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VERY SENSITIVE OPTICAL SYSTEM WITH THE CONCENTRATION AND DECOMPOSITION UNIT FOR EXPLOSIVE TRACE DETECTION

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Abstract

The vapour pressure of most explosives is very low. Therefore, the explosive trace detection is very difficult. To overcome the problem, concentration units can be applied. At the Institute of Optoelectronics MUT, an explosive vapour concentration and decomposition unit to operate with an optoelectronic sensor of nitrogen dioxide has been developed. This unit provides an adsorption of explosive vapours from the analysed air and then their thermal decomposition. The thermal decomposition is mainly a chemical reaction, which consists in breaking up compounds into two or more simple compounds or elements. During the heating process most explosive particles, based on nitro aromatics and alkyl nitrate, release NO_2 molecules and other products of pyrolysis. In this paper, the most common methods for the NO_2 detection were presented. Also, an application of the concentration and decomposition unit in the NO_2 optoelectronic sensor has been discussed.

Keywords: explosives trace detection, NO_2 optoelectronic sensor, concentration and thermal decomposition.

1. Introduction

Over the last few years the threat of terrorism has increased. Therefore, the demand for reliable and rapid explosive detection systems is very important. But the design of such a system is a very difficult task. Especially in the case of trace amounts of explosives (carried on clothing, hands, luggage, etc.), an efficient detection is very complicated [1].

Explosive molecules, in general, are organic compounds. They can be categorized by their vapour pressures and vapour concentrations. Carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) are the main elements in the chemical structure of explosives (Fig. 1).

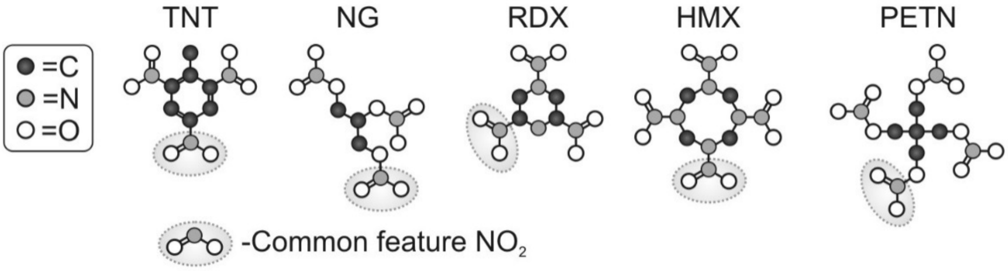

Fig. 1. Structures of selected organic explosives.

Moreover, most explosives also contain nitro groups ($-NO_2$). That is why a lot of detection techniques do not search for explosives in particular, but for the groups containing nitrogen [2]. Therefore, a large importance was placed on the construction of novel, compact and sensitive sensors of nitrogen dioxide (NO_2).

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Generally, NO_2 detection methods can be classified into three groups: the methods based on the electrical variation with various materials, the electrochemical methods and the spectroscopy methods (Fig. 2).

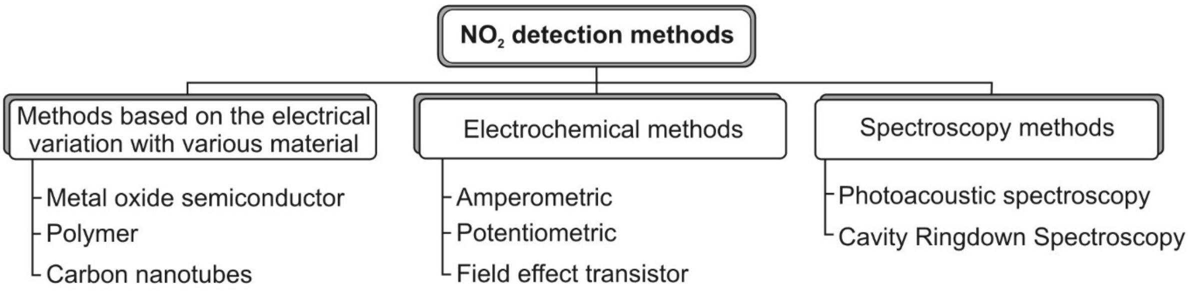

Fig. 2. Most common NO_2 detection methods.

