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Photoionization Detectors (PID) in the Fire Safety

Lead OMÓWIENIE

The proper use of the measuring devices in rescue and firefighting operations is extremely important, it is so, especially in the terms of safety increase in the incidents with an uncontrolled release of hazardous substances. The article describes the scope of the photoionisation detector (PID) use. It is related to the limitations of measuring devices based on the catalytic combustion sensors (explosimeters) by the characteristics of the method sensitivity range. The simulation of the incident involving both flammable and toxic substances indicating the proper use of devices to determine the toxicological and flammable hazard zones have been carried out.

Keywords: photoionisation detector, the PID, explosimeter, rescue and firefighting operation, ethylene oxide, catalytic combustion sensor.

1. Introduction

First Photoionization Detectors (PID) in Polish State Fire Service were introduced in the first decade of the 21st century. They are commonly integrated with the oxygen sensor and the explosimeters. Nowadays Polish State Fire Service is equipped with 24 Photoionization Detectors, including devices owned by the schools of fire service. Statistical analysis of emergency incidents reveals, that in the years 2010-2013 in Poland there were 10605 hazmat incidents, in which detectors were used. It is clear that, the number of incidents involving the use of detectors increases rapidly (1117 events/year) which is shown by the factor of the slope at Fig. 1. It is worth to mention that the PID were used only in few of them. The fact is that quantity of these devices is relatively small but the survey among firefighters indicates that a little use of the PID in emergency response

is related to difficulties in interpretation of the device output. Another problem is the lack of knowledge while answering the question why instead of the traditional explosimeter it is better to use the PID in the real situation. Firefighters do not realize the benefits of the device. Usually they only know that to use any instrument to obtain information about the concentration, first of all they must know what the substance is. If they already know this and as in the case of the explosimeter the value has to be multiplied by the calibration factor. Why should the firefighters use the PID then?

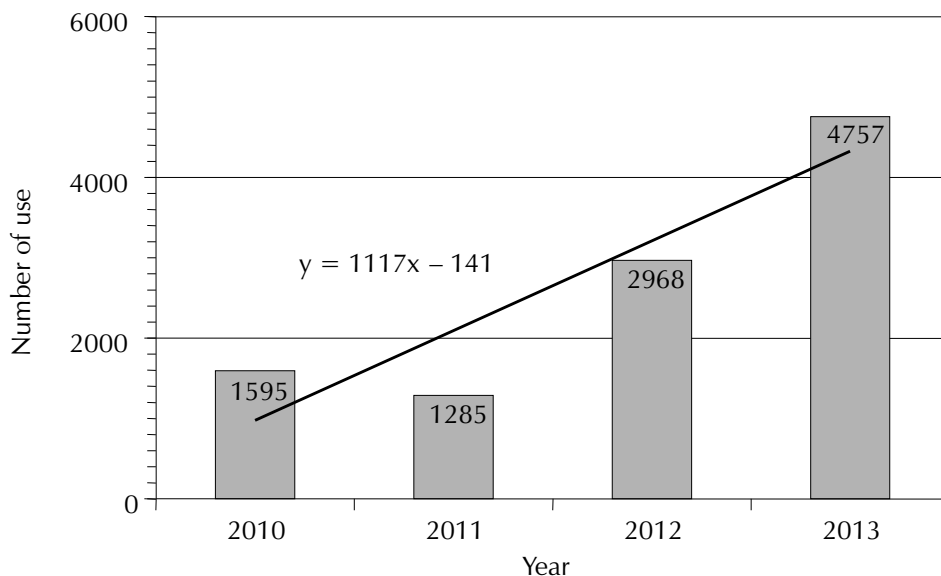


Fig. 1. Number of hazmat incidents (2010–2013) where measuring devices were used – statistical data from Headquarters of Polish State Fire Service [1]

2. Principle of operation

The photoionization detector operation principle is ionizing gas or vapor using ultraviolet radiation. In measuring a cell there is an ultraviolet lamp emitting the wave with strictly defined frequency. Because the quantum energy is related to the wave frequency with formula: $E=h\nu$, where h – Planck's constant ($6.63 \cdot 10^{-34}$ [J/s]), ν – frequency [Hz], quantum have uniform energy. This energy depends on gas filling the lamp – 9.6 eV for xenon, 10.6 eV for krypton and 11.7 eV for argon. The lamp's walls are made of special material, transparent for the ultraviolet radiation [2, 3].

