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SENSORS AND SYSTEMS FOR THE DETECTION OF EXPLOSIVE DEVICES – AN OVERVIEW

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Abstract

The paper presents analyses of current research projects connected with explosive material sensors. Sensors are described assigned to X and γ radiation, optical radiation sensors, as well as detectors applied in gas chromatography, electrochemical and chemical sensors. Furthermore, neutron techniques and magnetic resonance devices were analyzed. Special attention was drawn to optoelectronic sensors of explosive devices.

Keywords: Explosive device sensors, detection of explosive materials.

1. Introduction

Nowadays a lot of attention is being paid to the development of methods and instrumentation for the detection of explosives.

Initiated explosives have already killed thousands of people and injured several tens of thousands. Infrastructural facilities, like railway stations, airports, undergrounded railways; water supply, etc. are preferred targets involving up to thousands of people. Assuming, the methods will be found to early detect explosives by means of sensors [1].

New forms of bomb attacks are more sophisticated, more dangerous, using remote control of *Improvised Explosive Devices* (IED); initiation by mobile phones permits terrorists to initiate a bomb immediately. Therefore, detection systems with a reliable detection efficiency used in broad range of IEDs are an important problem.

An IED is an improvised explosive charge, equipped with a non-standard (home-made) or a professional detonator. But, an *Improvised Explosive* (IE) may be any chemical or mixture capable of an explosive reaction. Components of IE are typically inorganic salts containing molecular bound oxygen, like nitrates, chlorates, perchlorates or organic compounds with nitro-, nitamine- or nitrate-groups or peroxides.

There are more than one hundred types of military and civilian explosives and around twenty commonly used drugs. A number of explosive characteristics can be used for their detection [2]:

- geometry (the presence a metallic detonator can be detected using image shape analysis),
- material density (explosive material is denser than most organic materials),
- elemental composition (e.g. vapor emission analysis can be used to detect them),
- vapor emissions (e.g. nitrogen or its compounds can be detected in a vapor sample).

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IED detection techniques can be divided into two groups: bulk detection of explosives, and trace detection of explosives.

In bulk detection, a macroscopic mass of explosive material is detected directly, usually by viewing images made by X-ray scanners or similar equipment.

In trace detection, the explosive is detected by chemical identification of microscopic residues of the explosive compound. These residues can be applied in either or both of two forms: vapor and particulate.

Vapor detection refers to gas-phase molecules emitted by a solid or liquid explosive. The concentration of explosives in the air is related to the vapor pressure of the explosive material and to other factors, such as the duration of the presence explosive material in the given location, its packing, temperature, air circulation in the location, etc.

In particulate detection microscopic particles of solid explosive material adhering to the surface (i.e., by direct contact with the explosive, or indirectly, by its contact with someone's hands in handling the explosives).

Unlike bulk detection that aims to detect large quantities of explosives, vapor detectors search for very small quantities, less than a microgram. Hydrogen, Nitrogen, Carbon and Oxygen are the main components in an explosive.

The concentration of explosives can be divided in to three groups: high, medium, and low vapor pressure. Fig. 1 shows the maximum vapor concentration in air concerning several explosives at room temperature.

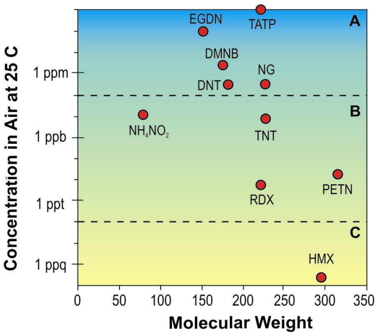

Fig. 1. Vapor concentration of explosives (A, B and C - high, medium and low respectively).

High vapor pressure of explosives includes ethylene glycol dinitrate (EGDN), nitroglycerin (NG), and 2,4-dinitrotoluene (DNT). These explosives have equilibrium vapor concentrations in air in the order of about one part per million (1ppm). Medium vapor pressure explosives have equilibrium vapor concentrations in air near one part per billion (1ppb), and low vapor pressure explosives - one part per trillion (1 ppt). The medium vapor pressure group includes TNT (2,4,6- trinitrotoluene) and ammonium nitrate (NH_4NO_3). The low vapor pressure group includes HMX (octogen), RDX (hexogen or cyclonite), and PETN (pentaerythritoltetranitrate). This vapor pressure concerns pure materials. The vapor pressure of mixtures containing these explosives may be even lower.

The relative values of the vapor pressures are important in the case of trace detection of explosives. High vapor pressure explosives are relatively easy to detect using sensors such as ion mobility spectrometers [3] or electron capture detectors. Thus, dynamites (containing EGDN and NG) can usually be detected from their vapor. Medium vapor pressure explosives are in many cases detected using surface swiping [4]. Low vapor pressure explosives do not produce enough volatiles to be determined in this way in any but only the most exceptional circumstances. Usually these compounds are detected using trace technology; especially swipe collections of particulate materials are preferred.

The vapor pressure of a substance increases exponentially with temperature rise. This means that one possible way increasing the chance of vapor detection of explosives is to heat the object.

2. Bulk detection systems

A number of techniques based on X-rays, gamma rays, infrared, terahertz-waves, and millimetre waves have been employed to detect weapons and explosives. The techniques of detection of explosives are detailed below.

The bulk detection method includes (Fig. 2):

- X-ray and gamma ray systems,
- neutron methods,
- electromagnetic systems.

Bulk detection is usually not applicable for the direct scanning of persons (health hazard).

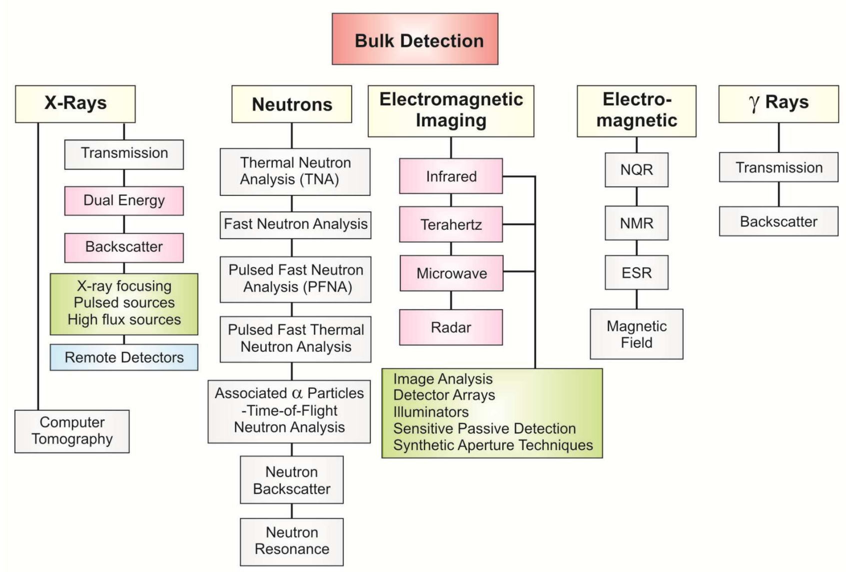

Fig. 2. Overview bulk detection of explosives.

In the X-ray detection method, the penetrating depth of radiation is high in most materials. This virtue makes it possible to investigate the contents in containers, packets, and suitcases. For the detection of explosives X-rays are used with energy from a thousand up to millions of electron volts (10^{-4} – 10^{-7} μm). In these methods the beam of X-rays passing through a material is absorbed. The attenuation coefficient depends on the energy of the X-rays and the effective atomic number of the material. The number of X-ray photons in the beam is determined by three effects:

- photoelectric absorption,
- Compton scattering,
- positron and electron production.

There are two main detection techniques based on analyses of radiation passing through the investigated material (transmitted radiation).

Single energy X-ray systems operated at airports use electron energies of 120 keV. They provide good resolution pictures to detect weapons with metal elements. In the case of explosives placed behind or within items characterized by a higher atomic number, the technique is inefficient. These devices cannot distinguish between a thin sheet of a strong absorber and a thick slab of a weak absorber. The standard system cannot identify the actual explosive material, but allows to detect control wires, batteries, detonators and other components of a bomb. Simplify, the system does not detect explosives but only explosive devices.

