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The detection of nitro compounds vapor using sensors based on MIS-structures manufactured by laser deposition

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Abstract. The conditions of the detection of nitro compounds vapors was investigated using the trinitrotoluene as an example. The detection method consists of pyrolysis and later registration by the MIS-sensor of gaseous products of thermal decomposition . It was shown that the offered method allows to achieve the detection limit of $1 \cdot 10^{-12}$ g/cm^3 (particles – 1 ng) with respect to the vapors of trinitrotoluene.

1. Introduction

This article is devoted to a new gas-analytical sensory method of detection of trace amounts of nitro compounds, allowing to create a device with a limit of detection of trinitrotoluene vapors not worse than $1 \cdot 10^{-12}$ g/cm^3 (particles – 1 ng).

The sensor is based on the metal-insulator-semiconductor (MIS) structure, developed in the National Research Nuclear University MEPhI [1]. The design and principle of operation of the sensor are described in details in [2].

2. Previous experience and statement of the problem

For the first time, the gas-analytical method of vapor detection of nitro-containing substances using a semiconductor sensor based on MIS-structure was proposed in 2006 by a group of researchers from Moscow Engineering Physics Institute [3].

The essence of the method was as follows. A gas sample with nitro compounds (trinitrotoluene, dinitrotoluene, nitroglycerin, hexogen, etc.) was heated to a temperature of 400 ° C and above. Then, the gaseous products of thermal decomposition (pyrolysis) were fed to the MIS-sensor and a useful signal was recorded. The nitrogen dioxide was used as a reference product of pyrolysis in this case.

It has been established [2] that MIS-sensors based on Pd-SiO_2-Si-Pd type structures obtained by laser deposition (Pd electrode thickness 30 nm, diameter 3 mm) have demonstrated the best sensitivity to NO_2 with a detection threshold of 1 ppb.

According to [4], at room temperature, the vapor pressure of TNT does not exceed 5...7 ppb or 60 pg per 1 cm^3. Thus, the sensitivity of the MIS-sensor to NO_2 is enough for its use in a vapor detector of nitro compounds.

This article presents the results of the research on the following tasks:

- studying the theoretical basis of the thermal decomposition reaction of nitro compounds,

- development of a procedure for preparing samples of nitro compounds of the required mass,
- development and creation of an experimental testing workbench,
- determination of optimal operating parameters of the experimental testing workbench,
- calibration of the experimental stand by trace amounts of nitro compounds.

3. The theoretical basis of the thermal decomposition reaction of nitro compounds

An experimental study of the regularities of the process of thermal destruction of molecules of nitro compounds has been conducted for more than half a century. However, the accumulated data are very contradictory. This can be explained by the competition of various channels of the primary act of the reaction of gas-phase monomolecular decomposition.

To describe the process of thermal decomposition of nitro compounds, it is customary to use the Arrhenius hypothesis, according to which a reaction involving molecules occurs only if they have some excess energy [5]. According to the kinetic theory of gases, the number of active molecules per unit volume is equal to their total number multiplied by the factor $e^{-\frac{E_a}{R \cdot T}}$, where E_a is the excess energy of the active molecule, J/mol (or activation energy); T is the temperature, K; R is the universal gas constant, $\frac{\text{J}}{\text{mol}\cdot\text{K}}$. Thus, if the reaction proceeds, the equation holds:

$$k = B \cdot e^{-\frac{E_a}{RT}}, \quad \text{or} \quad \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln B, \tag{1}$$

where k is the rate constant of thermal decomposition, c^{-1}; B is the pre-exponential factor characterizing the probability of a chemical reaction.

According to the modern theory of monomolecular decomposition mechanisms of 2,4,6-trinitrotoluene [6], the most likely scenarios of the primary reaction act are the following:

a) breaking the C-N bond with the abruption of the NO_2 group (E_a = 258-280 kJ/mol);
b) nitro-nitrite rearrangement (E_a = 190 kJ/mol);
c) aciform formation (E_a = 105-133 kJ/mol).

As seen, the process of intramolecular hydrogen transfer from the CH_3 methyl group to the NO_2 group with the formation of aciforms is energetically less expensive.