From the first group of methods, NO_2 sensors based on metal oxide semiconductors are the most common. This is related to their low cost and relatively high sensitivity. The sensing mechanism of the metal oxide based on gas sensors consists in an interaction of the searched gas with surface complexes, such as O^-, O_2^-, H^+ and OH^-, located on the metal oxide film. This interaction causes a change in the charge carrier concentration and - as a consequence - the conductivity of the semiconductor is also changed [3, 4]. The changes of conductivity depend on the semiconductor type (n or p) and the gas type (oxidising or reducing). NO_2 is an oxidising gas, therefore, for the n-type semiconductor the conductivity will decrease, whereas for the p-type it will increase [5]. Metal oxides, like WO_3, Co_3O_4, CeO_2, TiO_2, Al_2O_3, SnO_2 and ITO, are commonly used gas sensing materials in sensors for the NO_2 detection. The detection limit of metal oxide semiconductor based NO_2 sensors is typically a few dozen ppm [6-14]. An advantage of these sensors is their small weight, low cost, short response time, wide range of target gases and long lifetime - whereas a disadvantage is their relatively low sensitivity and selectivity, sensitivity to environmental factors and high energy consumption. However, this high sensitivity is mainly based on a high operating temperature, which is realized with a heated filament. Ederth, et al. showed that the sensitivity of the gas sensor can be significantly improved by measuring the fluctuation enhanced (stochastic) signal, instead of the dc resistance [15].

The next group are gas sensors based on polymer films. The most important advantage of this kind of sensors is their room operating temperature, thanks to which their energy consumption is low; therefore, they can be applied in portable detection devices. When the target gas is in contact with the polymer layer their physical properties, like mass and dielectric properties, can be altered. Depending on the occurring changes of physical properties, polymers can be classified into conductive and non-conductive polymers. In the first type of polymers, the electrical conductivity is affected by an exposure to various groups of organic and inorganic gases. The second type is widely used as a sorption coating on different sensor devices. These polymer layers could cause changes in the resonance frequency, the dielectric constant, etc. [3, 16]. However, in NO_2 sensors conductive polymers are commonly used. Among diverse conducting polymers, Polypyrrole (Ppy) and Polythiophene (PTh) can be applied in an NO_2 gas sensor. This sensor is characterized by a fast response and recovery time and is suitable for detecting the gas concentration gas within the range of 10-100 ppm [17, 18].

For the NO_2 detection, a gas sensor with carbon nanotubes (CNTs) is used. CNTs are characterized by a wide surface area, a great adsorptive capacity and a short response time. Due to this, a significant change in their electrical properties, such as the resistance and the capacitance, can be observed [19]. Sayago, et al. [20] presented a resistive sensor for the NO_2

detection with three different type networks of CNT materials. A sensitivity to the NO_2 concentration as low as 0.1 ppm was achieved. The highest NO_2 sensitivity values were obtained for temperatures ranging between 100 °C and 200 °C for all tested gas sensors. In another CNTs-based gas sensor, the bias voltage modulation improved the sensor performance by controlling the Schottky barrier potential. Thanks to this, the sensor was able to detect 50 ppb of NO_2 at a room temperature. The sensor response was repeatable without an auxiliary assistance of a heating system, a vacuum system or an additional film coating [21].

The second group are electrochemical methods. In general, the chemical gas sensors allow to directly translate the concentration of a tested gas into an electrical or optical signal. The amperometric, potentiometric and field-effect transistor based sensors are used to detect NO_2.

In amperometric sensors the current, occurring at the electrode surface as a consequence of an oxidation or a reduction reaction of the analyzed gas, is recorded as the analytical signal. This signal is linearly dependent on the tested gas concentration [22]. Mizutani, et al. [23] proposed a sensor constructed as a three-electrode cell system with 3 cm^3 of a 5M H_2SO_4 aqueous solution. The carbon–fluorocarbon mixture (C-F) was used as a gas permeable membrane of the sensing electrode. They obtained a detection limit of 3 ppm. A novel amperometric-type NO_2 sensor based on an $La_{10}Si_5NbO_{27.5}$ (LSNO) electrolyte and a nano-structured CuO sensing electrode was fabricated and tested by Wang, et al. [24]. In the range of 25-500 ppm at 600-800 °C they obtained almost a linear current response to the NO_2 concentration. In another NO_2 sensor, an LSNO electrolyte and a nano-structured NiO sensing electrode was applied. The sensor was able to detect 2 ppm of the NO_2 concentration at 450-600 °C [25].