In dual-energy X-ray systems two different attenuation coefficients are determined. It is possible to distinguish atoms of higher and lower atomic number in the investigated object, for example dense elements (metals) and less dense ones (food, clothes, etc.). But the X-ray intensities for each object are related not only to its material composition which reflects the intrinsic property, but also to some extrinsic parameters such as position, orientation and thickness. That is why the simple dual-energy analysis is better than single energy one, which can be easily confused without the knowledge of material density [5].

In Compton scattering, the energy of a scattered photon is determined by the wavelength of the incident photon and the scattered angle. This effect is used in *backscattered detection systems*. Compared with transmission radiation, the difference between the obtained image of organic and inorganic materials is higher. Practically, the backscattering system is usually more effective for the detection of materials with a low atomic number (e.g. explosives, narcotics) than the transmission system which is useful for metal imaging. There are several detection methods based on scattering radiation [6]. It has been observed that at large angles, it is possible to measure both scattered and transmitted photons. Both measurements indicate high-density, low atomic number materials, the signatures of explosives. There are also systems based on three detectors: two scattering and one transmission detector [7]. The detectors register both forward and backward photons. Basing on the registered signals, the profile of the investigated object is obtained. For the detection of sheet explosives (in passenger luggage), a low angle scattering method has also been proposed. Changing the scattering angle, the energy of the incident photons is modified by the diffraction effects. In this method, the obtained pattern of energy distribution is unique and defines the molecular structure of the material. Experimental results have shown that the method makes it possible to detect PE4 and Semtex (amount of 250 g, shape of sheet with 5 mm thickness and area of 280 cm^2). For the detection of explosives, also the high-energy X-ray imaging is applied. This kind of system is used to investigate large objects (containers) [8]. For the high-energy, e.g. 10MeV, increases the detection with the depth of penetration. The registered interaction (forward Compton scattering) is independent of atomic number; that is why two different energies have to be applied. In data analyses from the X-rays systems, the numerical reconstruction of a cross-section image is needed.

Computer tomography (CT) is one of the two of data analyses based on information from X-ray projections at several angles around an investigated object. The CT image is obtained using both absorption and scattering attenuation properties of each volume element. In the detection procedure, the transmitted radiation is measured. The detector does not provide the image but cumulates the amount of photons. The collected rays are processed to obtain a real image. The efficiency of such a procedure is determined by the number of projections used to form the CT scan image. The CT resolution is determined by the spatial and contrast parameters. The X-ray methods are still developed. There are a lot of new scientific ideas of obtaining a low fast alarm rate and a good resolution of imaging, for example angular dispersive X-ray diffraction (ADXRD) [9], multi-energy X-ray computed tomography [10], coded aperture imaging using backscattered X-ray radiation [11].

In the *neutron detection method*, instead of photons, neutrons are used. This technique provides better results, but at a higher cost and slower speed. Within the frame of this method, *Thermal Neutron Activation* (TNA), *Fast Neutron Analysis* (FNA), *Pulsed Fast Neutron Analysis* (PFNA), *Pulsed Fast Thermal Neutron Analysis* (PFTNA) and *Nuclear Resonance Absorption* (NRA) have been defined [12].

The TNA method bases on the identification of nitrogen in explosives. During the absorption of a neutron by a nucleus, the emission of gamma radiation is observed. The radiation energy is characteristic of the nucleus. The analysis of gamma rays intensity emitted by a tested object after its neutron exposure makes it possible to detect some explosive materials. The TNA method is also applied to generate a spatial distribution of nitrogen. It can be used to detect nitrogen but not oxygen or carbon. That is why the method does not distinguish nitrogen oxides in explosives and in the environment. This limitation leads to a high false alarm rate. In addition, the sensitivity of the TNA detection system is limited and its price is very high. It is applied for the detection of drugs and explosives in luggage and small packages, liquid explosive in bottles and bags, buried landmines and unexploded ordnance [13, 14]. Summarily, the TNA method is able to characterize High Explosives (HE) by their nitrogen and hydrogen signature, but with restricted sensitivity.

The FNA technique is the next step of TNA development. Using high energy neutrons, the gamma radiation at different energies is detected and distinguished [15]. For example, common explosives are characterized by the specific density ratio of nitrogen and oxygen. Moreover, the detection of carbon and hydrogen is also possible. That makes this technique more sensitive and false alarm resistant. In summary, FNA is sensitive to nearly all elements in explosives and permits to identify the analyzed substance but usually it is far more complex and expensive.

The same concept of detection has the *PFNA method* using a pulsed beam of neutrons [16]. However, the energy of penetrating neutrons is lower than FNA. In this technique, it is possible to obtain 3D position information, applying beam profile movement and special timing and image reconstruction. The main advantage of PFNA is not only the determination of the composition of explosives but also their spatial location and concentration. The main problem of the technique is to construct a specific pulsed energetic neutron source. The advantages of PFNA are: a highly informative, reliable and low level of the gamma-background, since gamma-rays are measured only between the neutron pulses. However, in order to have nanosecond neutron beams, a PFNA device must use accelerators of large particles, which are bulky and expensive.

Compared to this technique, *PFTNA* applies neutron beam pulses with higher duration time (10 microseconds) [17]. Nowadays, the PFTNA detection systems are portable. The main advantages of PFTNA are: high reliability, mobile construction, operation with one-side access to the object.

Nuclear magnetic resonance (NMR) *spectroscopy* identifies the atomic configuration of molecules. During the detection procedure, a characteristic absorption of energy by certain spinning nuclei in a strong magnetic field is observed. If the nucleus is placed in a magnetic field, interaction between magnetic moment and the magnetic field is observed. The energy of the nucleus changes with discrete values. Using an external electromagnetic field with a matched frequency, the photons are absorbed. The frequency of absorbed photons is called resonance frequency. By scanning the frequency of the transmitted RF field (perpendicular to the magnetic field), an absorption signal is detected. The resonating nuclear magnetic moments indicate a detectable RF voltage signal. A spectrum of signal amplitudes of different nuclei can be obtained using two ways:

- the magnetic field over the region is changed linearly round the resonance value,
- applying a constant magnetic field and varying the frequency of the oscillating field.

In the NMR, the determinants of the substances are: level of relaxations, spin-lattice relaxation time, spin-spin relaxation time and coupling constant. This technique may be used for the detection of explosives concealed in parcels, letters, and airline baggage. The principle of NMR usually involves two sequential steps: first, the alignment of the magnetic nuclear spins in constant-magnetic field, and then the perturbation of this alignment by radio frequency pulse. The perturbing frequency is dependent upon the static magnetic field and the nuclei of observation. The spin-spin relaxation time is characteristic of the molecular structure and the state of the sample material. Practically, in the detection of explosives, multiple transmitted pulses with specific energy and repetition rate are used. The pulses provide opportunity to obtain good selectivity of two relaxation times and the ^{1}H-^{14}N cross-coupling. The results showed that for the measured frequency of 3 MHz the values of relaxation times are very characteristic for explosives. The sensitivity of the method is affected by the density of the target nuclei in the material and by sensor parameters. NMR spectroscopy was used in detection of PETN [18], 1-Nitratoethyl-5-nitriminotetrazole derivatives [19].

The Electron spin resonance (ESR) or *Electron paramagnetic resonance* (EPR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons. The basic physical concepts of ESR are analogous to those of nuclear magnetic resonance (NMR), but these are electron spins that are excited instead of spins of atomic nuclei [20]. The magnetic field splits the spins into two groups (aligned and opposite with the magnetic field). Each orientation is associated with a different energy. Incident microwave radiation may induce transitions between the two states of the unpaired electron. In the case of the specific quanta energy resonance absorption is observed. Huge mass difference between nuclei and electrons makes that for ESR the lower magnetic fields and much larger microwave frequencies are applied than for NMR. The sensitivity of the method depends on the population ratio of the analyzed states. That is why the sensitivity of the method is improved by using of a low temperature. Thus, an ESR spectrum is obtained by recording the amount of microwave energy absorbed by the sample as a function of the magnetic field. In the case of the detection of explosives, the ESR spectroscopy is limited to some materials having free spins. In comparison with NMR, the ESR has a higher inherent sensitivity (around 15 000 times). The ESR instrument permits to detect black powder with a quantity of 18 mg.