Molecules of gas with ionization potential lower than the lamp energy are fragmented, releasing free electrons. These electrons are accelerated in the electric field, which can be observed as a current flow (Fig. 2). For pure substance, magnitude of current flow is linearly dependent on its concentration in air in wide range, which allows for quantitative determination.

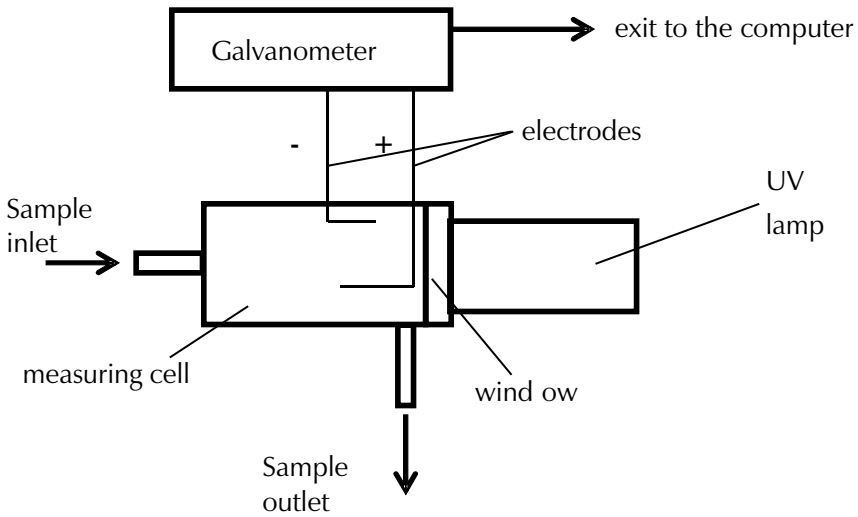


Fig. 2. Photoionization detector configuration [3]

Every substance has its own ionization potential, measured in [eV]. Gases with ionization potential greater than the lamp radiation energy like oxygen, nitrogen, carbon oxide, carbon dioxide are not ionized, therefore if clean air current flows magnitude is zero. Most organic volatile substances and some inorganic (e.g. ammonia) have smaller ionization potential, so if they are present in air, current flow is observed. Vapor of benzene is ionized by the lamp 9.6 eV, ammonia and ethanol – 10.6 eV, acetylene and formaldehyde – between 10.6 and 11.7 eV (Fig. 3).

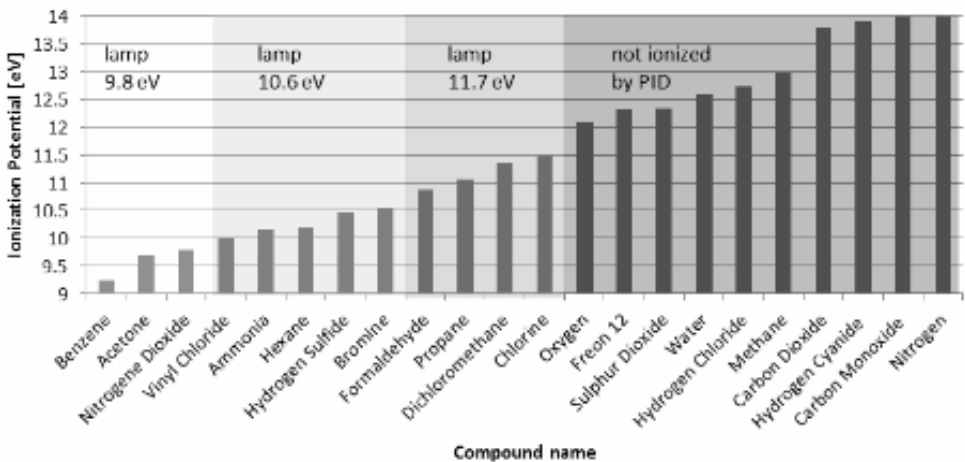


Fig. 3. Examples of compounds and their ionization potentials [5, 6]

