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Application of electrochemical sensors and sensor matrixes for measurement of odorous chemical compounds

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ABSTRACT

In this paper describes the principle of operation of the electrochemical sensors and the sensor matrixes comprised of electrochemical sensors intended for measurement of odorous compounds. Critical comparison of these sensors' advantages and disadvantages has been made. The fields of economy contributing to release of odours and the potential sources of their emission have been identified. Commercially available electrochemical sensors and sensor matrixes for measurement of odorous compounds have also been presented.

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1. Introduction

Compounds known as odorants unpleasantly perceived by the receptors of human sense of smell and they are identified as one of the main reasons of complaints lodged to different types of institutions [1–6]. Complexity of the problem of odour nuisance of indoor and outdoor air was emphasized in the Blacksmith Institute World's report, which classifies this issue as one of the most important problems as far as environmental protection is concerned [7]. The magnitude of odour nuisance impact is reflected in the statistical data of the complaints collected over last several years. For instance, the experts from the United States National Research Council Committee on Odours estimate that over 60% of the complaints on air pollution are connected with the exposure to unpleasant odours [8]. Prolonged odour presence on a given area and its high intensity can be a source of mental discomfort, so called odour nuisance [9–11], and in extreme cases it may lead to illness symptoms including headache, nausea, vomiting [12–15]. The attention paid to odour nuisance on selected areas increases not only with an increase in environmental protection awareness of the society but also with a progress in industrialization [16,17]. This situation enforces special care to be taken with respect to measurement of concentration and determination of the properties of emitted odorants. Obtaining information on concentration of particular odorants in ambient air is indispensable for comprehensive evaluation of the state of natural environment [10,18]. Suitable tools for

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Table 1
Chronological review of design solutions of sensors for identification of gas analytes characterised by unpleasant odour

Year	Sensor	Inventor
1957	Membrane sensor for dissolved oxygen	Clark
1961	Mechanical nose for odour classification	Moncrieff
1962	Semiconductor sensor utilizing metal oxides	Seiyama
1964	Sensor matrix utilizing redox reactions of odorants on sensitive element of an electrode	Wilkens and Hatman
1965	Conductivity modulation due to odorants	Buck
1967	Commercial semiconductor gas sensor	Figaro Eng. Inc.
1970	Semiconductor sensors with SnO_2	Taguchi
1972	Potentiometric gas electrodes	Frant, Ross
1975	Field-effect transistor with palladium gate for hydrogen measurement	Lundstroem
1982	Concept of electronic nose based on resistance gas sensors	Persaud and Dodd
1985	Application of chemical sensors matrix in intelligent nose for odour discrimination	Ikegami
1990	First scientific conference on electronic nose instruments	NATO Advanced Research Workshop, Reykjavik, Iceland
1993	Commercial electronic nose instrument	Alpha Mos
1999	Concept of ionic liquid application in amperometric sensor	Welton

measurement and control of atmospheric pollutants level as well as for identification of the odorants presence are employed for this purpose. Electrochemical sensors [19–24] and sensor matrixes comprised of electrochemical sensors named the electronic nose instruments [25–33] play an important role among numerous analytical techniques utilized for measurement of concentration of the odorous compounds. Table 1 presents information on the milestones in technological development of electrochemical sensors and sensor matrixes for identification of gas analytes characterized by unpleasant odour [25,34,35].

The electrochemical sensors utilized for measurement of the odorous compounds can be divided into three groups depending on the electrical signal measured [31,36–38]:

- potentiometric (measurement of voltage),
- conductometric (measurement of conductivity),
- amperometric (measurement of current).

The sensor matrixes are most commonly comprised of five types of sensors:

- semiconductor sensors with solid electrolyte (conductometric),
- semiconductor sensors with a layer of organic conductive polymers (conductometric),
- sensors utilizing surface acoustic wave (SAW),
- piezoelectric sensors utilizing quartz microbalance (QMB),
- photoionization detectors (PID);

where only the first two sensor types belong to a group of electrochemical sensors; this group is often narrowed to the electric-type sensors. However, the mechanism of the semiconductor sensors response to the components of gas mixtures, although being a complex process engulfing such phenomena as diffusion, chemisorption and desorption of gases, catalysed chemical reactions, electrical conductivity of semiconductors and electron surface phenomena [39–42], contains the elements of electrochemical processes.

In the case of single electrochemical processes the requirements involve best selective detection of particular odorant allowing for its quantitative determination at the lowest possible concentration level. The sensor matrixes are intended for holistic analysis and enable discrimination of the components of the samples with complex composition as well as allow identification of their characteristic properties. The sensors included in the matrixes may be characterized by limited selectivity due to an integral element of the matrixes' structure, which is a chemical image identification block intended for analysis of the signals of particular sensors [43–50].

In spite of the fact that an olfactometric technique is the approach most frequently employed to measurement of concentration of the odorous compounds [51–56], these are the electrochemical sensors that for many years have been consistently utilized in industrial analytical control, clinical chemistry, medicine or environmental protection due to their advantages (low price, satisfactory metrological parameters) [57–60]. A number of the sensor matrixes (the e-nose instruments) are also based on the electrochemical sensors, especially the semiconductor sensors with solid electrolyte. Development of this branch of industry resulted in the fact that these sensors are currently mass-produced [26,31,61]. Last few decades witness significant increase in interest in chemical (electrochemical) sensors, which is reflected in increasing number of the papers and conferences on that subject [26,30].

2. Characteristics of odorous chemical compounds

The odorants are volatile organic and inorganic chemical compounds sensed by animal and human smell receptors at very low concentrations and identified by brain as unpleasant ones. The compounds characterized by unpleasant odour include:

- inorganic compounds – hydrogen sulphide, ammonia, sulphur dioxide, nitrogen oxides, hydrogen fluoride, arsenic hydride,
- organic compounds – thiols, sulphides, disulphides, amines, carboxylic acids, aldehydes, ketones, aromatic hydrocarbons.

These compounds are characterised by relatively high volatility, hence the gas samples exhibit high vapour pressure. Human sense of smell is a natural sensor for air quality evaluation with respect to odour compounds presence. Information on odour characteristics can be perceived by human consciously or subconsciously. Unpleasant odours are naturally associated with danger, create the feeling of discomfort and can be the source of negative psychosomatic symptoms. Particular odorous substances present gas mixture can attenuate or amplify odour intensity and they can change hedonic quality of odour, hence it is advised to evaluate odour impact of the entire gas mixture [10]. In Table 2 are presented information on threshold levels of identification of selected odorous pollutants with sense of smell [17].

Minimization of odorous compounds emission becomes a priority for some branches of industry; it includes implementation of the deodorization systems in existing plants, appropriate design and localization of the structures to be built. In majority of cases ambient air quality in particular country depends on municipal waste management, agriculture and industry [6]. In Table 3 are presented a list of economy and industrial entities constituting potential source of odours [62].

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