Nuclear quadruple resonance (NQR) *spectroscopy* is based on specific characters of the material nuclei. The significant properties of the nuclei are magnetic moments and electric quadrupole moments. A nucleus may possess an intrinsic nuclear spin working as a little magnet with magnetic momentum. In some nuclei such as ^{14}N, ^{17}O, ^{35}Cl, ^{37}Cl large quadrupolar interactions (spin relaxations) may be observed. The relaxations are characterized by the large line widths. Quadrupole splitting can be observed directly using the NQR technique. In the NMR method the splitting is induced by a large external magnetic field. For this reason gas, liquid or solid, can be analyzed by NMR spectroscopy. In the case of the NQR method, the measurements are taken in the absence of any external perturbation. Therefore, NQR analyses should be performed in the solid phase at low temperatures. NQR can be used for a very precise determination of the local distribution of the electron density in molecules, providing more accurate results than NMR. Unfortunately, NQR signals are also inherently weak and vulnerable both to the thermal noise of the coil and any external radio frequency interference (RFI). In many NQR applications, RF interference (RFI) can be a major concern. There are also some methods to increase the signal-to-noise ratio [21, 22]. NQR is highly amenable to explosive analysis as these substances, such as TNT, RDX, HMTD [23, 24] etc., are typically rich in 14N (nitrogen) nuclei with a spin quantum number of 1, having electric quadrupole moments [25]. The registered spectra are unique for a given explosive material and are not susceptible to the interference of other materials containing nitrogen during the NQR measurement. The main advantage of ^{14}N-NQR resonance spectroscopy in the detection of explosives results from the high chemical and crystallographic specificity of NQR spectra. The spectra depend very strongly on changes in electronic charge distribution over the whole molecule. On the other hand, NQR detection is characterized by relatively low sensitivity caused by low resonance frequencies (0.5–6 MHz) [26, 27]. The results showed that the NQR technique can be used in the detection of explosives in luggage. Using specific transition frequencies of 3.4 MHz for RDX and 0.89 MHz for PETN, the relaxation times are 11 ms/0.9 ms and 32s/0.9 ms, respectively.

In γ–Ray detection, radiation emitted by atoms from the excited nuclei is exploited. Excited nuclei emit the γ–photon with definite energy due to transition to a lower state. The radiation from such source passes through the investigated object and is attenuated by three processes: photoelectric effect, Compton effect and pair production. The first effect is most significant in the case of heavy absorbing elements and for low photon energies. The Compton effect is important in the case of light elements and photon energies below the value of 3 MeV. Positrons and electrons are produced by heavy elements and high energy of γ–photons. In the case of the γ–Ray system based on pair formation, the γ–photons interact with the explosives activating the nitrogen. During the positron emission two coincident photons with energy of 511 keV are created. The photons are detected by a standard scintillator. The high energy photons penetrate easily most materials and permit to inspect big objects (luggage, cargo). The second method using γ–Rays is named γ–Ray nuclear resonance absorption (NRA). By scanning with high energy γ–Rays and by measuring the transmission profile of the photons, the regions characterized by high nitrogen concentration are imaged. The large absorption cross section makes the method sensitive to small amounts of nitrogen. But the whole detection procedure is complicated because of critical requirements concerning special target material and shape, as well as γ–Ray source intensity and stability.

3. Vapor detection methods

Vapor detection methods are non-invasive and measure traces of characteristic volatile compounds that evaporate from the explosive. Various explosives have different volatilities. Volatility is characterized by the concentration of saturated vapors near the surface of the explosive. The vapor concentration from some explosives at the temperature of 25ºC is equal to: nitroglycerine - $4{,}1\cdot10^2$ ppb, TNT - 7,7ppb, PETN - 18 ppt, RDX - 6 ppt [28]. However, the concentration of explosives vapor inside the sensors is many orders of magnitude lower than the pressure of saturated vapor on the explosives surface. Although the sensitivity of the respective methods depends on the vapor pressure, additional factors limit its sensitivity as follows: efficiencies of vapor collection, and enhancement (preconcentrators), as well as transport of vapor. Vapor pressure drops if the explosive devices (ED) are sealed, packed in a bag. Low temperatures and a strong wind decrease the detection sensitivity as well. Modern vapor sensors can reliably detect explosives with vapor pressure in the range of 10^2-10^3 ppb. Explosives with a vapor pressure less than 1 ppb (RDX, PETN, HMX) cannot be detected without preconcentrators.

Vapors and traces are currently detected by means of (Fig. 3):

- electronic/chemical sensors,
- optical sensors,
- biosensors.

Electronic/chemical sensors can be divided into four main groups (Fig. 3). The following subsections discuss specific detection technologies.

An electronic nose, or ENose, is usually composed of a chemical sensing system and a pattern-recognition system, such as an artificial neural network. Each vapor presented to the system produces a signature (‘fingerprint’). Presenting many different chemicals to the sensor yields a database of fingerprints, which the pattern-recognition system uses to recognize and automatically identify each chemical. Sensor arrays offer several advantages over single sensors; e.g. better selectivity, multicomponent analysis, and analyte recognition. Some electronic noses use fluorescent polymers, fiber-optic cables [29], arrays of different polymeric thin film sensors [30], gold nanoclusters deposited on interdigital microelectrode arrays [31], surface acoustic wave [32, 33], quartz crystal microbalance gas sensors, and micro-electromechanical systems [34]. In future these systems will replace some of the larger and more expensive detection devices. ENose can detect an electronic change of about 1 part per million [35].

In the *gas chromatography* (GS) method the carrier gas containing vapors of explosives moves inside a capillary whose internal surface is covered by a sorbent. The analyzed compounds reach the end of the capillary at different times depending on the relation between the solubility of the compounds in the sorbent and in the carrier gas. As the compounds exit the end of the column, they are detected and identified electronically [36]. An advantage of this method is its high sensitivity and the possibility of detecting various explosives (TNT, PETN, RDX, etc.) [37].

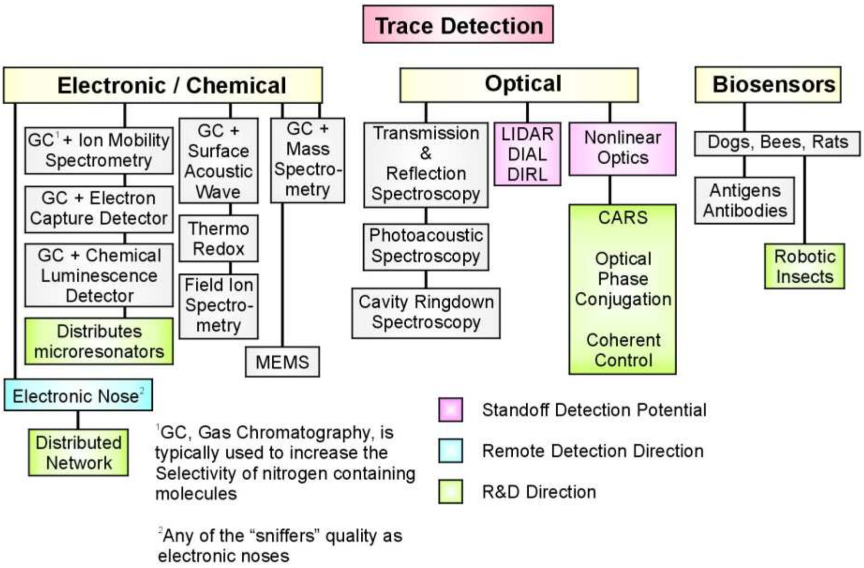

Fig. 3. Overview traces detection of explosives.

Ion mobility spectrometry (IMS) is one of the most widely used techniques for the trace detection of explosives. Typically, an IMS consists of an ion source region, an ion gate, a drift region and a detector. The radioactive source (e.g. radioactive 63Ni isotope) is used to produce ionized reactants which ionize the sample molecules. The sample flow is passed through an ionization chamber and then enters a measurement area where the ions are deflected into one or more measuring electrodes by a perpendicular electric field which can be either static or varying. The output of the sensor is characteristic of the ion mobility distribution and can be used for detection and identification purposes. The current collected at the electrode is measured as a function of time. Next the IMS spectrum is plotted as an ion current versus time, with different peaks representing different specific ions. An advantage of this method is its speed (measurements take only few seconds), but a disadvantage is its low selectivity.