The photoionization detector can be used to detect organic substances in air. Quantitative measurement is possible only when there is pure, known substance with known correction factor [4].

3. Correction factors

The photoionization detector is calibrated to isobutylene. In case of measurement of other compounds it is necessary to multiply output concentration by correction factor for particular substance. This correction factor depends on the type of substance and lamp energy. For example for the lamp 9,8 eV correction factor of 1,4-dioksan is 1,35 and for the lamp 10,6 eV this value is 1,06 [7]. Correction factors for chemicals commonly used in industry have been tabulated. It should be taken into account that correction factor depends, to some degree, on calibration conditions, humidity, and lamp material.

4. Concentration limits and sensor linearity

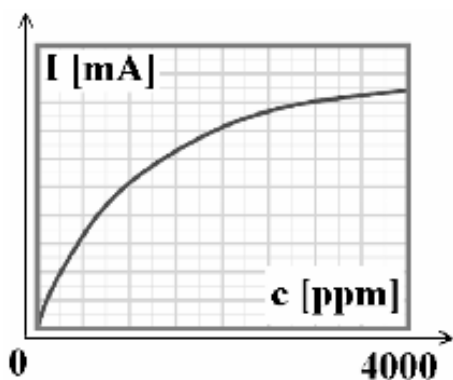


Fig. 4. Relationship between concentration and current for the PID calibrated vs. isobutylene [3]

As mentioned before, the relation between concentration and current is approximately linear in a wide range of concentrations. The chart below presents a deviation from the linearity for larger concentrations. Above 1000 ppm the relation is not linear and the measurement requires establishing a calibration curve (the use of correction factors may cause significant mistakes). Above 4000 ppm a detector is saturated and the measurement is not possible (Fig. 4). Typical resolution of output concentration is 0.1 ppm.

5. Application

The photoionization detector can be used in three general ways:

- to monitor concentration of a single, known compound,
- to detect the presence of some organic volatile in unknown environmental samples,
- as a detector at the end of GC column.

In case of mixture of several compounds, which ionization potentials are lower than the lamp energy, each of them will be ionized. This makes selective

detection of each substance impossible. Sometimes there is only opportunity to divide substances to groups using lamps with different energy.

The specific case of organic substance which cannot be ionized by the PID is methane. The ionization potential of methane is 12.98 eV. Therefore the PID cannot be used to detect leaks of natural gas, composed mainly of methane.

This method is especially useful when dealing with the organic volatile solvents, which can often be spilled in emergency conditions. The explosimeters measure only high concentrations, close to LEL (thousands of ppm), while even dozens of ppm can be a serious threat to human health. In that way the PID can be used to determine boundary of threat zone, when breathing apparatus should be used.

The PID offers fast response, high accuracy and sensitivity for detection of low concentration of the volatile compounds. Unfortunately the short life of a lamp and necessity of cleaning makes the PID not practical in stationary monitors, which continuously sample.

6. Maintenance and life expectancy of device elements

The UV lamp window is exposed to measured substances, which can lead to pollution. This can lead to serious deviation in output and often cleaning is required. Frequency of cleaning depends on the conditions in which a device is used, degree of the samples pollution and also on the acceptable level of errors.

Due to chemical properties of materials used in the lamp, they have only limited durability and must be periodically replaced. The 10.6 eV lamps have the longest life expectancy – that is approximately 6000 hours of continuous measurement.