A typical potentiometric gas sensor is a galvanic cell which consists of a solid electrolyte and two electrodes: the reference and the sensing ones, attached to both sides of the electrolyte. The chemical potentials formed between the electrodes and electrolyte result in an electrical potential drop, which can be measured as an electromotive force (EMF) of the galvanic cell [22]. The working electrode's potential depends on the concentration of the tested gas and the reference electrode is needed to provide a defined reference potential. Zhou, et al. [26] presented an NO_2 potentiometric sensor using yttria-stabilized zirconia (YSZ) as an oxygen-ion-conducting electrolyte. The working electrode was made of an oxide powder with a double-perovskite structure $(La_{0.8}Sr_{0.2})_2FeMn_{6-\delta}$ (LSFM). They obtained the response to NO_2 in a low concentration range from 10 to 100 ppm at 650 °C.

For the NO_2 detection a sensor based on a field effect transistor (FET) can be applied. Oprea, et al. [27] presented an NO_2 sensitive suspended gate (SG) FET where the insulator was the air and a sensitive thin layer (copper phthalocyanine – CuPc) was applied on the surface of the metal gate (Au/alumina wafer). The sensors have a low detection limit (<50 ppb) and a good sensitivity (20-70 mV/concentration decade). Andringa, et al. [28] presented a real-time FET NO_2 sensor where the gate metal was replaced by a catalytic metal (ZnO). They showed that the NO_2 pressure in the ambient air can be monitored for concentrations as low as 40 ppb.

The third group are spectroscopy methods. One of such methods is the photo-acoustic spectroscopy (PAS). It is based on the photo-acoustic effect where modulated light is absorbed by the target gas and converted to acoustic waves by a non-radiative relaxation of the excited energy levels of the interested gas. The photo-acoustic signal is detected with a resonant acoustic cell with a highly-sensitive microphone [29]. Saarela, et al. [30] developed a sensor using high-power LEDs (9 W at 453 nm) to excite the photo-acoustic signal in NO_2. A detection limit of 10 ppb was obtained. The next method is the quartz-enhanced photo-acoustic spectroscopy (QEPAS). This variant of PAS utilizes a quartz tuning fork (QTF) as a sharply resonant acoustic transducer to detect the pressure wave induced by the gas absorption from a periodically modulated light source. This solution allows to use extremely small volumes and removes restrictions imposed on the gas cell by acoustic resonance conditions [31–33]. Yi, et al. [34] applied a NO_2 detection sensor based on the off-beam QEPAS (OB-QEPAS) using a single mode broadband blue laser diode (7 mW at 450 nm). The same variation of the QEPAS technique was used by Zheng, et al. [35]. However, they applied a wide-stripe LED (1 W at 450 nm) and used the electrical modulation cancellation method (E-MOCAM) [1]. For this solution, detection limits of 18 ppb and 1.3 ppb were achieved, respectively.

The cavity ring-down spectroscopy (CRDS) is a highly sensitive optical absorption method for the trace gas monitoring. This technique uses the light intensity decay rate in an optical cavity to measure the target gas concentration. The laser pulses are injected into an optical cavity made up of two spherical and highly reflective mirrors. The radiation is many times reflected inside the cavity, resulting in path lengths in the order of kilometres. At each reflection, a small fraction of the laser radiation is transmitted through one end of the cavity and its intensity is measured with a photodetector [36–38]. The CRDS method allowed to obtain a detection limit of 0.06 ppb of NO_2 [39]. However, extreme demands on the stability of the high-finesse optical cavity and the sensitivity to mechanical instabilities make these systems complex and expensive to implement. The cavity enhanced absorption spectroscopy (CEAS) technique does not have this disadvantage. It is based on transmitting the radiation beam into an optical cavity at a very small angle to its axis. Therefore, dense structure modes are received. A weak mode structure of the resonance cavity causes that the whole system is not very sensitive to changes of the cavity and the laser frequency. Additionally, this approach eliminates an optical feedback from the cavity to the light source [40–42]. Wu, et al. [43] developed an NO_2 sensor based on the CEAS method with an incoherent broadband continuous–wave light source. For this configuration a detection limit of 9 ppb was obtained.