Chemiluminescence (CL) can detect the characteristic emission of radiation from a molecule, atom or effective fluorophore, in an excited state, produced in an exothermic chemical reaction. It can take place in gas, liquid and solid state. The analyzed vapors of explosives (NO_2 groups) are mixed with ozone, exciting NO_2 molecules. Characteristic light emitted by these molecules is then detected [38]. One of the most important disadvantages of these methods is the lack of selectivity. This can be improved by coupling CL by means of different separation methods (GS) [39].

Thermo-redox (reduction-oxidation) sensors are based on the thermal decomposition of explosives and subsequent reduction of NO_2 groups. The method is used to detect the presence of NO_2 molecules. The sensors cannot detect non-nitrogen explosives, and neither distinguish explosives in other substances containing NO_2 groups [40].

Electron capture (ECD) sensors can detect vapor of substances that strongly capture thermal electrons. The ECD sensor by itself cannot distinguish individual types of explosives from each other or certain interferents; so a gas chromatograph is placed at the front end to allow temporal identification of different explosives. This type of detector has a typical sensitivity of about 1 ppb for most electron-capture compounds [41, 42].

Surface Acoustic Wave/Gas Chromatography (SAW/GC) is a kind of technological method that allows to emulate hundreds of individual SAW sensors. In the system the gas mixture is separated using a chromatographic column and next each gas fraction from its outlet is detected using a SAW sensor. This principle is utilized in the Z-nose^{TM} [43, 44]. The SAW sensor signals give the information about intensity changes of testing fraction in time interval (depending on chromatographic column properties). In result a SAW/GC chromatogram is obtained. Each gas mixture has a unique chromatogram and can be identified. Using this technology method it is possible to distinguish the odors of different gas mixtures. It allows to investigate the quality of food, cosmetics etc. [45]. For military applications it permits to detect explosives, bacteria and toxins [46].

Field Ion Spectrometry (FIS) contains a unique ion filter using a dual transverse filter, which allows to eliminate electronically interferences, without using other physical separation methods. Its principle is based on filtering ion species according to the functional dependence of their mobilities with electric field strength. Field ion spectrometry eliminates the gating electrodes needed in conventional IMS to pulse ions into the spectrometer; instead, ions are injected into the spectrometer and reach the detector continuously, resulting in improved sensitivity. The detection is limited to explosives such as RDX, TNT, and PETN in the low picogram range. The obtained characteristic is the same as in IMS [47].

Biosensors are devices that integrate a biological element on a solid state surface, permitting its interaction with an analyte and signal transduction. Biological elements form such materials as: peptides, enzymes, receptors, single strand DNA [48]. Detection of TNT and DNT has been demonstrated using proteins immobilized on electrodes [49]. Immunoassays use antibodies as recognition elements in biosensors. Electrochemiluminescent immunoassays have been developed for TNT detection, in which enzyme-labelled antibodies bounding to paramagnetic beads on the electrode surface are used. TNT was detected by using this method in 80s to a sensitivity of 31 ppb [50]. To find hidden sources of explosive vapors some kind of animals (e.g. dogs, bees, rats) are trained. The animal is trained to adapt a particular behavior when is near the source. The sensitivity of a dog's nose is higher than even the best electronic detectors.

4. Detection of explosives using optical methods

All optical methods determining the chemical composition of air rely on the interaction between light and matter. The effects are divided into two groups: linear and nonlinear. Linear effects are divided into three main groups according to the type of interaction: light absorption, spontaneous Raman scattering and fluorescence. The absorption spectrum can be obtained in the form of a transmission spectrum, a reflectance spectrum, the spectrum of attenuation of the return signal in lidar technique, and a spectrum of optical losses of a resonator. The analysis of the absorption spectra allows to identify the species absorbing the light. Although optical spectroscopy is widely used in measurements of low concentration of the trace of atmospheric gases, they have not yet found wide application in the detection of explosives. This technique provides good results only in the case of long-path absorption. However, recently these methods have been attracting interest due to their use in future detection systems. Some of these methods are described below.

An analysis of nonlinear effects of optical interaction has not been dealt with in this paper. However, significant advances in the equipment are available, especially by using a femtosecond laser.

Ultraviolet-Visible-Near-Infrared (UV-VIS-NIR) *spectroscopy* is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials. This application usually requires recording at least a portion of the spectrum characterizing the optical or electronic properties of materials. Nevertheless, IR spectroscopy methods are used to detect and identify traces of explosives on the surface of explosive devices or in solids after condensing sample.

Spontaneous Raman scattering of light can be characterized as the interaction process of inelastic scattering of photons by molecules of a substance. This process results in changes of the energy states of interacted molecules and photons created by them having energy different than that of incident ones. The Raman spectrum consists of bands shifted with respect to the line of exciting radiation. This shift and shape of spectral bands are the fingerprints of detected material. The position of Raman spectrum on the wavelength scale is determined by the wavelength of excitation radiation, which will be optimized. The detectability thresholds for Raman methods are equal: ppm, ppb, and ppt for spontaneous Raman, resonance Raman, and surface-enhanced Raman scattering respectively (SERS) [51]. The sensitivity of the first method is insufficient to detect traces of explosives in the atmosphere. If the frequency of the exciting radiation approaches the allowed transition of the molecules, the efficiency of Raman scattering undergoes a resonant increase of about four orders of magnitude. Therefore, this method can be used to detect explosives, even by standoff sensors. The SERS effect is based on the enhancement of Raman scattering intensity by molecules, which are adsorbed on a rough gold or copper surface. The mechanism of this enhancement is related to locally high-strength electromagnetic fields that can appear at the surface in homogeneities. In this sensor the air probe is blown over the surface, which is illuminated by laser radiation. These sensors allow to detect mines in minefields.

Laser-induced fluorescence (LIF) is a commonly-used analytical tool for the detection and identification of many substances. It is a very valuable tool in combustion diagnostics and for the study of the decomposition of explosives. Researchers at the Gdansk University of Technology applied two laser excitation lines for identification, by comparing Raman spectra, of the popular explosive RDX (hexogen). Some selected peaks are more intensive in the case of 355 nm laser excitation than at 785 nm, which helps to identify the investigated sample. Such spectra are observed in the case of some common explosives but not all of them demonstrated these features [52].

Massachusetts Institute of Technology researchers have created a new detector, so sensitive that it can pick up a single molecule of an explosive such as TNT. In the sensor the target binds to the bee-venom protein coating the nanotubes, it shifts the fluorescent light's wavelength. Each nanotube-peptide combination reacts differently to different nitro-aromatic compounds. By using several different nanotubes coated in different bombolitins, researchers can identify a unique "fingerprint" for each explosive they might want to detect. This type of sensor is not influenced by ambient light. The nanotubes can also sense the breakdown products of such explosives [53].

Photoacoustic Spectroscopy (PAS) is based on the *photoacoustic effect*, i.e. the conversion of light to sound in absorbing materials. The photoacoustic signal is traditionally detected using a resonant acoustic cell equipped with a sensitive microphone. Recently, alternative transducers, such as a quartz tuning fork (TF) [54], optimized capacitive micro-electro-mechanical system microphones [55], or the silicon cantilevers [56] were used. Nowadays, a super-sensitive detector of explosives was demonstrated [57]. Using a laser and a device that converts reflected light into sound, researchers at the Department of Energy's Oak Ridge National Laboratory are able to probe and identify materials in open air instead of having to introduce a pressurized chamber, which renders photoacoustic spectroscopy virtually useless for security and military applications.

Microcantilever sensors operate by detecting changes in resonance response or deflection caused by mass loading, surface stress variation or changes in damping conditions. Specifically, microcantilevers designed as sensors of explosives are coated on one side with a chemical substance designed to absorb specific explosive molecules. An absorbed molecule induces the respective microcantilever to undergo immediately changes in deflection or resonance response. Induced changes in individual microcantilevers can then be detected and measured in real-time by a suitable microprocessor based system. Researches from the Wroclaw University of Technology used such system to recognize chemically volatile substances [58].

