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Towards optoelectronic detection of explosives

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Detection of explosives is an important challenge for contemporary science and technology of security systems. We present an application of NOx sensors equipped with concentrator in searching of explosives. The sensors using CRDS with blue – violet diode lasers (410 nm) as well as with QCL lasers (5.26 μm and 4.53 μm) are described. The detection method is based either on reaction of the sensors to the nitrogen oxides emitted by explosives or to NOx produced during thermal decomposition of explosive vapours. For TNT, PETN, RDX, and HMX the detection limit better than 1 ng has been achieved.

Keywords: explosives detection, absorption spectroscopy, laser spectroscopy.

1. Introduction

Nowadays the ensuring of safety becomes a grave challenge. There is observed a dynamic increase in number of terrorist attacks threatening various targets which are important for economy, administration or public activity. The past fearful experience showed that attack objects involving a large number of people were often selected. It concerns large buildings, public conveyances, as well as water supply systems, infrastructural facilities, etc. Therefore, a lot of attention is being paid to the development of methods and instruments for explosives' detection.

The terrorist attacks are usually performed with improvised explosive devices (IED). They are prepared with home--made constructions, which typically use inorganic salts containing molecular bound oxygen, like nitrates, chlorates, perchlorates or organic compounds with nitro-, nitamine- or nitrate-groups or peroxides, as well as any chemicals or the mixtures suitable for explosive reaction. Basing on IED principle operation and construction, the detection might be performed in two ways. Bulk methods detect IED markers such as characteristic shape, used materials or specific elements (wires, electronics). Trace sensors apply the searching of gases and particulates that are emitted by either applied explosives charges or deposited on the objects that were in contact with IED.

2. Detection of explosive devices

As far as several tens of methods of IED detection were already elaborated, this branch of science and technology is still under intensive development [1]. The methods are often

focused on bulk detection. Some of them are implemented in commercially available systems [2]. They are just used by the security services in the places of supposed threat. For instance the X-ray scanners, which are commonly used at the airports, are based on photoelectric absorption. They can detect dangerous objects (like characteristic metallic shell, detonators, etc.) due to the image analysis. More advanced systems, involving also Compton scattering or positron and electron generation are suitable for the detection of materials characterized by a low atomic number (e. g., explosives). This kind of apparatus is used to investigate larger objects like passenger luggage or even trucks and containers [3–5]. The most advanced systems of *computer tomography* are still under development [6–8]. Microwave thermography [9] provides opportunity to distinguish an ordinary object from a hazardous one, while the radio-wave active scanning enables to find the radio receiver circuits of the IED triggering systems [10]. Terahertz waves which penetrate many materials apart from metals or polar media can be used to detection of the species through packing, clothes, shoes, and bags. As long as this frequency range corresponds well to ro-vibrational spectrum of molecules, this radiation can be used for detection of various advanced explosives [11]. *Time domain spectroscopy* (TDS) is especially useful in the THz range [12,13]. Observation of explosives' transmission and reflection are conducted by using Teraview TPS 3000 instrument at the Institute of Optoelectronics, MUT. It makes it possible to detect some explosive materials – Hexogen, Penthrite and Octogen, due to recognition of their spectral fingerprints [14].

Ground penetrating radar (GPR) is used to scan near surface layers of the soil and to image the objects with a resolution of a few cm [15,16].
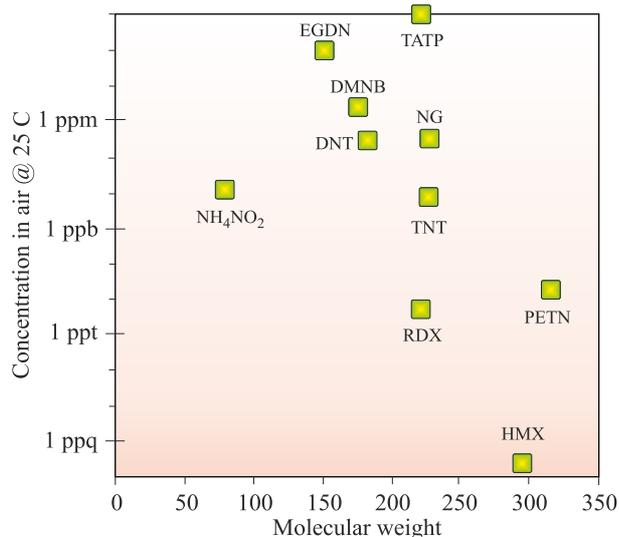
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Fig. 1. Vapour concentration of explosives [17].

Another approach to the explosives' detection is based on trace vapour investigation. Chemical identification of microscopic residues of the explosive compounds is performed. Vapour detection search for very small quantities of Hydrogen, Nitrogen, Carbon and Oxygen that are the common components in popular explosives. Figure 1 shows the maximum vapour concentration in the air for several explosives at the room temperature [17].

The main problem is that the vapour concentration inside the sensors might be even some orders of magnitude lower than the concentration of saturated vapour on the explosives surface. Moreover, the concentration level drops when the sealed packing is applied. Low temperatures or a strong wind decrease the detection probability as well. Modern vapour sensors can reliably detect explosives at vapour concentration in the range of 10^2–10^3 ppb.