However, due to the larger pre-exponential factor B at high temperatures, the rate of the TNT thermal decomposition reaction by the radical mechanism of the C-NO_2 bond breaking increases more rapidly with respect to alternative reactions and begins to predominate.

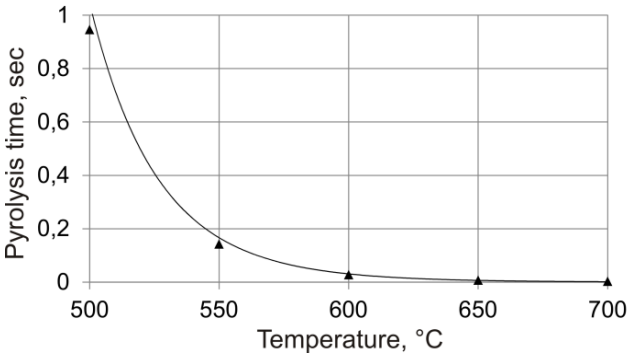


Figure 1. The dependence of the duration of thermal decomposition of nitrotoluenes from temperature

Using equation (1) and experimental data on the activation parameters of the thermal decomposition of nitrotoluenes [6] at temperatures of 230 °C and higher, in Figure 1 we show the dependency duration of the pyrolysis reaction of TNT (sec) from the temperature T, (C).

Thus, it is possible to estimate the conditions (time and temperature) necessary for the pyrolysis of vapors of nitro compounds with the formation of NO_2.

4. Development of a procedure for preparing samples of nitro compounds

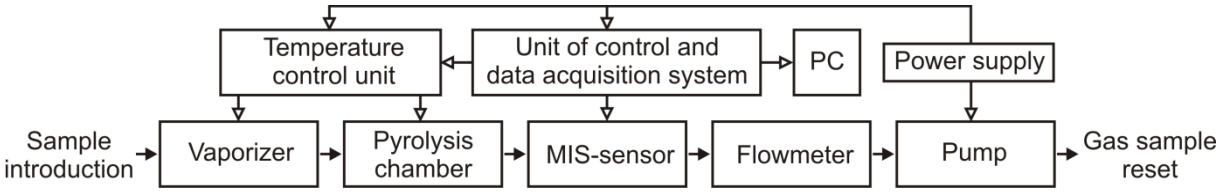
In this work, the following types of nitro compounds samples were used:
(a) – a sample of the solid substance dissolved by an acetone of special purity on an aluminum foil substrate 2.5 × 4 cm with a thickness of 0.9 μm;
(b) - a sample of the solid substance in a sterile container, dissolved by a fixed volume of acetone (0.5-10 ml), followed by precipitation of 100-200 μl of solution onto a substrate;
(c) – secondary dilution of a certain part of a solution of type (b) (100-500 μl) by a fixed volume of acetone (0.5-5 ml), followed by precipitation of 100-200 μl of solution onto a substrate;
(d) - secondary dilution of a solution of type (c);
(e) , etc - dilution of a solution of type (d): – next steps of the secondary dilutions by a fixed volume of acetone with precipitation of 100-200 μl of solution onto a substrate.

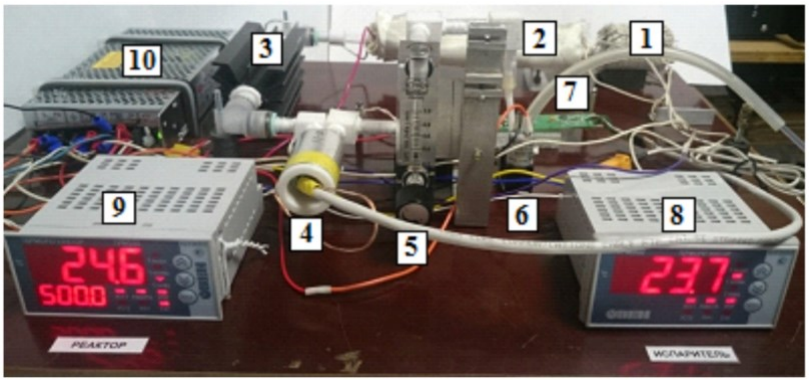
For example, to create a sample with a mass of about 10 μg it is necessary to take a dose of 100 μl from a solution of type (b) with a concentration 1 μg/μl (so 100 ± 3 μg of substance) and add 1 ml of pure acetone to it. In this way, we will obtain a new solution of type (c) with a concentration 91 ng/μl. Then, we can precipitate 100 μl of the solution on the foil, and after evaporation of acetone, we will get 9.1 ± 0.3 μg of the substance.