Cavity Ringdown Spectroscopy sensors will be described in detail in our research activity.

Separate group of vapor detection are *standoff detection systems*. These systems include:

- *Light Detection And Ranging* - LIDAR,
- *Differential Absorption Lidar* - DIAL,
- *Differential Reflectance Lidar*– DIRL.

Examples of military applications of LIDAR include the Airborne Laser Mine Detection System (ALMDS) for counter-mine warfare [59]. In this method the pulse of laser radiation interacts with the vapor of an explosive existing around the explosive device. The interaction yields an optical response, which is collected by an optical receiver. The main factors determining the signal power are the following ones: mean power of laser radiation, efficiency of the radiation interaction with the matter, solid angle within the scattered radiation, and efficiency of the receiving optics and electronics. As shown in literature [60, 61], the standoff optical methods have quite high sensitivity detecting low amounts of chemical substances.

Differential Absorption Lidar (DIAL) is a technique for the remote sensing of atmospheric gases. DIAL lasers transmit into the atmosphere pulses of radiation at two wavelengths: one of which is absorbed by the gas to be measured and one is not. The difference between the return signals from atmospheric backscattering on the absorbed and non-absorbed wavelengths is used as a direct measure of the concentration of the absorbing species [61]. Sometimes a differential reflectance lidar is used.

5. Experimental results

In this section our research activity in the detection of explosives will be described.

5.1. Laser Induced Breakdown Spectroscopy (LIBS)

LIBS is one of the atomic emission spectroscopy methods used for testing the elemental composition of materials. LIBS is based on plasma generation by a sufficiently intense laser pulse. The laser pulse is responsible for the atomization and ionization of the sampled material. Plasma plume formed during the interaction of laser radiation with a sample consists of excited atoms, ions and molecules. Its growth and decay is accompanied by many physical processes such as expansion, shock waves, continuum emission and light absorption, excitation and relaxation of species and chemical recombination. Most important for analytical purposes are de-excitations of the species by optical emission. Each excited atom, ion and molecule emits radiation during its relaxation which is characterized by its own discrete spectrum. In a LIBS sensor optical plasma radiation is collected and spectrally analyzed in the spectral range covering near UV, visible and near IR. The spectrum appears as the spectral signature of the sampled material.

The capability to perform non-contact real time multi-element detection makes LIBS a very interesting method for different applications [62-64], including the detection of explosives in trace amounts [65-69]. A typical setup of the LIBS sensor is shown in Fig. 4.

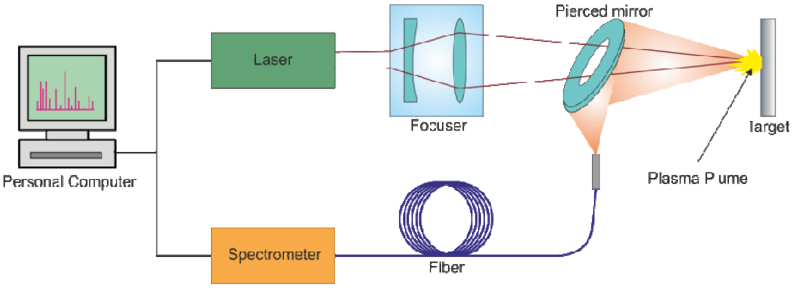

Fig. 4. LIBS experimental setup.

It consists of a laser delivering pulses with a duration 10^{-9} s (or shorter) and energy 10^{1}-10^{2} mJ. The laser beam is focused on the sample surface to reach an energy density in the range 10^{10}-10^{11} Jcm^{-2} sufficient to induce a breakdown. Optical radiation emitted by decaying plasma is collected by an optical system and passed to a spectrometer through a fiber cable. In the spectrometer optical radiation is spectrally resolved and digitized. In the form of a digital signal the spectrum is processed by means of numerical procedures to obtain information about the tested material.

Explosives are organic substances, typically containing carbon (C), hydrogen (H), nitrogen (N), and oxygen (O). LIBS spectra of energy materials contain atomic lines of these elements and molecular bands of CN and C_2 (Fig. 5), which can be attributed to native C=C and C-N bonds of explosive molecules and to radicals formed in chemical processes proceeding in the plasma plume [70, 71].

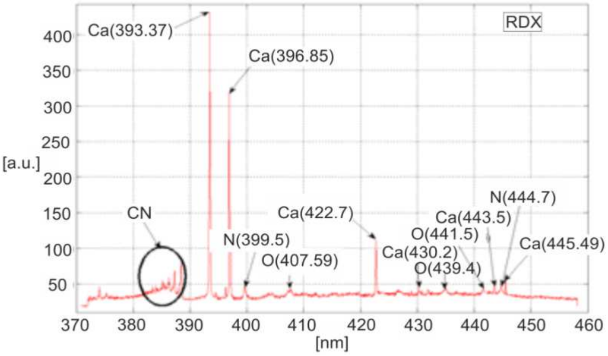

Fig. 5. LIBS spectra of hexogen (RDX) with characteristic emission lines used for identification.

The identification of energetic materials with LIBS has been recently based mainly on the analysis of several combinations of emission line ratios. The use of ratios improves the algorithm of the analysis of spectral data. Typically, for the classification of organic material purposes, intensities of the emission lines of C, H, N, O atoms and their ratios C/H, C/N, C/O [72] are used. Except atomic lines, many authors reported discrimination improvement by means of molecular lines of C_2, CN and their intensities ratios C_2/CN. In [73], the authors propose to use a set of 20 ratios: [O/C, H/C, O/N, N/C, O/H, N/H, C/CN, O/CN, O/CN, H/CN, N/CN, C_2/CN, C_2/C, (O+N)/(H+C), Ca/H, Ca/C, Ca/O, Ca/N, (O+N)/(C+C_2+CN+H), (O/N)/(H/C), CN/(N/C)]. The set of line intensities can be further expanded by adding a parameter resulting from a function of selected emission line intensities [67]. A different method of spectral signal normalization is used in [69], where the normalization of the signal relies on appropriately selected reference signals which are the functions of intensities H(O), N(O), N(H), O(C), N(C) and H(C). On the basis of calculated intercepts and slopes of the functions one can classify the spectrum and finally the material.

The analysis of explosive residues on an unknown support is difficult due to variable amount of ablated material from one point to another. In this case the matrix effect influences significantly the intensities of the analyzed emission lines even for the same type of substrate. This is the effect of the varying amount of the sampled explosive and the substrate, differences in the shape of the plasma, temperature and electron density. These factors are responsible for the variability of chemical reactions occurring in the plasma plume and eventually cause changes in the spectral signature of the sampled material.

At the MUT Institute of Optoelectronics the LIBS sensor for rapid LIBS detection of explosives was developed. It works in the atmosphere of air. The influence of air is reduced by use of double pulse laser excitation [74]. In double pulse configuration the shock wave following the first laser pulse reduces locally the air pressure and the second pulse induces the plasma plume in a cleaner environment with reduced amount of interfering substances.

Optimal time intervals for detection of explosive residues were found experimentally. The best results were obtained with the interval between the laser pulses t_{di}=10 µs and the delay between the last laser pulse and the beginning of plasma radiation integration t_d=4 µs. The time of plasma radiation integration t_b can be in the range 10^{-8}-10^{-2} s.

Collecting the spectrum of an unknown substance is only the first step in explosive detection. Next, the spectrum has to be classified as an explosive or non-explosive one. The comparison method can be based on a linear correlation algorithm [75, 76] in the case of bulk materials. In the systems of explosive residue detection more sophisticated algorithms are usually used. Multivariate analysis algorithms are most frequently applied to identify the

LIBS spectra [77, 78]. A different approach to spectrum identification is the application of an artificial neural network for spectral signal processing and classification [79].