There is a lot of instruments which can be used for explosives vapour detection. The instruments can be used as hand held, portable or fixed devices for either remote or stand-off detection. One of the most complex systems is based on neutron techniques. Although the systems are characterized by high sensitivity their use is limited by high false alarm rate or high price [18–21]. *Nuclear magnetic resonance* (NMR) *spectroscopy* can identify the atomic configuration of molecules. It may be used for the detection of explosives concealed in parcels, letters and airline luggage [22]. Additionally, *electron paramagnetic resonance* (EPR) can be about 10^4 times more sensitive in some cases. These instruments permit to detect the samples of black power of tens of a milligram. The experiments with *nuclear quadruple resonance* (NQR) *spectroscopy* are carried as well [23–27], however, the sensitivity of this method is not satisfactory by now [28,29]. Finally, it can detect and image the volumes of high nitrogen concentration with γ-ray systems by measuring the transmission characteristics of the objects. The systems are enough sensitive to detect trace amounts of nitrogen, but the

applied procedure is complicated because of critical requirements concerning special target material and shape, as well as γ-ray source intensity and stability.

Many compact detection devices, e.g., *electronic nose* are also designed nowadays. The devices perform multi-component analysis and analyte recognition. In the sensors, fluorescent polymers [30], arrays of different polymeric thin film [31], gold nanoclusters deposited on microelectrode arrays [32], surface acoustic wave [33,34], quartz crystal microbalance devices, and micro-electromechanical systems (MEMS) [35] are used. Their detection limit reaches the value of about 1 ppm [36]. In the future these sensors will be able to replace some of more complicated and more expensive instruments. In comparison, the *gas chromatography* coupled with mass spectrometry or other sensors like *Surface acoustic wave/gas* provides a high sensitivity (even ppb-level or lower) and various explosives detection (TNT, PETN, RDX, etc.) [37,38]. *Ion mobility spectrometry* (IMS) belongs to the most widely used techniques for the trace detection. The samples of the investigated gas are ionized by a radioactive source. Then, the sample flows to the measurement area where the ions are deflected into the measuring electrodes. The output signal corresponds to ion mobility distribution that can be also used for samples' identification. Modification of this method leads to *Field ion spectrometry* (FIS) that consists in the filtering of ion species. The filtering effect is performed according to the functional dependence of samples mobilities on electric field strength. The detection is limited to explosives such as RDX, TNT, and PETN in the low picogram range [39]. *Chemiluminescence* can be applied for detection of a characteristic light emitted from excited molecule, atom or fluorophore [40]. The light is produced during an exothermic chemical reaction. Sample of the analysed gas is mixed with ozone or NO_2 excited molecules. The mixing procedure induces the chemiluminescence of the investigated molecules. The observed chemiluminescence is a presence marker of the explosives [2]. *Thermo-redox* (reduction-oxidation) sensors are based on the thermal decomposition of explosives and subsequent reduction of NO_2 groups. But the sensors cannot neither detect non-nitrogen explosives, nor distinguish the explosives from other substances containing NO_2 groups [41]. *Electron capture* (ECD) sensors can detect vapour of substances that strongly capture thermal electrons. This method is usually used together with gas chromatography. Typical detection limit of ECD sensor is about 1 ppb [42].

Biosensors are devices that integrate a biological element on solid state surface. They provide possibility of TNT detection with detection limit of 31 ppb [43]. Finally, in order to find hidden sources of explosive vapours the animals (e.g., dogs, bees, rats) have been also trained [44].

3. Optical detection of explosives

There are linear and nonlinear optical methods of chemical composition determination. For the first class, light absorption and fluorescence have been qualified. On the other

hand, a nonlinear method is represented by spontaneous Raman scattering. Some progress of analysis with other nonlinear effects is recently observed, especially by using femtosecond lasers [45,46]. But these methods are still under development.

Spontaneous Raman process results in inelastic scattering of photons which energy is different than that of the incident ones. The spectrum of scattered light consists of bands which frequency is shifted down (Stokes process) or up (anti-Stokes process) with respect to an exciting laser line. While this shift corresponds to the scheme of energy levels of the investigated matter, the spectrum is its fingerprints. This method is mainly used for the trace detection of deposits on a target surfaces etc. Cross section of Raman scattering is usually about three-four orders of magnitude lower than that for Rayleigh process, therefore, the sensitivity of Raman methods is insufficient to detect traces of explosives in the air. An improvement can be achieved when the frequency of the exciting radiation approaches the allowed transition of the molecules. In this case the efficiency of Raman scattering can raise even four orders of magnitude. This approach can be used for explosives sensing even with the remote techniques (Raman lidar). Increase in Raman methods sensitivity can be also obtained by using surface enhancement [(*Surface enhanced Raman scattering* (SERS)] [47]. For this setup, the cross section of Raman scattering is increased by about several orders of magnitude for molecules, which are adsorbed on a rough gold or copper surface. Today such SERS systems have been successfully used to detect mines in minefields.

