MONITORING METODS OF NITROGEN DIOXIDE

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In the article nitrogen dioxide detection methods are presented. Particularly, the ideas of methods based on surface acoustic wave propagation in layered structures and photoacoustic method as well as the plasmon resonance method are discussed. Advantages described methods and their measurement possibilities are analysed. Methods recommended by the Polish Standard are described, too. Devices just used in nitrogen dioxide monitoring, their construction and principle of an operation are discussed. Examples of commercial solution of this kind of gas detectors are shown.

Keywords: surface acoustic wave propagation, dioxide nitrogen detections, photoacoustic gas monitoring, the plasmon resonance

1. INTRODUCTION.

Nitrogen oxides are very toxic substances and their presence in air impend over people and environment. In Poland, measurements and inspections of nitrogen oxides by Polish Standard ware regulated [1,2,3]. Nitrogen dioxide control at the workstands are regulated by Order of Minister of Work and Social Politic [4], and in natural environment – by Order of Minister of Environment Protection and Natural Resources [5]. In the work [6] methodological and legal basis of the toxic gases monitoring and an influence of nitric oxides on the environment and health people have been presented. On the base of this normative and lawful conditions many devices were elaborated, which can be used for air monitoring at workstands and for using of air ambient monitoring. Measurement methods of gases (also nitrogen oxides) described in Polish Standard are permissible ones for adjudication using about air state in a work environment by agencies entitled to it, such as Sanitarial-Epidemiological Stations. These methods are mostly chemical ones and for this reason they are time consuming and often troublesome in practical application. There is research necessity of new measurement methods, which will bring new possibility of technical solutions of the nitric oxides monitoring.

Between wide spectrum of physical-chemical measurement methods [6] there are many methods, which can be used for toxic gases monitoring. The special attention ought to concern on new measurement methods of toxic gases such as: the surface acoustic wave (SAW) method, the photoacoustic method and plasmon resonance method. These methods in next part of the elaboration will be described. For market there are existed devices, which applied different physical-chemical effects. These devices as gas alarms, analysers and detectors mono- and multigases are presented. Some of devices, in this elaboration will be presented.

2. GAS SENSOR USING SURFACE ACOUSTIC WAVE.

Among many methods of toxic gas detection noteworthy is new acoustic method. The method is based on the effect of surface acoustic wave(SAW) propagation in a layered structure. Principal feature of the surface wave (of Rayleigh's type) is, that during propagation of the wave, displacements of particles are largest on free surface and particles oscillation are exponential fading with depth [7, 8]. The transport of mechanical energy by the wave is concentrated in zone with range of a wavelength below of a wave propagation surface [7].

The configuration with propagating SAW on interface: waveguide - semiconducting film of the organic compounds can create a sensor element which may be sensing on low concentration of toxic gases [6]. In a case of phthalocyanine films, a propagation of SAW is strongly disturbance by adsorption of toxic gases such as: CO, NH_3 and NO_2 on a surface of a layer. An adsorption effect of gas molecules on semiconductor surface (metallophthalocyanine) changes essentially electric properties of the layer, which strongly depends on molecule concentration of absorbed gases (particularly NO_2). In case of NO_2 their molecules influence with electron cloud at peripheries of macrocyclic ring of metallophthalocyanine molecules. In result this influence so-called compounds with charge transfer complex is formed (CTC) [8,9]. The result of these influences may change the conductivity (electric effect) and change of surface density (mass effect) of metallophthalocyanine films [6]. Both effects influence on the propagation conditions which may be additionally disturbed by change of gas concentration and by temperature of environment. Investigations the effects in works [7,8,9,10,11 have been presented. In [7] Authors have described the sensor of toxic gases, designed on the base of configuration of the piezoelectric $LiNbO_3$ waveguide and semi-conducting film of metallophthalocyanine, obtained by sublimation method in vacuum [6]. On the $LiNbO_3$ two identical acoustical tracks were made, the one with metallophthalocyanine film (MPc) delay line and the second – the free track on a crystal, as a track relation [6].

Such configuration enables measurements of difference frequency Δf in both tracks. Wave propagation in the track with metallophthalocyanine film is imperceptibly disturbanced. This disturbance consists in a reduction of a surface wave velocity and increase of its attenuation. Reduction of velocity propagation is caused by a mass load effect of the surface crystal as well as an electric load, which results from influence of electric potential associated with the surface wave with active charge carriers in the semiconductor layer [6].

Described in work [7] the differential configuration consists of two acoustic oscillators.