An NO_2 sensor using the CEAS method has been also developed in our research team. Figure 3 shows the NO_2 optoelectronic sensor scheme. Its construction consists of a pulsed laser, an optical cavity equipped with two high reflectance mirrors and a photo-receiver. The laser radiation wavelength well matches the absorption spectrum which is a fingerprint of the interested gas due to the specific scheme of the energy levels. Thanks to this, a very good selectivity was obtained. For the NO_2 detection a pulsed laser (TopGaN Ltd.) operating at the wavelength of 414 nm and a photomultiplier from Hamamatsu were applied. With this sensor a detection limit of 1 ppb was achieved [44].

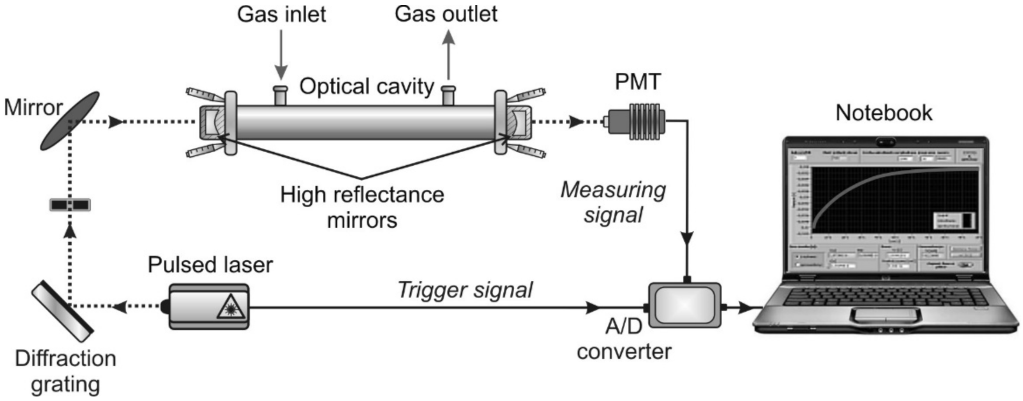

Fig. 3. A scheme of the NO_2 optoelectronic sensor.

All of the above sensors allow for the detection of NO_2. However, using them for the explosive detection becomes quite problematic. This is related to the extremely low vapour pressure of explosives [45]. Thus, the NO_2 concentration value resulting from the explosive degradation is also small. Therefore, very sensitive detection instruments are necessary.

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[1] E-MOCAM - electrical modulation cancellation method - suppressed the background noise caused by the stray light by three orders of magnitude

In this paper a novel system for the trace explosive detection has been proposed. For this purpose, an NO_2 optoelectronic sensor was integrated with a prototype concentration and decomposition unit based on the thermal decomposition process. This unit captures the explosives from the air and converts (decomposes) them to the compounds, such as nitrogen oxides. This approach allows to improve a detection limit at least by two orders of magnitude.

2. Explosive vapour concentration and decomposition unit

The concentration and decomposition unit is a component of the explosives detection system, which operates basing on the adsorption process. This means that an explosive vapour present in the analysed air is captured and accumulated on the surface of another substance called an adsorbent (Fig. 4). Then the adsorbent is heated to enable a thermal decomposition of explosive particles. Thanks to this, the explosive compound breaks up and NO_2 molecules are obtained [46-50].