LIBS data processing algorithms commonly lead to a dimensional reduction of spectral signals. This is essential for a subsequent classification. The most widely used method for the classification of LIBS signals is the partial least squares discriminant analysis (PLS-DA) [78]. In the sensor model built at the MUT Institute of Optoelectronics the algorithm based on prior knowledge was applied. The method is based on supervised principal component analysis (SPCA) [80]. SPCA uses information about the distance between the signals from different classes in the training set. From the set of distance data the Laplacian matrix is formed and next incorporated in the eigenvalue problem. In this way the nonlinear dependence of the between-class distance is imposed on the typical PCA eigenvalue problem.

In the case of SPCA specific groups of signals may be assigned to any number of classes. In the chart of Fig. 6 the result of SPCA is shown concerning three types of explosives (groups: 3 – HMX, 4 – HX, 5 – tetryl) and material substrates (groups: 1, 6, 2). The signals have been divided into two classes: explosive and NOT explosive. The chart shows the results of the algorithm in the direction of maximizing the separation of classes; so it becomes possible to define clearly the border between both classes (black line in the graph). A reliable detection of explosive residues is difficult, usually based on a statistical evaluation of probability. The Bayes rule might be the basis for the assessment of probability of detecting explosives after each LIBS event for a tested target.

The LIBS sensor has an attained effectiveness on the level of ~90% for true positive rate and ~1% for false positive rate in an experiment performed for distance in the range 20-30 meters. Worse results were obtained at longer distances between the sensor and the target. Promising direction for future LIBS sensor development is fusion of LIBS and Raman spectroscopy in one device. This is possible without changes in the sensor setup [81]. The fusion of the two spectroscopic methods may increase significantly the effectiveness of trace explosive detection and lower false alarm rate.

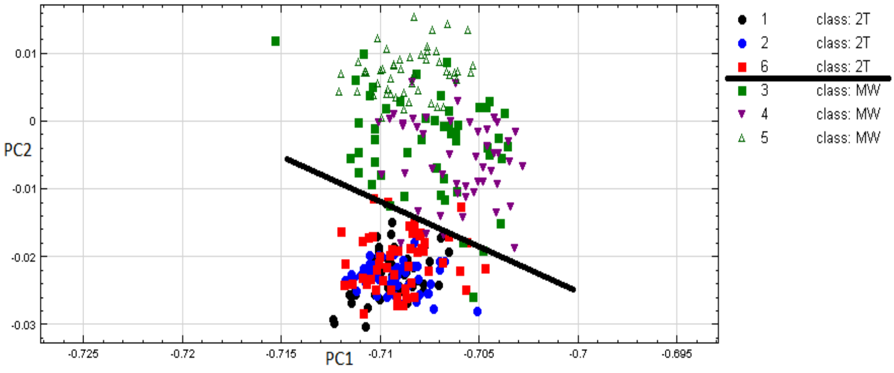

Fig. 6. The result of LIBS spectra classification by the SPCA algorithm.

5.2. Microwave sensors

Microwave radiation can be basically utilized for detecting explosive devices in two ways: passive and active. The operating principle of passive detectors is based on measuring very small temperature differences (microwave thermography) [82]. Physically there is a difference between characteristics of the heating and cooling time of the ground surface with and without buried objects. These phenomena can be utilized to obtain thermal maps of the ground surface. Next, using recognition pattern methods, it is possible to distinguish an ordinary object from a hazardous one. A much more promising technology seems to be active scanning using radio waves in the range of microwave radiation. Assuming that explosive devices to be detected contain high frequency radio receiver circuits, it is possible to excite them using a very short radio pulse or other ultra wideband emission [83]. Such a wideband emission is necessary because the center frequency of the receiver is usually unknown. The emission cannot initiate the explosive device because internal receiver filters are tuned so that they recognize dedicated signals only. For example, a mobile phone (a very popular component of IED) is activated when it receives a unique call from the station.

5.3. Metal detectors

Metal detectors (MD) are kind of sensors designed originally to detect metal parts of explosive devices. There are two possible constructions: static and dynamic ones. Static ones generate a constant magnetic field and measure its distortion caused by ferroelectric materials close to it. The dynamic version generates and sends into the ground magnetic pulses and next analyses their echoes. Such a type of MD is able to discriminate different kinds of objects as well as different metals [84].

5.4. Ground Penetrating Radars

Ground penetrating radar (GPR) utilizes electromagnetic waves to scan near surface layers of the soil [85, 86]. Distinct from dynamic metal detectors it analyses both the magnetic and electric properties of the target. In its simplest form GPR sends into the soil structure short electromagnetic pulses and receives echoes from underground structures. As the electromagnetic waves propagate in all directions a compact buried object is visible as a deeper one when GPR is placed farther away from it. As a result the echoes from such an object make a characteristic hyperbola with the top indicating the situation of the object (Fig. 7a).

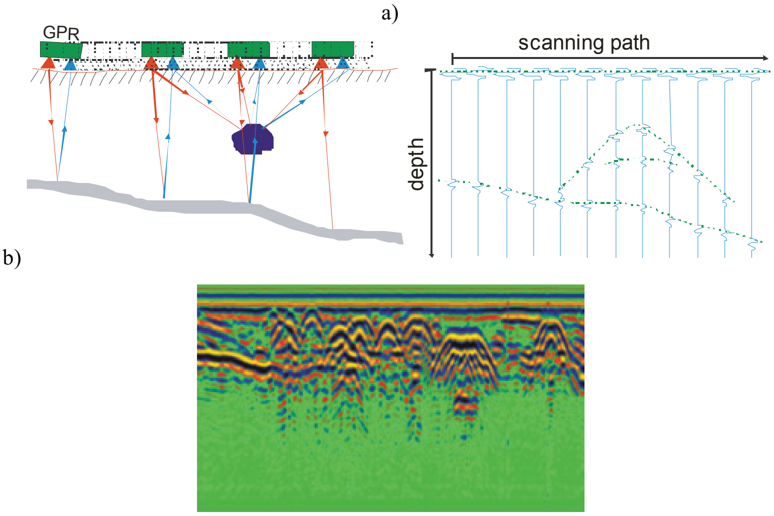

Fig. 7. GPR operational principle (a) GPR exemplary imaging (b) - cross section of the ground structure (B-scan).

When single scans are dense enough and the amplitudes are represented using a color map, the resulting imaging may have the form shown in Fig. 7b. The hyperbolas shown in Fig. 5b. indicate underground objects. This raw imaging is usually analyzed utilizing various methods to obtain final information about the depth shape and reflectivity of the object under detection. Modern GPRs reach a spatial resolution of the order of cm. By collecting more parallel B-scans it is possible to calculate transversal cross sections as well as a 3D image. The consecutive steps of four types of GPR imaging are shown in Fig. 8.

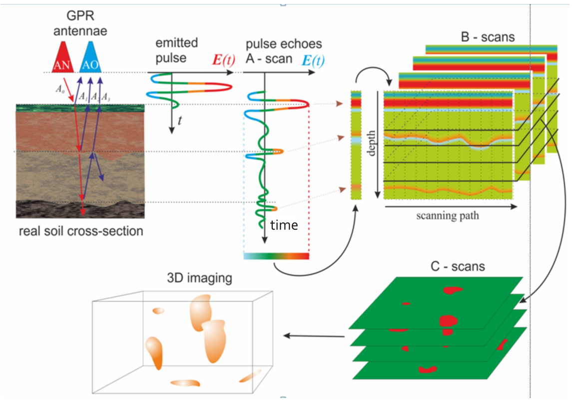

Fig. 8. Different kind of GPR imaging formation.

Regardless of the type of imaging it is necessary to use a pattern recognition system in order to obtain a correct classification of the target.

5.5. Detection of explosives in the terahertz range

Detection and identification of hidden explosives represent a promising application of the terahertz range (0.1÷10 THz) of the electromagnetic spectrum. Terahertz waves penetrate many materials apart from metals or polar media (as water). Therefore, terahertz radiation can “see” through packing, clothes, shoes, and bags. The next major factor contributing to this interest is that THz radiation is non-ionizing and is of rule minimum health risk for a suspected person or the system’s operation because the photon energy is very small (4,4 meV @ 1THz). The main factor that limits the propagation through air is its humidity because of strong absorption by water vapor. Attenuation is about 10dB/km at frequencies below 1 THz and even more than 100dB/km at frequencies higher than 1 THz [87].