Laser-induced fluorescence (LIF) is a commonly used tool to study decomposition of explosives. In this technique the fluorescence observation is often replaced by matter identification using Raman processes. Efficiency of the method can be optimized operating with well-defined wavelength of exciting laser [48] or using specialized bulks prepared with nanotechnology methods [49].

Laser induced break-down spectroscopy (LIBS) consists of plasma generation from surface of a target irradiated by a laser pulse and an analysis of plasma fluorescence. Experimental scheme of the LIBS system which was constructed in the Institute of Optoelectronics, MUT is shown in Fig. 2 [17]. The atomization and ionization of the sampled material are induced by laser pulses. The processes provide a plasma plume. Therefore, a luminescence can be observed. This radiation is analyzed by a spectrometer. The excited species can be identified by their characteristic fluorescence spectra. The capability to perform non-contact real time detection of trace amounts of matter makes these techniques very promising [50–53].

Absorption spectroscopy is a simple and non-invasive technique for tracing matter detection. It can be used for *in situ* or for remote investigation and has great potential in the detection and monitoring of the components in the gas phase. These methods are characterized by high sensitivity and good selectivity.

Differential absorption lidar (DIAL) is a technique that applies the absorption spectroscopy for remote sensing of gases in the air. DIAL laser operating at two wavelengths transmits radiation pulses to the atmosphere. One of them is tuned to the absorption line of the investigated gas. The second one is not absorbed by this gas and serves as a reference signal. The registered signals occur due to laser light scattering on atmospheric aerosol. The difference between the signals is used to determine the concentration of the absorbing species [54]. Examples of military applications of LIDAR include the *Airborne laser mine detection system* (ALMDS) for counter-mine warfare [55]. In the system, explosives' vapour existing around the explosive devices is searched. The interaction yields an optical response, which is collected by an optical receiver. As were described in literatures the standoff optical methods deliver the sensitivities reaching even the ppb level [56–58].

In optical absorption methods the concentration of the absorber N is determined by measuring of the light quenching in a chamber (optical cell) of the length d. The concentration is calculated by using the formula following from Lambert-Beer law

$$N = \frac{1}{d\sigma(\lambda)} \ln\left[\frac{I_0(\lambda)}{I(\lambda)}\right], \qquad (1)$$
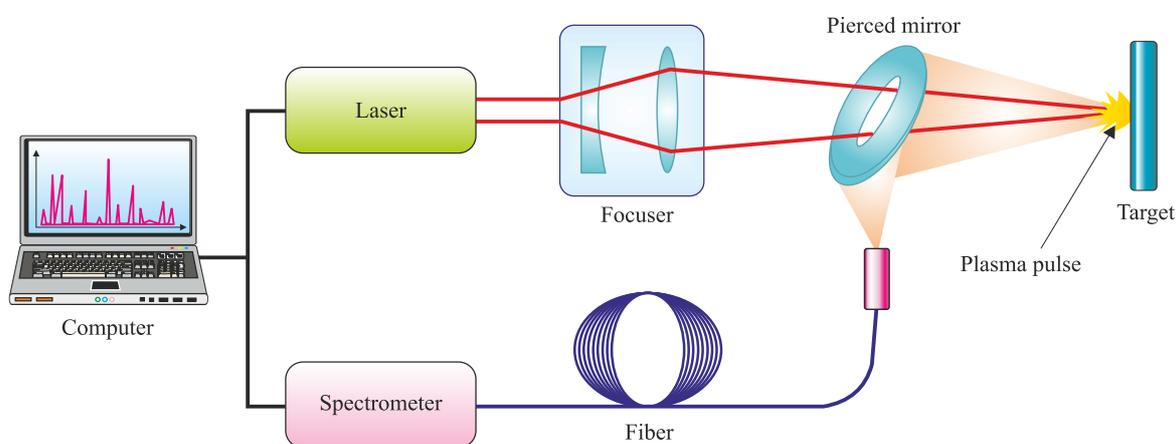

Fig. 2. LIBS experimental setup [17].

where $I_0(\lambda)$ and $I(\lambda)$ denote the intensity of radiation at the input and at the output of the cell, respectively, while $\sigma(\lambda)$ is the absorption cross section at the wavelength of λ. Typical values of molecular absorption cross sections are from σ ~10^{-20} to ~10^{-18} cm^2 [59]. As seen in Fig 1, for majority of explosives the detection limit should be better than a few ppm (N ~10^{13} cm^{-3}). For some of them it should reach even the level of parts of ppb ($N < 10^{10}$ cm^{-3}). These concentrations are so low that even in the most favourable circumstances the absorption coefficients are: $\alpha = N{\cdot}\sigma << 10^{-4}$ cm^{-1}. Due to that the detection of explosives cannot be easily performed with common spectrophotometers which sensitivity reaches a similar level. There are some improvements of the methods (i.e. modulation technique) but they do not cause so high sensitivity increasing. In DIAL techniques the detection limit of *ppb* level is achieved due to the averaging of the signal over relatively long absorption path ($d > 10$ m). For *in situ* apparatus where the absorption path is much shorter, the laser spectroscopy techniques of higher sensitivity must be applied.

