour concentration;	Dincer, Odabasi, & Muezzinoglu, 2006
GC-MS & 8 E-NOS	Municipal solid waste	in most cases a good correlation was found between the results obtained with GC-MS and electronic nose;	Delgado-Rodriguez et al., 2012
GC-MS-O & DO & E-NOS	Waste management plant	demonstrated the potential of the techniques used to identify, distinguish and quantify odor concentrations of compounds released by the operation of waste management facilities	Giungato et al., 2016
DO & E-NOS	WWTP	complementary character of both presented techniques for efficient monitoring of odour concentration was revealed; it was found that both presented approaches provide objective, repeatable and reproducible results, typical for traditional chemical methods.	Littarru, 2007
	Municipal waste plant	it was found that sensor sets are an interesting solution for monitoring of odours.	Romain, Molitor, Adam, & Bietlot, 2016

abbreviations: DO – dynamic olfactometry; E-NOS – electronic nose; FO – field olfactometry; GC-MS – gas chromatography – mass spectrometry; GC-O – gas chromatography – olfactometry; WWTP – wastewater treatment plant.

Literature reports that are devoted to theoretical bases and principles of electronic nose operation and practical possibilities of their use are the basis for concluding that the development of odour analysis is connected with the use of electronic noses. It seems that many countries will soon extend reference methods in the analysis of malodorous substance to include the possibility of using the electronic nose; this mostly applies to countries where such legal regulations exist. While observing the potential and the rate of development, it can be supposed that the role of electronic noses in odour monitoring in the air will keep growing and this technique, apart from supplementing olfactometric techniques may also replace them in some aspects. For short-term odour nuisance (episodes), it will be possible to register them using electronic nose devices, which, in turn, is often not possible after qualified personnel arrives on site to perform field olfactometry measurements.

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