The detection of nitro compounds by using MIS-sensor

A.V. Litvinov¹, N.N. Samotaev¹, M.O. Etrekova¹* and A.A. Mikhailov²

¹ National Research Nuclear University MEPhI (MEPhI), Kashirskoe shosse 31, Moscow, 115409, Russian Federation
² Scientific production company "INKRAM", Lyublinskaya Street 151, office 222, Moscow, 109341, Russian Federation

Corresponding author’s e-mail address: Etrekova@mail.ru

Abstract. It was shown the possibility of using MIS-sensors as detectors sensitive elements of the nitro-containing organic trace. The detection is carried out due to the nitro groups, formed during the reaction of pyrolysis of the nitro compounds molecules.

1. Introduction

As shown by years of international experience in the design of gas analysis systems [1, 2], the combination in a single device of high sensitivity, of simplicity of equipment, of low requirements for operator skill, of portability and of price acceptable for mass production and implementation in the security systems is a very difficult task. Therefore, the search for optimal solutions remains relevant.

A number of studies we have conducted [3, 4] show the possibility of using MIS-sensors as detectors sensitive elements of the vapor nitro compounds (for example, explosives) with the use of gas detection technology study, called thermo-redox. Its essence lays in the thermal decomposition (reaction of pyrolysis) of molecules nitro-containing explosives with subsequent detection of nitro groups (NO₂). Competitive advantages of this technology are the absence of radioactive source and carrier gas, as well as compact and easy maintenance. The disadvantage is the inability to distinguish the type of explosives and the difficulty of detection of substances with low vapor pressure such as RDX or PETN.

2. Experimental

The basis of the MIS-sensor is the structure (Fig. 1a), which is a MIS-capacitor consisting of the silicon plate (3), a layer of insulator SiO₂ (2) and palladium metal electrode of the shutter (1). Such a capacitor has the capacitance C. The sensor’s temperature is maintained in the range of 100-150 °C with the help of miniature film heater (6) and stabilized due to electronic unit by using a thermistor (9). Standard dimension of the sensor in the housing is 1 cm³ (Fig. 2).

For the manufacture of MIS-structures we have used laser technology for the deposition of thin films of metals and insulator, the essences of which consists in evaporation of the substance of the target with help focused laser beam with subsequent condensation of evaporated substances on a substrate. Used solid-state yttrium aluminum garnet laser with a radiation wavelength λ = 1.06 μm. The laser worked in the mode of modulated q-switched with pulse duration of 10 ns, pulse energy 0.1 Joule and a pulse frequency of 50 Hz.
In Fig. 3 shows a typical C-U-characteristic of the MIS-sensor. Principle of operation the sensor consists in the following. During the deposition of molecules of the investigated gas on the surface of the paddle (Pd) C-U-characteristics shifted along the axis U (the dashed line). If we hold on the capacitor DC voltage, $U_{dr}$, there is a capacitance change $\Delta C$, which is converted by electronics into an analog (or digital) signal.

According to the works [5, 6, 7], the model of sensitivity of MIS-sensor is as follows. Due to the porous structure of the palladium film (Fig. 1b) of the gas molecules freely penetrates to the boundary of metal-insulator, where they create a layer of charge, which generating the changing electric field in the semiconductor. This leads to a shift of the C-U-characteristics of the sensor.

The experimental setup was as follows: the pump (outlet side of the gas path) ensured flow of atmospheric air through a reactor made of quartz glass, where the gas mixture is heated up to
200...500 °C required for pyrolysis of explosives molecules, and after cooling, was fed into the chamber with the MIS-sensor. Output signal (capacity MIS-sensor) is processed by electronics and displayed on a PC.

The MIS-sensor was calibrated using a graduated source micro flow NO\textsubscript{2} on a concentration of 0.25 ppm (0.46 mg/m\textsuperscript{3}) in air at the operating sensor’s temperature of 150 °C. The results are shown in Fig. 4.