One of them, *photoacoustic spectroscopy* is based on the *photoacoustic effect*, e.g., the energy conversion from light to acoustic wave in the absorbing material. The signal is usually detected in a resonant acoustic cell equipped with a sensitive microphone. Recently, alternative transducers, such as a quartz tuning fork (TF) [60], optimized capacitive micro-electro-mechanical systems of microphones are used [61,62]. The detection limits better than α_L ~10^{-7} m^{-1} are available. As a consequence the detection and identification of explosive materials in open air was demonstrated with this technique [63].

In order to improve the sensitivity, absorption path should be lengthened. This approach is realized in *multipass spectroscopy*. Absorption cell with two mirrors of high reflectivity is applied. The laser beam is introduced to the cell through a hole in one of the mirror and after several tens of reflections (or even hundreds) it leaves the cell in the same way (or through the second hole in the mirror). The leaving optical signal is registered by a photoreceiver. While the detection limits reaching α_L ~10^{-7} cm^{-1} (and even better) are available, the multipass spectroscopy system can successfully be applied in explosive detection [64,65].

In *Cavity ring-down spectroscopy* (CRDS) the high sensitivity is achieved in a similar way. The idea was proposed by O'Keefe and Deacon [66]. This technique exploits high quality optical cavity (resonator) consisting of two spherical and high-reflective mirrors. The laser pulse is injected into the cavity and, then, it is reflected multiple times. When the cavity is filled with investigated gas and the laser wavelength is tuned to the gas absorption line, the Q-factor has been decreased. This provides the opportunity to determine the absorption coefficient with the detection limit better than 10^{-9} cm^{-1} [67,68]. Various modifications of this approach have been already elaborated and different methods of Q-factor measurements have been applied [69].

In the Institute of Optoelectronics, MUT in cooperation with the Institute of Experimental Physics, WU various models of optoelectronic sensors employing CEAS technique have been developed. The models were designed to measure trace concentration of nitrogen dioxide (NO_2), nitric oxide (NO), and nitrous oxide (N_2O), which are the most common vaporization products of explosives.

Detection of NO_2 is performed in the blue-violet spectral range ($400 \div 450$ nm) where the absorption bands ($^2A_1 - {}^2B_1$ and $^2A_1 - {}^2B_2$) are observed. Maximum of the absorption cross section varies from values of about 3.5×10^{-19} to 6×10^{-19} m^2. In this wavelength ranges, no absorption interferences from other gases or vapours normally existing in the air are noticed. The simplified scheme of the sensor is shown in Fig. 3(a). This sensor has been described in details in some papers [70,71].

Briefly, the light pulses are generated by a pulsed blue-violet laser diode (TopGaN, lasing at the wavelength of 410 nm with peak power of 500 mW, pulse duration of 50 ns, and repetition rate of 1 kHz). The radiation is introduced to the optical cavity (50-cm long) consisting of two mirrors of high reflectivity coefficient (Los Gatos Research Inc.). Of-axis beam configuration (CEAS method) is also applied. In order to eliminate the broadband fluorescence, a system of diffraction grating and a diaphragm is used. The output signal (leakage radiation from the cavity) is registered by a photomultiplier (Hamamatsu). Acquisition of the experimental signal is achieved with two channel A/D converter (Cleverscope). Temporal method of Q-factor determination is applied [67,72]. Analysis of the signals and determination of NO_2 concentration is performed with special software. The light scattering by some aerosols and smokes existing in the air is reduced due to application of a coalescence filter. Moreover the mirrors of the cavity are heated to the temperature of 50°C in order to avoid water vapour condensation on their surface. The sensor is characterized by detection limit of 1 ppb, and uncertainty of 2%. Its compact construction, as well as low energy consumption, provides the opportunity to be used in different application (Fig. 3b).

Detection of NO and N_2O is performed at the wavelengths of 5.26 μm and of 4.53 μm, respectively (Fig. 4). Within these ranges the absorption spectrum of NO_x consists of series of narrow separated lines corresponding to ro-vibronic transitions in the molecules. Therefore, precise matching of the laser spectrum to selected absorption line is crucial for the sensitivity of such sensor. For this purpose, quantum cascade lasers (QCL) from Alpes Lasers SA are applied. These light sources are characterized by very narrow lines which can be precisely tuned to the desired wavelength by precise setting of temperature and driving current. Proper selection of the absorption lines (Fig. 4) enables to avoid the interferences induced by other gases existing in the atmosphere (H_2O or CO_2) [73,74].