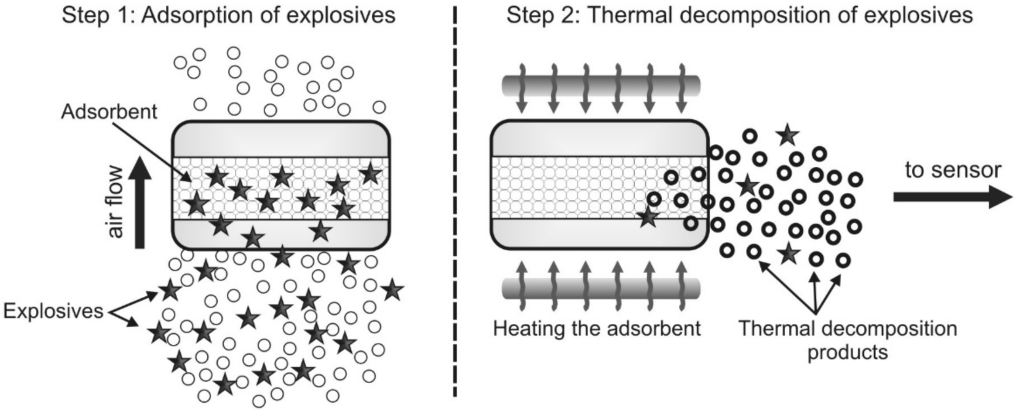

Fig. 4. The conception of the concentration and thermal decomposition process.

For the described system, a *concentration coefficient* is defined as the ratio between the NO_2 concentration measured before and after the thermal decomposition process. This is one of the fundamental concentration and decomposition unit parameters. Its value depends on the gas flow rate [l/min], the heating temperature, the surface area of the adsorbent [m^2/g] and the collection volume for explosives vapour [cm^3].

The concentration and decomposition unit consists of two subsystems: an adsorber with the adsorbent material and a control system. A photograph of the adsorber construction and the applied adsorbent material is presented in Fig. 5. The explosive vapours are collected with molecular sieves in a special container made of gilded copper. The air flows through a perforated glass tube situated inside the container.

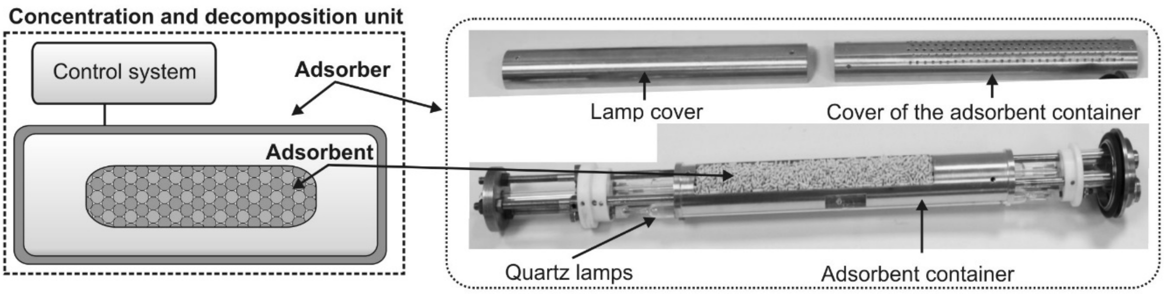

Fig. 5. A scheme of the concentration and decomposition unit construction and the adsorber components.

To achieve a high gradient of the decomposition temperature (about 100 °C/min), quartz lamp heating was applied. Additionally, the control system was equipped with an AR601/S1/S (APAR) temperature controller. It allows to change the temperature inside the adsorbent's container by setting the lamp switching temperature to T_{SET}.

3. Measurement results

During the measurement procedure with the thermal decomposition of explosives, it is very important to know the dynamic characteristics of the adsorber heating. This characteristics shows temperature changes inside the adsorbent's container during the heating process. Measurements of this characteristics were performed for several temperature settings T_{SET} in the range from 140 °C to 190 °C with steps of 10 °C (Fig. 6). The temperature was measured by a thermocouple placed inside the adsorber and a digital multi-meter. The signal was recorded using a computer with dedicated software for this device.