7. The use of the PID detector and limiting conditions for the explosimeters

The PID detector unlike the explosimeters is characterized by a significantly higher accuracy measurements. The standard explosimeters used in the rescue operations have only 1% LEL of accuracy. In case of calibration to methane (LEL 5%) that means the accuracy of 500 ppm. For measurements of concentrations below 10,000 ppm, it is possible to switch to the mode of ppm measurement with better accuracy equal to 50 ppm. In case of uncontrolled release of toxic substances this range of precision is definitely unsatisfactory. In order to understand the importance of the problem it is worth to consider the ethylene oxide example, both a flammable and toxic substance. In this kind of usage the explosimeter gives us only the opportunity to examine one of the characteristics – flammability.

The simulation was carried out using ALOHA v. 5.4.4. The parameters presented by the program are more than sufficient for the presentation of the

risks posed by substances unless we take into account the effects related to the difference in the relative height or changing weather conditions. The most unfavorable weather scenario involving failure of the tank with a capacity of $V = 50 \text{ m}^3$ in the sunny warm day was considered. The air relative humidity is low, $H = 5\%$, while the air temperature is $T_1 = 35^\circ\text{C}$ (308 K). At low wind speed $v = 1 \text{ m/s}$, there are typical conditions for the stability of the atmosphere corresponding to the class A (unstable), wherein the simulating conditions are without atmospheric inversion.

As a result of the valve break of liquid phase there took place the emission of the ethylene oxide contained in a liquid state at a pressure of 1 MPa and the temperature of $T = 2^\circ\text{C}$ (275 K). The most likely scenario, loosening the set screws in the cistern valve, similarly to the incident with the ethylene oxide in Nowy Sacz 2000 [8] was assumed.

The ethylene oxide is released from the damage of equivalent diameter $d = 0.25 \text{ cm}$ creating a fast evaporating pool of predetermined maximum surface equal to $S_1 = 1 \text{ m}^2$. The rate of emission is $q = 0.223 \text{ kg/min}$. The range of toxicological contamination is determined for NDSC (1.72 ppm = 3 mg/m³), for ERPG-2 (50 ppm) and for ERPG-3 (500 ppm). The analysis carried out for the concentration [ppm] in function of the distance from the place of release [m] showed that the first value of NDSC (which is determined according to the most threat zones and represents the highest momentarily permissible concentration) is exceeded at a distance of 252 meters, the second zone for ERPG-2 (denoting the maximum concentration for which no irreversible health effects are observed) is exceeded at a distance of 45 meters, and the third zone for ERPG-3, indicating the maximum concentrations for which no irreversible life-threatening effects are observed, is exceeded just at only 13 meters (Fig. 5, Table 1).

Table 1. Ethylene oxide concentration values for open space c_{zew} [ppm] and inside buildings as a function of distance x [m] from the center of pool. Break equivalent diameter $d = 0,25 \text{ cm}$. relative humidity $H=5\%$, air temperature $T_1=308 \text{ K}$, ethylene oxide temperature in tank $T=275 \text{ K}$, $v=1 \text{ m/s}$, atmosphere stability class A, atmospheric inversion – no, pool surface $S = 1 \text{ m}^2$

x	c_{zew}	c_{zew}	x	c_{zew}	c_{zew}
[m]	[ppm]	[ppm]	[m]	[ppm]	[ppm]
13	497	156	50	40	13
20	267	84	80	16	5
30	114	36	100	10	3
40	63	20	252	2	0
45	49	15			

It should be noted that the model of heavy gases (as well as Gaussian) gives only the approximate values for distances smaller than $x = 50$ meters, however, they can be successfully used as an estimate.