Scheme of the sensor designed for detection of NO and N_2O is presented in Fig 5. The sensor consists of a laser control system, optical system, sample module, and a signal processing unit. The main task of the first unit is to stabilize
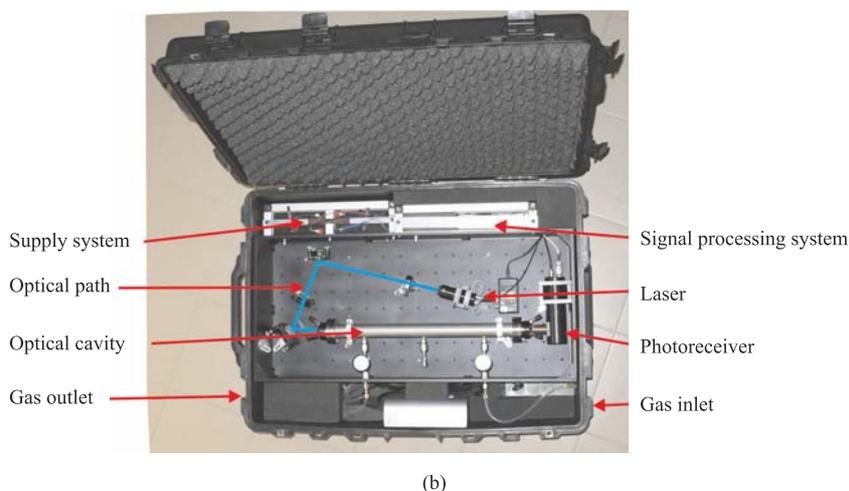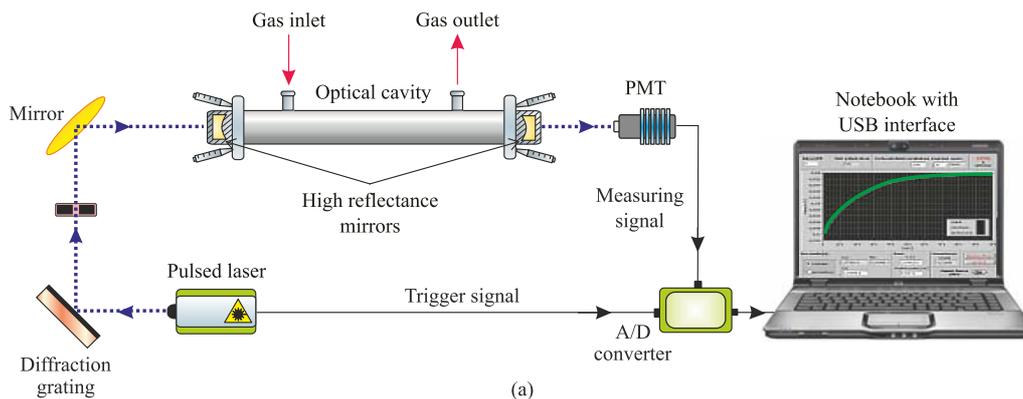
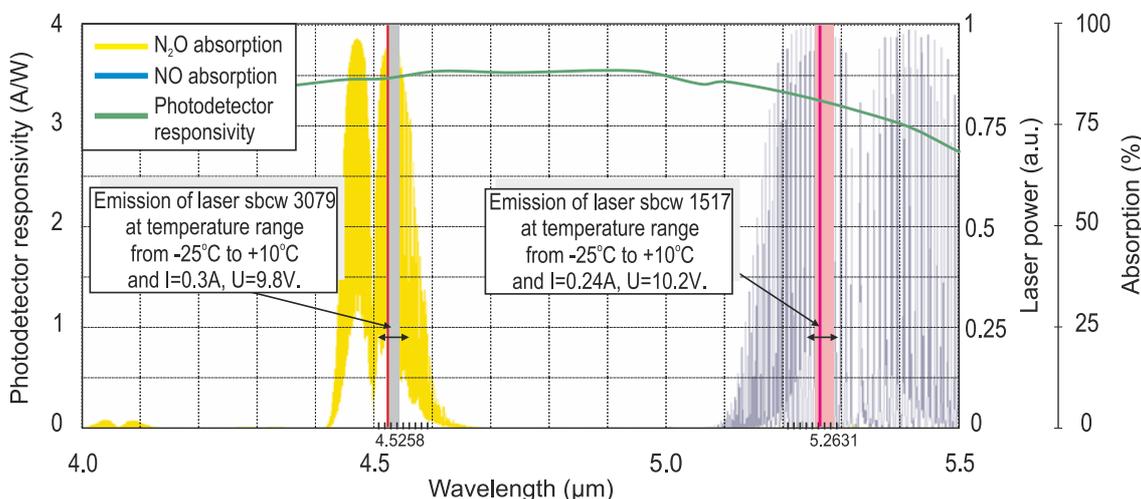Fig. 3. Scheme (a) and photography (b) of portable NO$_2$ sensor.

Fig. 4. Absorption spectra of NO and N$_2$O compared with tuning ranges of QC lasers and responsivity of photodetectors.

the operating conditions of the mentioned QC lasers. Their pulses illuminate two cavities. The two-channel construction enables simultaneous detection of both gases. Signals from the cavities are registered with HgCdTe (MCT) photodetectors (VIGO System S.A.). The sensor provides to detect investigated gases with the detection limit of 47 ppb for N$_2$O, and of 75 ppb for NO. The uncertainties measurements reach value of about 13% [75].