The relative error in the mass of the nitro compound in the sample was for a solution of the type (a) – 2 %, (b) – 3 %, (c) – 4 %, (d) – 5 %, (e) – 6 %; (f) – 8 %; (g) – 10 %; (h) – 12 %.

In the framework of this work, 2,4,6-trinitrotoluene was used as a sample of a nitro-containing substance. Dilution with acetone was carried out in sterile containers of glass and polypropylene. The shelf life of samples obtained by the multiple dilution methods with acetone at room conditions was no more than 7 days.

The substance was weighed using laboratory electronic scales CAUW-120D from manufacturer CAS with mean square deviation ≤ 0.02 mg. The dosage of acetone for the dissolution of the TNT samples was performed using single-channel pipette dispensers with a volume of 100 μl and 1-10 ml from manufacturer Thermo Fisher Scientific.





(a)

(b)

Figure 2. (a) Schematic diagram and photograph of the experimental testing workbench. Notation: 1 – the vaporizer; 2 – the pyrolysis chamber (or reactor); 3 – the device for cooling the gas mixture; 4 – MIS-sensor; 5 – the flowmeter; 6 – the pump; 7 - the electronic board; 8, 9 - thermoregulators, 10 - the power supply. (b) Photo image of the MIS-sensors.

5. Development and creation of an experimental testing workbench

Taking into account the above-described theoretical and experimental data, a test stand (Figure 2) was developed and constructed for a detailed study of the proposed method and determination of optimal operating modes.

The work on the test bench was carried out as follows.

A sample of the nitro compound on the foil was placed in an evaporator, where it was heated to 40-100 °C to increase the vapor pressure. The evaporator was made of a quartz glass tube 9 cm long with an inside diameter of 1.5 cm and a wall thickness of 2 mm. The nichrome filament was wound on the outer surface of this tube (d = 0.5 mm, R = 12 Ω).

Using a miniature diaphragm pump with a flow rate of 0.1-0.5 l/min, the carrier gas supplied to the evaporator inlet was withdrawn along with the TNT vapors and sent to the reactor. The reactor was also made of a quartz tube 25 cm long (heated working length 16 cm) with an internal diameter of 7 mm and a wall thickness of 1.5 mm. Nichrome wire was wound on the outer surface of the reactor tube (d = 1 mm, R = 3 Ω).

The nichrome heaters with the installed temperature sensors were fixed on the evaporator's and the reactor's quartz tubes by a heat-resistant electrically insulating compound and thermostated with glass fiber and heat-resistant glass cloth. Under the influence of high temperature in the reactor thermal decomposition of TNT vapors leads to NO_2 emission, which is registered by the MIS-sensor.

In this work, we used MIS-sensor of the Pd-SiO_2-Si-Pd type. The signal from the sensor was processed by an electronic circuit board and outputted using the appropriate software on the PC via the RS-485 interface.

Based on the geometric dimensions of the reactor and according to Figure 1, it was assessed of the required ratio "temperature of reactor - flow rate" (or what amounts to the same thing, time of the vapor residence in the reactor at a given temperature) in order to meet the conditions for the pyrolysis reaction by the radical C-NO_2 bond breaking mechanism.

The flow of sampling was regulated by a panel-type rotameter made of acrylic plastic with an adjusting valve. The temperature of the evaporator and the reactor was regulated by industrial thermoregulators. The power supply of all elements of the installation was carried out from a two-channel switching power supply.

6. Determination of optimal operating parameters of the experimental testing workbench

Before the experiments the MIS-sensor was calibrated by low NO_2 concentrations. The calibration results are shown in Figure 4.