The terahertz range of radiation corresponds well to the frequencies of normal modes (vibrational and rotational) of molecules of chemical compounds at room temperature. Accordingly, some explosives like Hexogen, Trinitrotoluene, Octogen, Penthrite and drugs (e.g., methamphetamine) have characteristic transmission and reflection features in the THz range, often called spectral fingerprints, distinguishable from other common materials like clothes, human skin or metal materials.

Scanning of pure explosives in the transmission mode is limited to samples with a thickness less than about 1 mm, which is connected with a relatively high attenuation, especially in absorption peak regions, where the absorption coefficient can reach the value of the order of 10^3 cm^{-1}. Due to flat transmission spectrum of paper, scanning of mails with suspicious powder or a tablet is possible. In the case of thicker samples or packages one should consider a reflective way of measurements. One can observe few percentage changes in the reflection of explosives at frequencies connected with absorption peaks. Identification of explosives from a distance of meters seems to be a real challenge, because relatively weak and broad features of explosives can be masked by the combined effects of atmospheric water vapor absorption, barrier attenuation and scattering from both clothing and the target explosives [88]. A more promising technique of safe applications seems to be passive or active imaging using scanners or cameras with frequencies below 0.5 THz. It is possible to detect a suspicious object hidden under clothes (guns but also non-metallic items), which can be further analyzed by other techniques.

Time Domain Spectroscopy is a commonly used technique in the THz range and has been described in detail in many books and papers [87, 89]. For Time Domain Spectroscopy measurements, at the MUT Institute of Optoelectronics, a Teraview TPS 3000 unit with accessories in transmission and reflection configurations was used. The main parameters of the systems are: spectral range 0.06-3.0 THz, signal-to-noise better than 4000:1 and spectral resolution 0.06 THz. In transmission, the samples were placed at a medium distance between the emitter and detector, perpendicularly to the incident THz beam. In reflection measurements, the incidence and collection angles of the beam were 45°. The chamber was purged with dry air to eliminate water vapor. Fig. 9 presents transmission and reflection spectra of three commonly used explosive materials - Hexogen, Penthrite and Octogen [90].

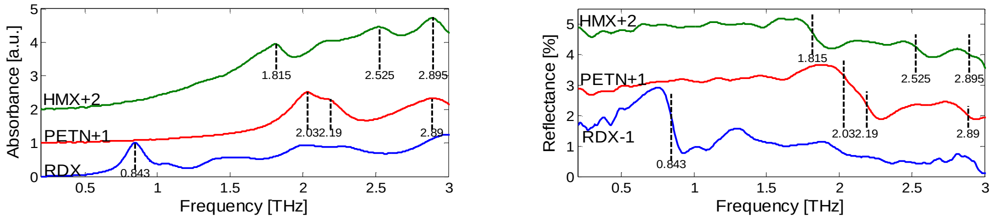

Fig. 9. Transmission and reflection spectra of RDX, HMX and PETN. Offsets (e.g.+1) for clarity.

In reflection, we examined 100% pure samples while in transmission, due to high attenuation, we mixed explosives with transparent Polyethylene powder. The mixing ratio was 10% (weight of explosive versus total weight of mixed samples). The sample was pressed into pellets with a diameter of 13 mm, using a hydraulic press. It can be noted that peaks in absorbance of all measured substances are associated with their features in reflectance. These results reveal that reflection measurement can be used for stand-off detection of explosives but a considerable technological progress is required in the field of generation and detection of THz radiation as well as signal processing and recognition.

5.6. Cavity enhanced absorption spectroscopy

Cavity enhanced absorption spectroscopy belongs to the spectroscopic measurements based on the light absorption phenomenon. Absorption spectroscopy is a simple, non-invasive, in situ technique for obtaining information about different species. However, the sensitivity of traditional spectroscopic methods is limited to the range of absorption coefficients of 10^{-4} – 10^{-5} cm^{-1}. In order to improve the sensitivity, a longer absorption path length should be used. For this reason, multipass spectroscopy is applied (in White or Herriott cells) [91, 92]. Absorption spectroscopy with a modulation technique could be also used [93]. O'Keefe and Deacon proposed a novel measuring technique called *cavity ring-down spectroscopy* (CRDS) that provides a significant increase of absorption sensor sensitivity [94, 95]. In this technique, the laser pulses are injected into a stable optical cavity (resonator) consisting of two spherical and high-reflective mirrors. Radiation is multiply reflected inside the resonator. After each reflection, a small part of laser radiation leaves the cavity due to the residual transmission of mirrors, and is registered by a photoreceiver. The amplitude of single-mode radiation trapped within the cavity decays exponentially with time. When the system is filled with the analyzed gas that is able to absorb the radiation, the Q-factor of the cavity decreases and the decay time is shorter.

Effective storage of light in the resonator is ensured only when the laser frequency is well-matched to the cavity mode. Then the best sensitivity can be achieved. However, the major disadvantage of this method is a strong dependence of the frequency of resonator modes on mechanical instabilities. The instabilities can degrade the high-finesse of the cavity and provide fluctuations of the output signal. Such a disadvantage was minimized in the cavity enhanced absorption spectroscopy (CEAS) based on an off-axis arrangement of the resonator [96].The radiation is injected at a very small angle versus the cavity axis. As previously, the beam is repeatedly reflected by the mirrors; however, the reflection points are spatially separated. In result a dense structure of weak modes is obtained or the modes do not occur due to overlapping. The system is much less sensitive to mechanical instabilities. CEAS sensors attain a detection limit of about 10^{-9} cm^{-1} [96, 97]. Another advantage is that due to off-axis illumination of the front mirror the interference of the light source (a laser) by the optical feedback from the cavity is eliminated.

At the Institute of Optoelectronics MUT in cooperation with the Institute of Experimental Physics of Warsaw University some different types of the optoelectronic sensors employing CEAS were developed. They were designed to measure trace concentration of nitrogen dioxide (NO_2), nitric oxide (NO), and nitrous oxide (N_2O).

In the case of NO_2, the maximum of the absorption spectrum is at the wavelength range of 400 ÷ 450 nm. The absorption cross section at the range exhibits several minima and maxima varying from about $3.5\cdot10^{-19}$ till $6\cdot10^{-19}$ cm^2 [98]. Moreover, there are no absorption interferences from other gases or vapors normally existing in the air. The influence of scattering by some aerosols and smokes existing in the air was minimized using special filters. The developed sensor consists of a blue-violet pulsed laser diode (TopGaN), diffraction grating and mirror, an optical cavity (Los Gatos Research Inc.), a photomultiplier tube (Hamamatsu), an analogue to digital converter (Cleverscope), and a computer with special software (Fig. 10a) [99].

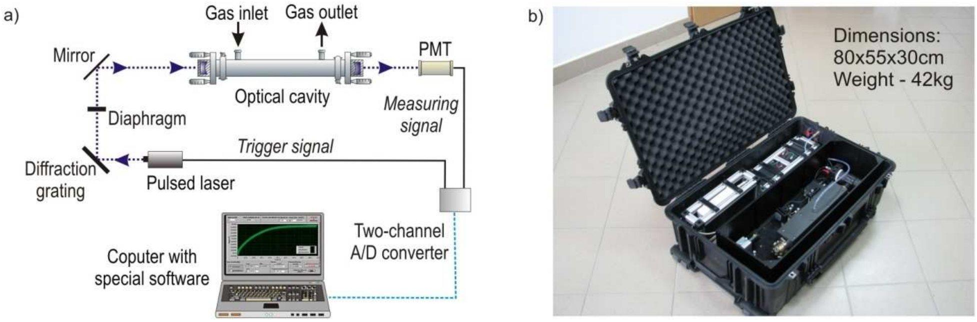

Fig. 10. Scheme (a) and photography of a portable nitrogen dioxide sensor (b).

Investigations of the laboratory model of the NO_2 sensor showed that it is characterized by a high selectivity, its sensitivity reaches the level of 1 ppb, and a measurement uncertainty of 2%. This idea was applied in the mobile construction of the sensor, and similar parameters were achieved (Fig. 10b) [100].