Oscillations frequency through a propagation velocity of the surface wave v and geometric parameters of the acoustic configuration is designated. Parameters of acoustic interdigital transducers don't change, thus don't change wavelengths of the surface acoustic wave, which is equal: $\lambda \approx 80$ μm, and frequency of the acoustic wave will be function only of a wave propagation velocity (v). For the free track f_0 = 43,6 MHz and is constant. For the measurement track f depends on adsorbed gases. Oscillations frequency (f) in the measurement track with the active layer is directly proportional to velocity of the surface wave (v) and the differential frequencies for both tracks is direct proportional to their difference of velocity and from this – to concentration of gases [15].

Direct measurements of nitrogen dioxide (and other gases, too) by means of this sensors in the differential configuration by measurements of relative difference frequency Δf are realized.

Presented the differential configuration has got many qualities [7, 12, 13, 14,15]:

- compensation of temperature influence on acoustical properties of a foundation (niobate lithium has got large temperature coefficient),
- compensation of not large fluctuations of atmospheric pressure,
- reduction of measurement frequency from range of some tents MHz to some kHz.

In investigations presented in work [7] were showed, that lead phthalocyanine is very sensitive on nitrogen dioxide already at room temperature. At the same time one doesn't observe the influence of another toxic gases. Problem of acoustic gases sensors on phthalocyanine films in works [11-15] are widely described.

3. PHOTOACOUSTIC METHOD OF GASES MONITORING

In monitoring of gases it seems to bee that the methods based on a photoacoustic effect in gases may find wider applications [16, 17, 18]. The base of the theoretical model of a photoacoustic effect it is generation of local heat source in gas, created as a result of light absorption in this gas. Created in gas a head source causes acoustic wave generation [16]. In the case of using for measurement of a modulated light beam, the power density of emitted heat to absorption coefficient and to intensity of the incidence beam is proportional. The conversion of thermal energy into an audible signal by Morse's and Ingard's theory has been described [16,17]. As a source of light incident energy most frequently lasers are applied. The amplitude of a photoacoustic signal is proportional to power density of heat and depends on parameters of the absorbed light gas [16]. For unary gas the amplitude S of the photoacoustic signal can be presented by formula $S = CPN\sigma$, where: P – power of source light beam, N – molecule concentration, σ - absorption cross-section of gas particles, C –a constant of a photoacoustic chamber (experimentally determined) [16].
The photoacoustic method gives possibility of gases measurements at ultra-low concentration [16] but unfortunately, it is complicated and expensive one.

4. HIGH SELECTIVE SURFACE PLASMON RESONANCE SENSOR FOR NO_2 MONITORING

In a plasmon sensor is applied the effect of changing of attenuation and light reflection coefficients in layered metal-dielectric structure, caused by changes of environment in presences of surface plasmon resonance (SPR) [19]. The surface plasmon wave can be created on a separation surface between substances: metal-dielectric, when on this surface an electromagnetic wave incidences [19, 20]. Vectors of electric field intensity and magnetic field in plasmon wave are reach maximum value on a separation surface and disappear inside both materials. The idea of plasmon resonance sensor depends on equalization of a propagation constant SPW (β_{SPW}) and a propagation constant of an electromagnetic optical wave ($\beta_{e\text{-}m}$) [21]. Such fitting of wave vectors secures resonance transfer of electromagnetic energy from an incident wave to a surface plasmon wave. Then a resonance absorption of energy of an incident optical wave is observed. The changes of optical parameters of investigated medium can be detected by analysis of interaction between the SPW wave and the optical wave by measuring of intensity of an optical signal. The surface plasmon resonance effect among other for detection of nitrogen dioxide was used. [21].

Sensors based on the plasmon resonance are very sensitive for changes of optical property of gas medium (NO_2) adherent to metal layer [19].

The NO_2 plasmon sensors are very highly selective and the presence of other gases: NH_3, H_2, CO, CO_2, SO_2, HCl, Cl_2 i H_2S, do not have influence for NO_2 measurements, because SPR effect for this gases is imperceptible by using gold layer [19].

Literature of this problems informs about possibility of applications of silver and copper and cobalt phthalocyanine films in plasmon sensors for nitrogen dioxide detection [21].

5. NON - ACOUSTIC METHODS OF NO_2 DETECTION

Presented below methods of NO_2 detection by Polish Standard are recommended.

5.1 Determination of nitrogen oxides on workstands by colorimetric analysis [1,22,23].

The colorimetric method is often used one to mark at workstands of NO_2 concentration. Air (containing nitric dioxide) is forced through absorptive solution, which in a result of a chemical reaction with nitrogen dioxide changes its tint in colour range from light-pink to violet. Intensity of the tint as a function of intensity of solution after absorption for wavelength λ = 560 nm in colorimeter is measured. The of NO_2 concentration from a calibrated characteristic is determined.