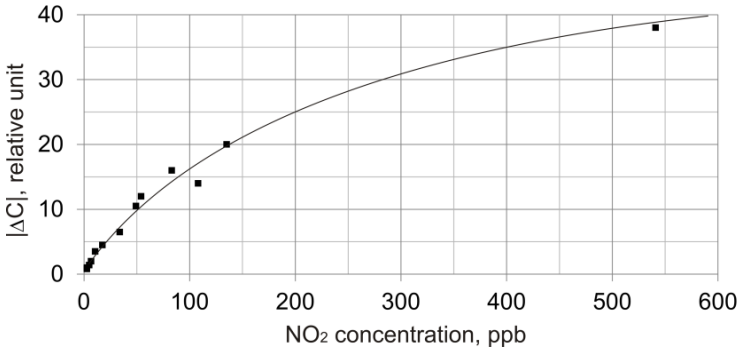


Figure 3. MIS-sensor calibration with respect to NO_2.

According to [7], MIS-sensors do not exhibit sensitivity to organic compounds, including nitro-containing ones. Therefore, assuming that at least one of the three nitro groups is detached from each TNT molecule, one can judge the amount of a substance successfully subjected to pyrolysis.

It was shown that the evaporation rate of TNT sample with a spot area S ≈ 5 cm^2 (type (a)) from the foil surface at an evaporator temperature of 70 °C is 3.0 ± 0.5 μg/min (the influence of the flow in the range 0.1-0,5 l/min can be neglected).

The optimal temperature of the reactor was established with a fixed heating of the evaporator to 70 °C, a flow of 0.5 l/min, and the evaporation area of the TNT sample spot on the foil of 5 ± 1 cm^2. The time duration influence of the TNT vapor residence in the reactor on the response of the MIS-sensor ΔC_{MIS} was also studied. The results are shown in Table 1 and Table 2.

Table 1. Optimization of pyrolysis chamber temperature.

M_{TNT}, ±0,01 mg	$T_{reactor}$, °C	ΔC_{MIS}, rel.un.	$t_{rel.}$	$K_{rel.}$
1,60	700	12	370	0,1
1,16	600	27	25	0,4
1,29	550	51	5,3	1,6
1,44	500	37	0,8	0,9
1,76	400	1	0,01	0,01

Table 2. Influence of the flow rate or residence time of TNT vapors in the pyrolysis chamber.

M_{TNT}, ±0,01 mg	$T_{reactor}$, °C	Flow, l/min	ΔC_{MIS}, rel.un.	$t_{rel.}$	$K_{rel.}$
1,49	700	0,1	4	1850	→0
1,49	700	0,3	14	615	0,1
1,60	700	0,5	12	370	0,1
1,34	500	0,1	57	3,9	0,3
1,44	500	0,5	37	0,8	0,9

Notations: $t_{rel.}$ – the coefficient of the ratio of the duration of the actual and theoretically sufficient time of heating (see Figure 1) for pyrolysis of the TNT vapors; $K_{rel.}$ – the ratio of the measured NO_2 concentration (according to Figure 3) and the TNT concentration supposed.