4. Concentrator

For many detection systems based on trace explosives' analysis, the level of sensitivity is insufficient. Then, the enhancement of the sensitivity can be achieved due to concentrator application. This special unit makes it possible to increase either the vapour pressure of explosives or concentration of their traces (like nitrogen oxides).
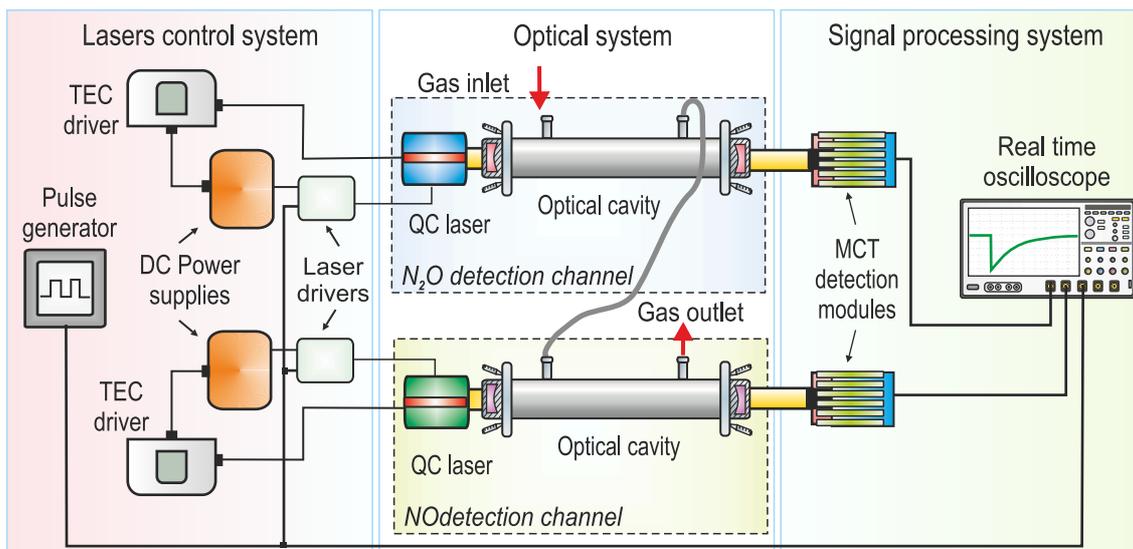
Fig. 5. Scheme of two-channel CEAS sensor for NO and N_2O detection.

The idea of the concentrator operating procedure is shown in Fig. 6. The sorption of trace material is performed from a large incoming flow of the investigated air. An adsorber is used for the collection of interest matter. Next, the emission of characterized gases is carried out during the desorption and thermal decomposition procedures. As a result, there is observed a strong increase in NO, NO_2 and N_2O concentration. It also leads to growth in the detection limit of the explosive detection system. In the concentrator, various adsorbing materials can be applied. In its simplest constructions CuO_2 layers and molecular sieves were used. During the first tests, the cooling and heating of the cooper oxide layer (which is necessary for sorption and desorption process, respectively) was done with Peltier modules. The most important feature of that concentrator was a low-temperature operating range (up to 60°C). Therefore, desorption process could be performed simply in the air. Additionally, a low temperature range does not induce the nitrogen oxidation and enables to avoid NO_x production from the air components which may adversely affect results. Situa-

tion is different in the case of molecular sieves. They are characterized by much higher sorption capacity. However desorption process must be performed in a neutral gas because of need to operate at significantly higher temperature (even higher than 200°C). Successful concentrator with nanotubes of ZnO or TiO_2 in the polymer structures was described by the science group from Silesian University of Technology, Poland [76–78].

As a result of our research two types of concentration units have been developed. The first one provides opportunity to achieve the air flow of about 0.2 l/min. The vapours of the explosives are collected with the adsorption material in a special container. The volume of the container is about 0.4 l. To achieve a rapid thermal decomposition procedure (with temperature of about 100°C/min) a 2kW halogen lamp is applied (Haloline 64784, Osram).

In the second solution the sorbent is heated with an induction generator (Fig. 7). Thanks to this a dynamic increase of the sorbent temperature is achieved (up to 1200°C/min.) in a small volume of the sorption material
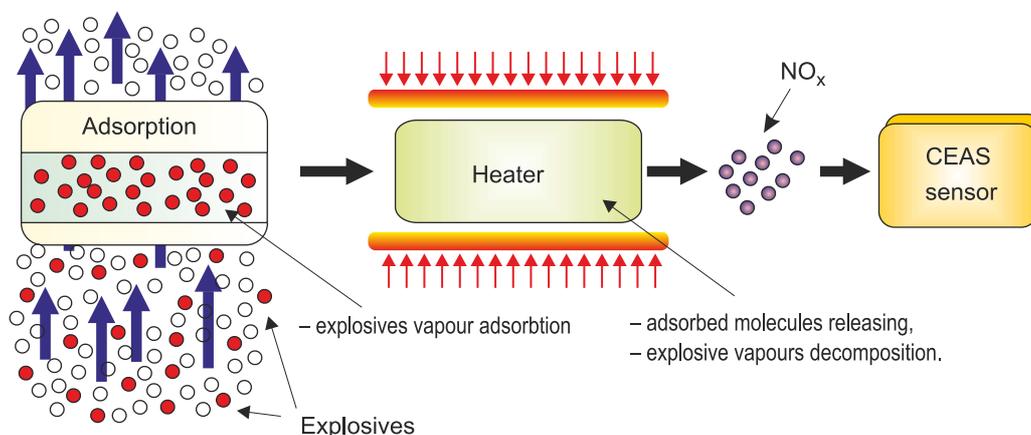