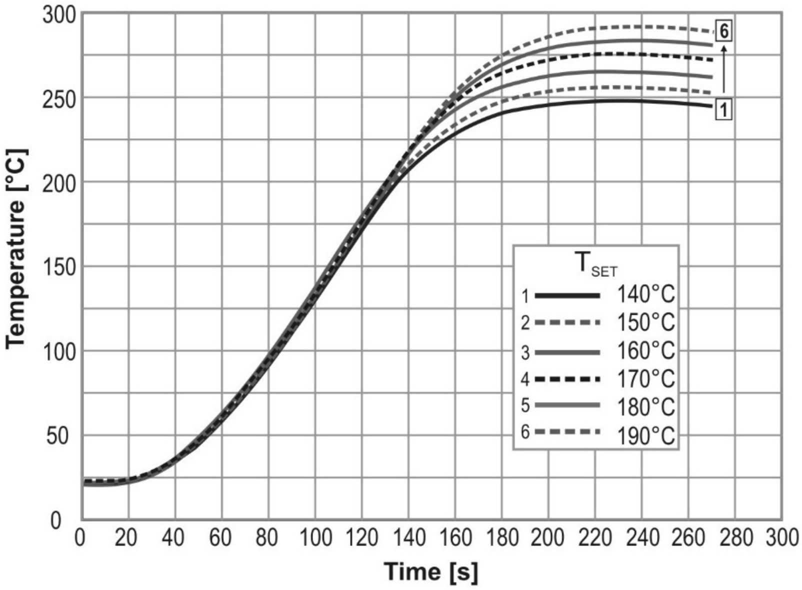

Fig. 6. Temperature changes inside the adsorber during operation.

From the temperature of 30 °C to T_{SET} + 60 °C a linear increase in the temperature is observed. After that, the temperature grows due to the thermal time constant of the adsorber. That is why the final temperature reaches the value of T_{SET} + 100 °C. The presented characteristics indicated that in order to provide a decomposition temperature above 250 °C in the shortest time (t_{off} =160 s), the lamp switching temperature T_{SET} must be set to at least 170 °C. Furthermore, the registered characteristics of the adsorber heating allows to identify the moment of commencing the thermal decomposition.

For the experiment with explosives, an optoelectronic NO_2 sensor based on the CEAS method was applied. In the first measurement stage the compounds formed during the thermal decomposition process were investigated. Knowing them is important because some compounds could influence the sensor parameters. For this purpose appropriate research was performed. The investigations were carried out using a gas chromatograph (HP 6890 type) and an atomic emission detector (AED).

Initially, the adsorbent (13 x 1.6 mm molecular sieves from Sigma-Aldrich) was annealed at 320 °C for 2.5 hours. After that, it was cooled in a desiccator at a room temperature (25 °C) for 24 hours. Such prepared empty (clean) molecular sieves were analysed. During the thermal decomposition (with a temperature of 300 °C), the air from the concentration and decomposition unit was collected to a Tedlar bag. The sampled gas from the bag was dispensed into the chromatograph using a gas-tight syringe. Chromatograms were recorded at different wavelengths specific for each element at the same time – the detection of nitrogen (N 174 nm), carbon (C 496 nm, C 179 nm), chlorine (Cl 479 nm), hydrogen (H 486 nm) and bromine (Br 478 nm). The obtained results showed that during the thermal decomposition no compounds were formed which could influence the uncertainty of the NO_2 measurement.

In the next step of the testing procedure, the explosive detection capability using the designed setup was determined. The experimental setup consists of an NO_2 optoelectronic sensor, the concentration and decomposition unit and a computer with specialistic software for determining the NO_2 concentration (Fig. 7).

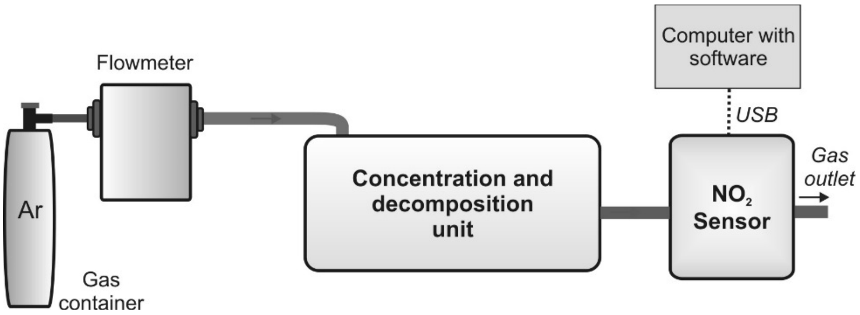

Fig. 7. A scheme of the experimental setup.