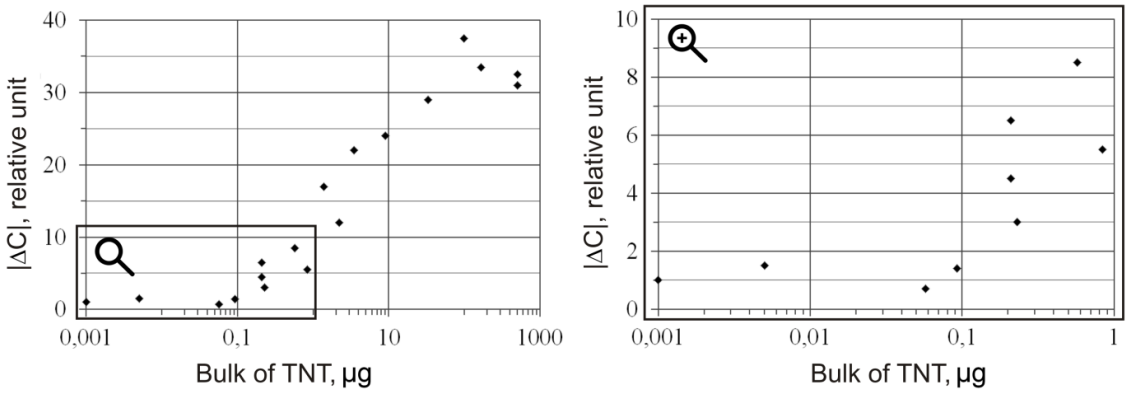


Figure 4. Calibration of the experimental stand by trace amounts of TNT.

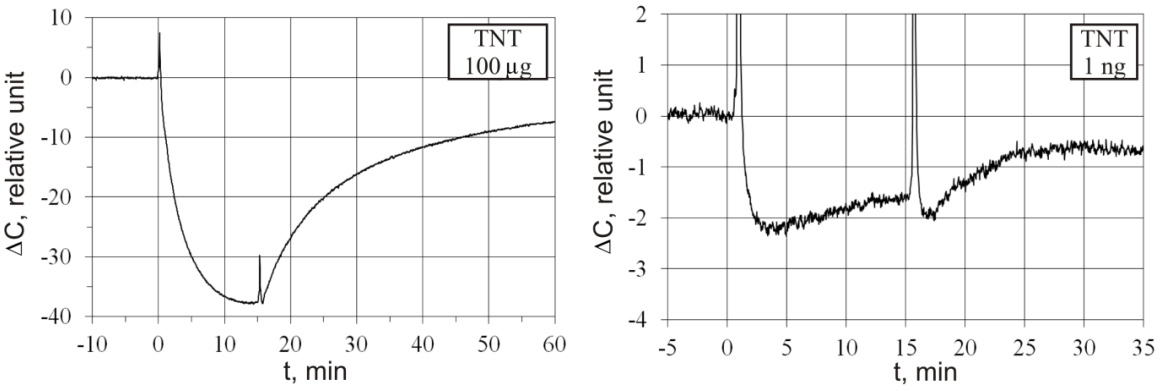


Figure 5. Example of the response of a MIS-sensor per 100 μg and 1 ng TNT.

If the sample productivity, the carrier gas flow rate and the duration of each sample supply (15 min) are known, one can estimate the concentration obtained and the total mass flow of TNT as:

$$3\ \frac{\mu g}{min}/0{,}5\frac{l}{min} = 6\frac{\mu g}{l}\ \text{(or 635 ppb under normal conditions);}$$

$$0{,}5\frac{l}{min}\cdot 15\ min = 7{,}5\ l\ \text{(total volume of gas sample);}\quad 6\frac{\mu g}{l}\cdot 7{,}5\ l = 45\ \mu g.$$

The calculated data were confirmed by weighing results on the microbalance.

Analyzing the experimental data, we note:

1) at the optimum temperature of the reactor of about 500-550 °C the pyrolysis of TNT molecules occurs with the detachment of 1-2 nitro groups, judging by the expression $1 \leq K_{rel.} < 2$;

2) the optimal value of the mass flow of gas is selected in dependence on the geometric parameters and temperature of the reactor in such a way that the obtained regularity is correlated with the calculated one shown in Figure 1.

After determining the optimal operating parameters, the experimental stand was calibrated by TNT masses in the range from 500 μg to 1 ng (samples type (b)-(h)). The calibration results are shown in Figure 4. An example of the MDP sensor responses is in Figure 5.

7. Conclusion

We demonstrated efficiency of the method based on pyrolysis of TNT and following detection by a MIS-sensors of trace amounts of nitro-containing substances (including explosives). The method has a number of competitive advantages:

- a long service life of the sensor,
- an absence of consumables,
- the simplicity of operation and maintenance,
- stability of work and reproducibility of results,
- the possibility to create a miniature device (really achievable overall dimensions LWD of 80x50x50 mm and a mass of not more than 0.5 kg),
- an advantageous price-quality ratio,
- high sensitivity (detection threshold for TNT vapors is 10^{-12} g/cm^3 or 1 ng).

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