The based element of the set-up is a spectrofotocolorimeter of a SPECOL type[1].

5.2 Method using tubular detectors with direct read-out [3,24]

The method uses of chemical reactions of nitrogen oxide with some chemical compounds. The degree of tint created compounds testifies of a concentration of investigated matter. The most often used chemical reactions are as follows:

- reaction with N,N'-diaphenylbenzidinne (colour changes from grey to blue-grey):

$$NO_2 + C_6H_5\text{-NH-}C_6H_4\text{-}C_6H_4\text{-NH-}C_6H_5 \rightarrow \text{coloured compounds}$$

- reaction with dihydrochloride N-(1-naphthlyl)etylenediamine (colour changes from white to red)

$NO_2 + C_{10}H_7\text{-NH-}CH_2\text{-}CH_2\text{-}NH_2 \cdot 2HCL + H_2N\text{-}C_6H_4\text{-}SO_3H \rightarrow$ diphase compounds

- reaction with O-toluidine (colour changes on yellow-orange)

$$NO_2 + NH_2(CH_3)C_6H_3\text{-}C_6H_3(CH_3)NH_2 \rightarrow \text{coloured compounds}$$

Mentioned above chemical substances are placed in glass pipes with sealed ends forming tubular detector. After broking both pipes ends the NO_2 measurements are realised by flow of investigated air by tubular detector. Intensity of tinge of the tubular detector shows suitable nitrogen dioxide concentration.

Using of tubular detectors should remember about factors which disturb measurement results. Halogens and chlorine dioxide and few other oxidized substances create tints similar to tints created by nitrogen dioxide. In exact marking NO_2 prevents sulphur dioxide disturbs when the concentration is higher than 100 mg/m^3 of air [3].

5.3 Marking of nitrogen dioxide in atmospherically air (low emission) by spectrophotometrical method with Saltzman's reagens [2,22].

This method is elaborated on the base of a method which by American Environment Protection Agency (EPA) EQN-1277-026 is recommended [2].

The method for NO_2 samples taken at every 30 minutes is applied or for samples taken continuously by 24 hours, in range from 0,03 μg to 2 μg in 1 ml absorbed air.

The method in [25] is exactly described.

6. MONITORS OF NITROGEN DIOXIDE.

Monitors – it is the name of methods of environment air monitoring.

The monitors for testing of toxic or dangerous substances are used.

For the main group of monitors belongs:

- Chemiluminescence monitors [26,27].
- Elektrochemical monitors (coulometer) [26,27].
- Electrochemical monitors (potentiometers) [23,26,28].

The main futures of monitors are not so high their accuracy (above some percents) and relatively low sensitivity. [29,30].

7. SEMICONDUCTOR SENSORS OF NITROGEN DIOXIDE.

Among many types of nitrogen dioxide sensors, the literature of last years informs about employment of semiconductor NO_x sensors in which semiconducting metal oxides are applied [30,31,32,33].
The sensor with an active surface in a form of a tungstic trioxide film (WO_3) on the foundation of Al_2O_3 is presented in [31]. The sensing element composes of a WO_3 layer, on which is evaporated gold digital electrode and with a heating element made of ruthenium dioxide (RuO_2). The sensor works basing on the resistance measurement in range from 0,01 to 2 MΩ. The work temperature of the sensor is up to 350°C. The sensors of this kind detect NO_2 as well as NO, too. They can be used for monitoring of waste gases, for inspection and air quality monitoring, working in range of concentration: 0 ÷ 50 ppm.

8. PRACTICAL APPLICATION OF NO_2 DETECTORS

The detectors are sometimes produced as multigases detectors, not only for nitric oxides control but also for carbon monoxide, ammonia or sulphur dioxide. There are, so called gaseous alarm, designed for two sills of detection. This sills are connected with two values: maximum permissible concentration (MPC) and maximum permissible concentration momentary (MPCM). The other type of detectors are monitors applied at workstand and emission monitors as well as low emission monitors to check of ambient air. This detectors can work in temperature range from -20 to +50°C. Their measurement ranges of gases concentrations may be very various.

Table 1 shows technical parameters of some multigases detectors, which in polish market are presented. Shown in table detectors are first of all the gas alarms in which electrochemical sensors are applied [34]. All presented detectors are produced by Canadian BW Firm – one of the biggest producers of this type gas detectors in the world.

In Table 2 some examples of gas detector used at the workstand are presented.