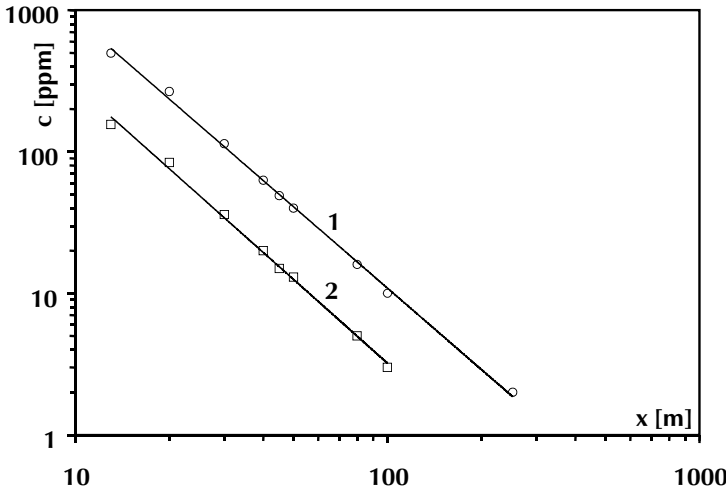


Fig. 5. Concentration values c [ppm] 1) in open space c_{zew} [ppm] 2) inside buildings c_{wev} [ppm] as a function of distance x [m] from the center of pool. Break equivalent diameter $d = 0,25$ cm. relative humidity $H=5\%$, air temperature $T_1=308$ K, ethylene oxide temperature in tank $T=275$ K, $v=1$ m/s, atmosphere stability class A, atmospheric inversion – no, pool surface $S = 1$ m²

Even the value of ERPG-2 is exactly the same as the accuracy of the explosimeter (50 ppm). The result shows that depending on the distance the significant differences between the real value and the read value can be observed. They will be greater, the closer the source of release is. This is a consequence of the fact that the dependence of $c = f(x)$ is a power function dependence. For example, the concentration in open space, can be represented by the function $c = 71995x^{-1,91}$ which means that the difference in concentrations for example between 50 and 100 metro is 30 ppm, between 100 and 150 metro is 6 ppm and between 150 and 200 metro is just 2 ppm. All these values are out of range and accuracy of the explosimeter but very easily distinguished by the PID.

Conclusions

Analyzing specifications for the PID and the explosimeters as well as a sample scenario of an uncontrolled release of the ethylene oxide, we can clearly see a separate area of ?? the application for both types of detectors. The explosimeters inaccuracy typically used in rescue operations is 50 ppm. This causes that the results can be regarded as accurate at the concentrations equal to at least 1000 ppm. For this threshold a relative error of $B = 100\% |\Delta c/c|$ concentration is 5% what is in agreement with standard statistical rules for experimental accuracy. This is a cause of the limitation of explosimeters use, primarily to determine the flammable threat zone and the toxic threat zone only for substances which have threshold values (e.g. ERPG-2) at least equal to those of 1000 ppm. This gap can be filled by the PID which have much higher sensitivity and the time of reaction much shorter.

What emerges from there, it is the need for training of first responders of how to use measuring devices during rescue operations. Lack of knowledge concerning the interpretation of the displayed results makes the devices unused which is unacceptable from the safety and the economic rules point of view.

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Detektory fotojonizacyjne (PID) w jednostkach ochrony przeciwpożarowej

Właściwe wykorzystanie urządzeń pomiarowych jest niezwykle ważne w aspekcie podniesienia bezpieczeństwa działań ratowniczo-gaśniczych podczas zdarzeń związanych z niekontrolowanym uwolnieniem substancji niebezpiecznych. W ramach artykułu określono możliwości wykorzystania detektora fotojonizacyjnego (PID). Odniesiono je do ograniczeń pomiarowych urządzeń bazujących na czujnikach spalania katalitycznego (eksplozometrach) poprzez charakterystykę zakresu czułości metody. Przeprowadzono także symulację zdarzenia, z udziałem substancji o właściwościach jednocześnie palnych oraz toksycznych, wskazując właściwe wykorzystanie urządzeń do określania stref zagrożenia toksykologicznego oraz palnego.

Słowa kluczowe: detektor fotojonizacyjny, PID, eksplozometr, akcje ratowniczo-gaśnicze, tlenek etylenu, czujnik spalania katalitycznego.