![Figure 4](image)

**Figure 4.** The results of the calibration of the MIS-sensor on NO\textsubscript{2} (0.46 mg/m\textsuperscript{3} in the air)

In the first series of experiments on the experimental facility was tasked to determine the response of the sensor for heating of gas sample with help the reactor, without explosive vapors. It was also to check depend whether the sensor response on to known concentrations of NO\textsubscript{2} from heating temperature of the reactor. It was established that the stabilization of the readings of sensor after we enable heating of the reactor takes 30...50 min. In addition, it was shown that heating (in the temperature range 250...450 °C) gas mixture containing a known concentration of NO\textsubscript{2} has no effect (within the error of measurement of 15 %) on the magnitude response of the MIS-sensor mounted in the calibration. Thus, it was shown the ability to start main research using samples of explosives.

In this work, we studied the reaction of MIS-sensors on the trinitrotoluene (TNT). Samples of TNT were prepared in two versions: Test No. 1 was a glass cylindrical container with a volume of 0.1 l, on the inner surface of which is uniformly distributed a solution of TNT in acetone of high purity, followed by removing acetone vapors; Test No. 2 — test paper strips (2 x 5 cm) which was impregnated with a solution of TNT in acetone of high purity and carefully dried.

During the experiments with Tests No. 1 the reliable response (0.7 ± 0.3 Rel. units) managed to capture at the temperature of the gas mixture containing vapors of TNT, at least 420°C. To increase the effective area of the heating of the reactor, it was decided to optimize its design. For this the inlet nozzle of the reactor was filled with chemically pure heat-resistant glass fiber (~50% Al\textsubscript{2}O\textsubscript{3}, ~50% SiO\textsubscript{2}). By the microscopic fibers in the composition of the glass molecules of TNT were holding in the gas circuit of the reactor a longer time, which increased the reaction efficiency of thermal destruction. The experiments conducted with the use of advanced reactor showed an increase the response of the MIS-sensor ceteris paribus to 1.5 ± 0.3 Rel. units. It should be noted that the containers of glass were heated to 30...55 °C in all experiments with the Tests No. 1, for increasing the vapor pressure of explosives. Indeed, according to [8], the vapors pressure of TNT at room temperature does not exceed 5...7 ppb (60 µg/m\textsuperscript{3}, or 60 pg of 1 cm\textsuperscript{3}). However, with increase in temperature for every 5°C, saturated vapor pressure of TNT has doubled [8].

During the experiments with Tests No. 2 (at the temperature of the reactor 400 °C and with application glass fiber - concentrator) was established the dependence of the response of the MIS-
sensor from temperature of heating of test strips with the TNT microcrystals. The results are as follows: when heated to 30 °C, the response was 2.0 Rel. units; at 50°C – 6 Rel. units; at 70°C – 10 Rel. units (temperature measurement accuracy is ±2°C, the noise level of the signal ± 0,3 Rel. units) – Fig. 5. Note that the reaction of MIS-sensor on a clean test strips as well as the strips which were moistened with acetone high purity and subsequently were dried, were recorded.

![Figure 5](image)

**Figure 5.** The dependence of the MIS-sensor’s response on Tests No. 2 from the temperature of heating a sample of TNT. Arrows indicate the moments of filing and removing test strips

According to our estimates, the mass evaporated from the surface of the test strip of TNT when it is heated to 70 °C was about 1 µg.

3. Conclusions

Proved the possibility of using MIS-sensors as detector sensitive elements of the nitro-containing organic trace. Since MIS-sensors does not have sensitivity to the molecules of organic substances [9] that is why in the proposed method of the detection the sign of the presence of nitro compounds is the gas NO₂ which is emitted during the reaction of pyrolysis of the molecules of explosives.

4. References

[1] David J and Lewis A M 2008EUR 23023 EN
[2] Applications. National Institute of Justice 1999
[3] Nikolaev I N, Litvinov A V and Emelin E V 2007 Sensors and systems 5 p 66 (In Russian)
[4] Nikolaev I N and Emelin E V 2004 The measuring technique 11 p 54 (In Russian)
[5] Emelin E V and Nikolaev I N The measuring technique 2006 5 p 68 (In Russian)
[6] Emelin E V, Nikolaev I N and Sokolov A V Sensors and systems 2005 10 p 37 (In Russian)
[7] Nikolaev I N, Litvinov A V and Emelin E V Sensors and systems 2006 7 p 66 (In Russian)
[8] Qxley J C., Smith J L, Luo W and Brady J 2009 Propellants Explosives Pyrotechnics 34(6) pp.539 - 543
[9] Nikolaev I N and Onishenko P O 2006 Sensors and systems 3 p 34 (In Russian)