Then the research was focused on multi-channel detection. Laboratory systems were developed involving different operating ideas. Fig. 11a shows the experimental CEAS system with two lasers. Their radiation is directed towards the optical cavity with a special optical setup. In order to register optical signals from two channels a technique based on time division multiplexing was applied. Each laser is assigned to the suitable measurement channel within the strictly determined temporary window. Within this window, the relevant signal from the optical cavity is registered.

The system provides an opportunity for simultaneous detection of trace concentration of two non-interacting gases with different absorption spectra [101,102]. Then the wavelengths of both channels should be appropriately matched to the absorption spectra of the investigated gases. Another possibility is the application of one channel for control of the optical system alignment. The controlling process is performed continuously. The control wavelength is located outside of the absorption spectrum of the investigated gas. The sensor presented in Fig. 11a was applied for simultaneous measurement of nitrogen dioxide concentration and the control of the cavity Q-factor.

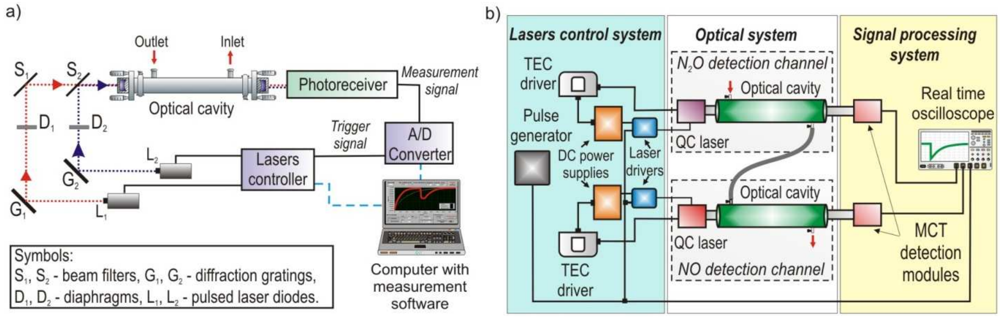

Fig. 11. Scheme of two-spectral CEAS sensor (a), simplified scheme of the experimental setup and example of the cavity output signals (b).

Another two-channel sensor is designed for simultaneous detection of NO and N_2O. The experimental setup consists of two pulsed lasers with the control electronics, an optical system and signal processing system (Fig. 11b). Two optical cavities were used, for the detection of NO and N_2O respectively. As far as precise matching of the laser wavelengths to the absorption spectra of NO_x is required, the main task of laser electronics is to stabilize operation parameters of QCL's (Alpes Lasers SA). The tuning was ensured using the temperature and power supply control. The stability was guaranteed by high-quality power supplies and a precise thermoelectric cooling system.

For registrations of the optical signals from the cavity the detection modules with HgCdTe (MCT) photodetectors were applied (VIGO System S.A.). The MCT modules use monolithic optical immersion technology and thermoelectric cooling. These photodetectors offer a high detectivity (about 10^{11}cmHz$^{1/2}$/W) and a wide bandwidth (up to 1 GHz). The modules include special transimpedance preamplifiers that match the output parameters of the photodetector to the measuring circuits. Signals from the detection modules were observed and analyzed using a real-time oscilloscope. The best sensitivity was obtained at wavelengths of 5.26 µm and of 4.53 µm respectively. The developed system provides the opportunity to detect N_2O at the level of 225 ppt, while the sensitivity of NO channel is about 8 ppb [103].

5.7. Preconcentration system

The sensitivity of the sensors designed to detect trace amounts of explosives depends on the type of explosive, since various compounds are characterized by different vapor pressures (Fig. 1). To enhance the sensitivity, a special preconcentrator can be applied. The system allows increasing the vapor pressure of explosives, and the concentration of their products: nitrogen oxides mainly. Its operating procedure includes measurements of concentration and the effect of thermal decomposition processes. During the concentration control, a trace sample of explosives is collected from a large incoming flow using a special sorptive material (adsorbent). Then the adsorbent is heated to a temperature affecting the thermal decomposition of the explosives. Due to that, additional compounds including NO, NO_2 and N_2O occur. Finally, the products can be analyzed with the NO_x sensors. These processes are schematically presented in Fig. 12.

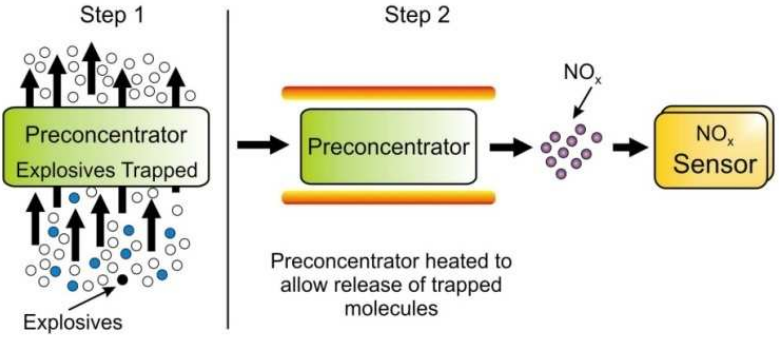

Fig. 12. Idea of the concentration and thermal decomposition of explosives vapour.

The preconcentrators can substantially improve the threshold sensitivity of the whole detection system. However, the detection of explosives is an extremely complicated challenge. This is evidenced by the fact that only few significant research centers all over the world perform research in this field [104]. At the Institute of Optoelectronics (MUT), in cooperation with the Institute of Experimental Physics (Warsaw University) and the Electric Power Research Institute (Warsaw University of Technology) as well as the Department of Optoelectronics at the Silesian University of Technology attempts have been made to develop such systems [105-106]. As results of these common research works two types of preconcentration units have been developed.

The first one provides an opportunity to achieve a high air flow of about 38 L/s. Vapors of the explosives are collected with the adsorption material in a special container. The volume of the container is about 0.4 L. In order to achieve quick heating of the sorbent to the decomposition temperature (about 100ºC/min) a quartz lamp was applied. The preconcentrator operation is controlled by an electronic system. In the second solution, induction heating by a power generator was used. Due to that an extremely quick rise of the temperature (up to 1000ºC/min) of the sorptive material (about 1 cm^3) was achieved. This system provides an air flow of about 5L/min. The adsorption and decomposition process is controlled by a microprocessor unit and a portable computer with special software. Moreover, the whole system is supplied by a battery power supply (two 12V, 7Ah batteries).

Another idea of a device that increases the sensitivity of the explosive sensor has been designed. It consists in collecting of NO_x molecules directly from the explosives or from the decomposition system. Its most important feature is low-temperature operation (below 60ºC) which provides an opportunity to avoid the use of inner gases. Otherwise at higher temperatures the decomposition is affected by production of NO_x from O_2 and N_2 molecules contained in air. The main elements of the preconcentrator are Peltier modules (thermoelectric coolers, TEC) coated with a sorption material. In this case copper oxide was used. TEC modules allow to adjust an appropriate sorbent temperature. When the investigated air sample is injected into the preconcentrator, the sorbent is cooled to a temperature near the dew point and nitrogen oxides are deposited on the sorption material. In the next step, the sorbent is heated by TEC modules and the desorption process is carried out. This process causes the release of collected nitrogen oxides from the sorptive layer.

In the Department of Optoelectronics at the Silesian University of Technology very intensive investigations have been carried out dealing with the development of preconcentrative and sensing systems for the detection of explosive vapors [105, 106]. The sensing systems are based on nanotubes of ZnO, TiO_2, polymer structures. Applications of the nanotubes in sensors of explosive vapors permit to miniaturize the systems and to reduce essentially the cost of their production. At present, the results of investigations are being patented.

6. Conclusion

The presented work concerns a very important problem of hazard for people, because of the danger of terroristic activities as well as of breakdowns in the production of explosives or dangerous materials. The paper deals with actually applied methods of detecting vapors of explosives. It may be said that all the methods of detecting them require complex and considerably advanced systems. The presented methods are characterized by a high degree of technological development. Basing on analyses which have been carried out, the problem of producing commercially available, inexpensive devices for the detection of explosive vapors requires further investigations. Many investigations are so far rather scientific attempts, and the achieved results are still far from being able to be practically applied widely.

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