Devices used for monitoring nitric oxides in the ambient air in Table 3 are shown. Under mentioned devices, actually work in the automatic testing stations to control of air quality in the Katowice agglomeration [35]. n automatic stations are realized measurements of NO_2 and NO as well as carbon monoxide, sulfur dioxide and dusts too.

Table 1.

Type of Detectors	Gas	Accuracy	Measurement range		Notices
			1	2	
Gas detectors of series CD-420 (BW Firm)	CO	1 ppm	0-500	0-1000	Four-channel system of detection;continuity of control gas concentration
	NH_3	0,5 ppm	0-50	0-100	
	NO_2	0,1 ppm	0-10,0	0-20,0	
	SO_2	1 ppm	0-100	0-50	
Spark safety gas detectors of series I.S. Plant (BW Firm)	CO	1 ppm	0-500	0-1000	Low necessities of preservation
	SO_2	0,5 ppm	0-100	0-50	
	NH_3	0,5 ppm	0-50	0-100	
	H_2	1 ppm	0-100	0-200	
	HCL	0,1 ppm	0-10,0	0-20,0	
	NO	0,5 ppm	0-50,0	0-100	
	NO_2	0,1 ppm	0-10,0	0-20,0	
Local gas detectors type: ALARM RAT (BW Firm)	CO	0,5 ppm	0-500	0-1000	Sensors of pin type; three alarm levels of gas concentration
	NH_3	0,5 ppm	0-50	0-100	
	NO_2	0,1 ppm	0-10,0	0-20,0	
	NO	0,5 ppm	0-50	0-100	
	SO_2	0,5 ppm	0-100	0-50	
	H_2	1 ppm	0-100	0-200	

Table 2.

Detector name	Gases	Measurement range and accuracy	Type sensor
Multigase detectors LTX 310 (INDUSTRIAL SCIENTYFIC CORPORATION USA)	Explosive gases, oxygen and toxic gases	Nitric oxide 0-999 ppm with step 1 ppm; nitrogen dioxide 0-99,9 ppm with step 0,1 ppm	Electrochemical detectors
Monogase detectors series 200 (INDUSTRIAL SCIENTYFIC CORPORATION USA)	Nitrogen dioxide	0-199,9 ppm; threshold alarm 3 ppm	Electrochemical detectors
Analyser CMS (Chip-Mes-System) DRAGER Comp.	Nitric oxides and others gases	0,5-15 ppm or 10-200 ppm	Chip with reagent
Pump Accuro (DRAGER Comp.)	Toxic gases	0,5-10 ppm, 5-100 ppm, 2-50 ppm	Tubular detectors

Table 3.

Type analyser	Sensor measurement method	Measurement range and accuracy	Quantity sensitivity
Analyser of nitric oxide concentration type ML 8841	Chemiluminescence	1,5 ppb 0-500 ppb	0,5 ppb
Analyser of nitric oxide concentration typ ML 9841	Chemiluminescence	0,5 ppb lub 1% odczytu 0-500 ppb	1 ppb
Analyser of nitric oxide concentration typ ENVIRONMENT AC 30 M	Chemiluminescence	0-1000 ppb	2 ppb

9. CONCLUSION.

After analysis of detection nitric oxide methods recommended by Polish Standards one can ascertain, that the methods (in most of cases) based on chemical analysis from many years are used. The Polish Standards rarely recommended automatic methods, which are simple and usefriendly. As mentioned in this elaboration, there are exist many detection methods of nitric oxides (and other toxic gases, too). Some of methods found commercial application for production of gas alarms used industry and as gas detectors and analysers.

Analysed in the elaboration the new method based on surface plasmon resonance is very perspective one and it seems to be applied for air monitoring in near future. As one shows in the works [20,21], the gas detection by plasmon sensor can be realized by measurements of optical wave intensity, resonance angle, resonance length wave and changes of polarization [36]. The plasmon method is very sensitive and can be used for concentration measurements in wide range.

Presented here the surface acoustic wave method is attractive for measurements of higher concentration of nitrogen oxide and other gases [14,15].

Summing up one can notice, that in group of new investigative methods, the special position among gas detection methods can occupy plasmon one.

Market of detectors grows continuously and ensures the demand for sensors of high quality.

Investigations over possibility of application of surface plasmon resonance sensors and the sensors based on surface acoustic wave propagation in layered structure for measurements of nitrogen dioxide and other gases monitoring, are carried from few years in Institute of Physic at Silesian University of Technology in Gliwice. The results of experimental investigations of nitrogen dioxide detectors based on the plasmon resonance and the SAW propagation are actually realized and their results will be published in near future.

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