Fig. 6. Idea of concentrator operation: sorption, desorption and thermal decomposition of explosives vapour.
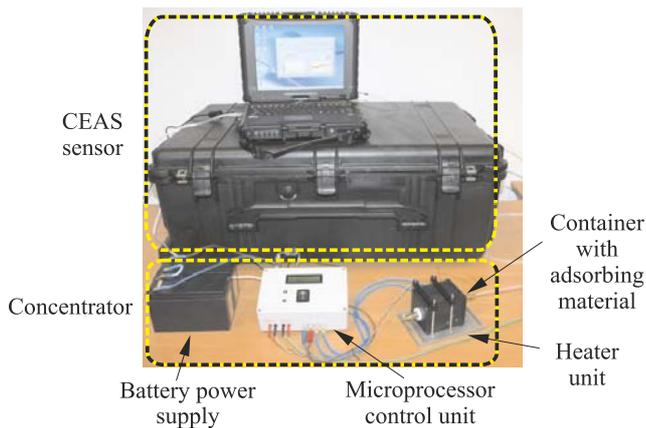
Fig. 7. Portable NO$_2$ sensor with concentrator.

Fig. 8. Detection of explosives with NO$_2$ optoelectronic sensor in Polish mine.

(about 1 cm^3). The air flow of about 5 l/min is available. Both adsorption and decomposition processes are controlled by microprocessor unit, and portable computer with a special software. Due to low energy consumption the unit can be supplied with a battery (two 12 V, 7 Ah).

5. Detection of explosives with NO$_x$ sensors

The constructed optoelectronic sensors of NO$_x$ were used for detection of explosives and explosive devices. Preliminary practical studies with the portable NO$_2$ optoelectronic sensor were performed in one of the Polish mines, where the explosive devices with NG and ammonium nitrate were investigated.

The measurements were carried out in specific and harsh conditions at the ground depth about 1100 m. Several scenarios of investigation were prepared. Figure 8 presents an example of results of nitrogen dioxide concentration measurement, which was performed for 40 min. with repetition of 8. The determined value of background concentration of NO$_2$ was of several ppb. During the first step of experiment, the explosives were searched in various containers. The peak detection signal of 30 ppb was observed at the time moment of 6.5 min. when the sensor inlet was treating a non-hermetic package. The second investigation concerned people, their clothes and equipment. The peak of about 40 ppb was recorded at the time of 8.3 min. which corresponds to investigations of hands the workers who had touched the explosive. Particles of dynamite which remained on the hand were decomposed at an elevated temperature (e.g., the temperature of human body – see Tab. 1). That is why higher signal than in the first step was noticed. The results registered in the time interval of 10 min. and 30 min. correspond to passage of a miners' group of 50 people using machines and vehicles equipped with diesel engines. Therefore, the maximum concentration of NO$_2$ was increased even to the level of 60 – 100 ppb. Additionally, the group presence caused a growth in a background concentration to the value of ~20 ppb. Nevertheless, the subsequent investigation of the hands of a miner who was in frequent
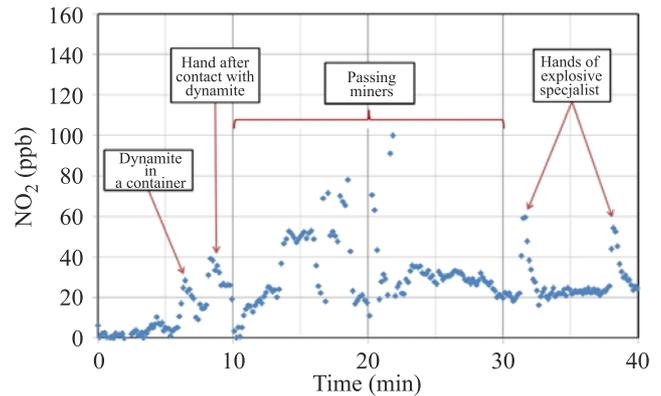
contact with the dynamite generated next two signal peaks of 60 ppb (at 33 and 38 min).

The experiments showed that NO$_2$ sensor enables to distinguish peoples and objects that had got contact with the explosives characterized by high pressure of the vapours, as well as to find the explosive in a non-hermetic package.

Next experiment concerned a detection of nitrogen oxides produced during a thermal decomposition of explosives. Special adsorbent composed of Al$_2$O$_3$(95%) and CeO$_2$(5%) was prepared. It was obtained due to a 4-hour heating of slurry of aluminium oxide powder in an aqueous solution nitrate hexa (V) and ceric ammonium (NH$_4$) 2Ce (NO$_3$)$_6$] at

Table 1. Vapour pressure of explosives at various temperatures [79].