The experiment was performed using the reference probe. For the tests, the concentration and decomposition unit was filled with specially prepared molecular sieves (volume of 10 cm^3) containing 1g amount of TNT. Argon was used as the inert gas. The reference measurement of the NO_2 concentration was performed for the “empty” sensor (filled with argon). The base line of 10 ppb of the NO_2 concentration was achieved. Next, the concentration and decomposition unit was heated to 300 °C and the constant flow of argon of 1.5 l/min was set. The measurement was carried out online. Thanks to this, the NO_2 concentration before (1) and after the thermal decomposition process (2) could be compared (Fig. 8). At 200 °C a significant increase in the NO_2 concentration was observed. After 140 s from the start of heating, the *concentration coefficient* increased by more than 300 times in relation to the initial NO_2 concentration. Further growth of the temperature caused the saturation of the sensor.

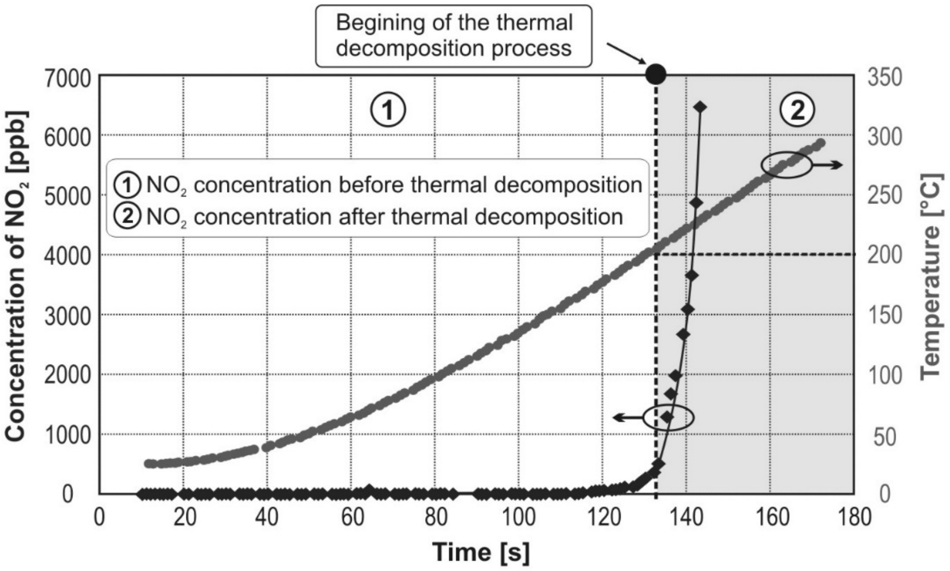

Fig. 8. The NO_2 concentration before and after the thermal decomposition.

4. Summary

In the paper, an indirect detection of explosives by the NO_2 measurement was discussed. Different types of NO_2 detection methods were presented. Depending on the sensor type, the detection limit is in the range between dozens of ppm to single ppb. The amount of NO_2 molecules from explosives can be increased by using a special concentration and decomposition unit.

An explosive trace detection system consisting of two devices that are able to operate together: an optoelectronic gas sensor and a concentration and decomposition unit, was presented. The gas sensor is designed to detect an ultra-low concentration of NO_2 using the CEAS technique. The concentration and decomposition unit is constructed to collect and decompose the explosive vapour.

The compounds formed during the thermal decomposition process were analysed. It was shown that the adsorbent material (molecular sieves) did not form any compounds that might affect the correct measurement of the NO_2 concentration. Therefore, the application of both the NO_2 optoelectronic sensor and the concentration and decomposition unit as an integral detection system is very reasonable. Using a sample with 1g of TNT, the determined concentration coefficient exceeding 300 was achieved. This means that by using the concentration and decomposition unit, a minimum increase of the NO_2 concentration in the range of two orders of magnitude was obtained. Furthermore, because the concentration and decomposition unit can operate as an independent unit, its use in other NO_2 sensors is possible and can improve their detection limit.

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