Explosives name	Temperature (°C)	Saturation pressure	
		ppm/ppb/ppt	Torr
Trinitrotoluene (TNT)	25	7.7 $\cdot 10^{-3}$ ppm	5.8 $\cdot 10^{-6}$
	85	70 ppm	0.053
	100	140 ppm	0.106
	150	4 $\cdot 10^3$ ppm	3.0
	200	14 $\cdot 10^3$ ppm	10.5
Hexogen (RDX)	25	6.0 $\cdot 10^{-3}$ ppb	4.6 $\cdot 10^{-9}$
	43	0.1 ppb	7.6 $\cdot 10^{-8}$
	100	100 ppb	7.6 $\cdot 10^{-5}$
	200	1.2 10^5 ppb	0.09
Octogen (HMX)	100	3.95 ppt	3.0 $\cdot 10^{-9}$
Penthrite (PETN)	25	18 ppt	1.4 $\cdot 10^{-8}$
	97	1.1 ppm	3.38 $\cdot 10^{-4}$
	139	93 ppm	7.08 $\cdot 10^{-2}$
Nitroglycerine (NG)	20	0.34 ppm	2.6 $\cdot 10^{-4}$
	26	0.41 ppm	3.1 $\cdot 10^{-4}$
	93	400 ppm	0.31
Ammonium nitrate (NH$_4$NO$_3$)	25	12 ppb	9.1 $\cdot 10^{-6}$
	35	29 ppb	22 $\cdot 10^{-6}$
	50	103 ppb	73.8 $\cdot 10^{-6}$
	80	870 ppb	661 $\cdot 10^{-6}$

the temperature of 300°C. Thanks to this developed surface of the high adsorption capacity material is achieved. Such sorbent catalyses the thermal decomposition process additionally. It also provides opportunity to increase the frequency of adsorption-decomposition cycles. During the experiments, Tenax and Carboxen sorbents were investigated, as well.

The explosive samples were diluted in acetone. The samples containing 1 ng, 10 ng and 100 ng of TNT solution were prepared, respectively. The samples were subsequently placed in the concentrator with the induction heater where thermal decomposition was performed. The gas products of this process were transported to the sensor in argon flow (2 l/min). In the sensor, the measurements of nitric oxide and nitrous oxide were made.

In the first step of investigations, the calibration procedure of the system was performed. During that step, the value of Q-factor of the sensor cavity was determined. Then two-steps' preparation procedure of the sensor was started. During 60s the sensor cleaning process using argon was performed. After that the sensor sensitivity was verified with a reference mixture from a gas bottle (10 ppm of NO or N_2O).

Thermal decomposition of explosives was carried out in the argon atmosphere and at different values of sorbent temperatures. The measurement showed that the highest concentrations were recorded using Carboxen sorbent. The concentration of nitrous oxide varied in the range from tens to hundreds of ppb for all samples with mixture of 1 ng. In the same setup, the concentration of nitric oxide reached much higher values, for example for Carboxen the level of ppm was obtained. For TNT and PETN the significant increase in NO_x concentration was observed at the temperature of 160°C. In comparison, for RDX and HMX the growth in concentration of nitrogen oxides was observed at the higher temperatures. It can be explained by different values of their vapour pressure. Hexogen and octogen are characterized by lower vapour pressure than TNT and PETN. As a consequence the concentration of nitric oxide and of nitrous oxide was lower, as well. The results are listed in Tables 2 and 3.

Table 2. Concentration of NO and NO_2 registered during thermal decomposition of selected explosives using Carboxen sorbent.

Explosive	Adsorber Temperature (°C)		Nitric oxide concentration [ppb]		Nitrous oxid concentration [ppb]	
	MIN	MAX	MIN	MAX	MIN	MAX
TNT	250	350	670	3600	120	660
PETN	160	350	100	1500	300	590
RDX	230	350	50	2100	100	560
HMX	280	350	20	2500	20	640

We can conclude that the developed systems enable to detect the explosives portions of 1 ng such as TNT, PETN, RDX, HMX. However, for some explosives characterized by low vapour pressure (Tab. 1) the use of vapour concentrator might be necessary.

Table 3. Concentration of NO and NO_2 registered during thermal decomposition of selected explosives using Tenax sorbent.

Explosive	Adsorber Temperature (°C)		Nitric oxide concentration [ppb]		Nitrous oxid concentration [ppb]	
	MIN	MAX	MIN	MAX	MIN	MAX
TNT	170	250	10	170	100	360
PETN	250	300	15	130	100	440
RDX	270	300	10	300	80	160
HMX	300	330	5	220	20	135

6. Conclusions

Effective detection of explosive devices requires development of complex and advanced sensors. Beside various techniques of bulk detection, there are also systems searching traces of explosive materials. For these systems, explosive vapours, as well as emitting gases, are very useful. We have shown that the designed optoelectronic sensors of NO_x applying the achievements of modern laser spectroscopy (like CEAS detection technique with QC lasers) and the concentrator provide to detect nanograms of TNT, PETN, RDX, HMX. Similar sensor of NO_2 (with blue-violet diode laser) operating without the concentrator enables quick and successful detection of dynamite in a non-hermetic package as well as both people and objects that have got a contact with the explosives. There is observed a fast progress in the developments of optoelectronic elements which can be used in the described experiments. That is why in the nearest future a high increase in detection limit of such sensors is also expected.

Acknowledgements

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