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Review

Analysis of Standard Methods for Determining the Properties of Explosive Materials in Ukraine

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Abstract: Standardized methods for determining the basic properties of energy-saturated materials in Ukraine are considered. The optimal directions for the use and development of explosives testing methodology in Ukraine are presented. All of the methods considered can be applied under certain conditions, depending on the initial requirements for the test explosive.

Keywords: explosive, test method, thermal sensitivity, mechanical sensitivity, water-resistance, density, detonation velocity, thermodynamic properties

1 Introduction

The current pace of development of science and technology has taken the industry of energy-saturated materials to a new level. The technologies for the production

of components and the production of the final explosive products from them are improved every year. It is also worth noting the development of various methods for increasing the level of safety during the transportation of explosives and for their testing. For this purpose, special standards and methodologies are created and developed.

Most of the methods for determining the basic properties of explosives in Ukraine are upgraded versions of the methods from the Soviet Union. These methods are also standardized in the CIS countries, but they may differ from those used in the countries of the European Union [1, 2]. It is worth noting that European technologies for determining certain properties of explosives can also be used in modern factories and enterprises in Ukraine.

The purpose of the present research is an analytical study of the methods for determining the basic properties of explosives in Ukraine, as well as an assessment of the appropriateness of their use and compliance with modern technologies. Test methods for high explosives are considered in this paper, because of their comprehensive and wide use in mining and the military industry.

2 Test Methods in General

78 national standards relate to civilian (brisant) explosives in Ukraine. According to the Ukrainian implementation of the European Standard Series 13631 (from [3] and [4]), there are several regulated basic properties of explosives to be tested for, such as:

- heat resistance,
- friction sensitivity,
- shock sensitivity,
- water-resistance,
- resistance to high hydrostatic pressure,
- transmission of detonation (concerning intermediate detonation),
- charge density,
- detonation velocity,
- thermodynamic properties (mostly concerning the evolution of heat and temperature of an explosion),
- toxicity of gases.

The determination of propellant explosive properties is mainly governed by GOSTs from the Soviet Union. Each of these GOSTs provides its own regulatory and technical documentation, which depend on the type of gunpowder. It is worth noting that the testing of the various grades of smoke powder are regulated by [5].

At that time, each type of smokeless powder has its own GOST, for example [6]. Despite some differences in the test methods, all types of gunpowder include testing of properties such as:

– velocity/time of combustion of the gunpowder,
– bulk density,
– hygroscopicity,
– velocity of the fraction,
– pressure of evolved gases.

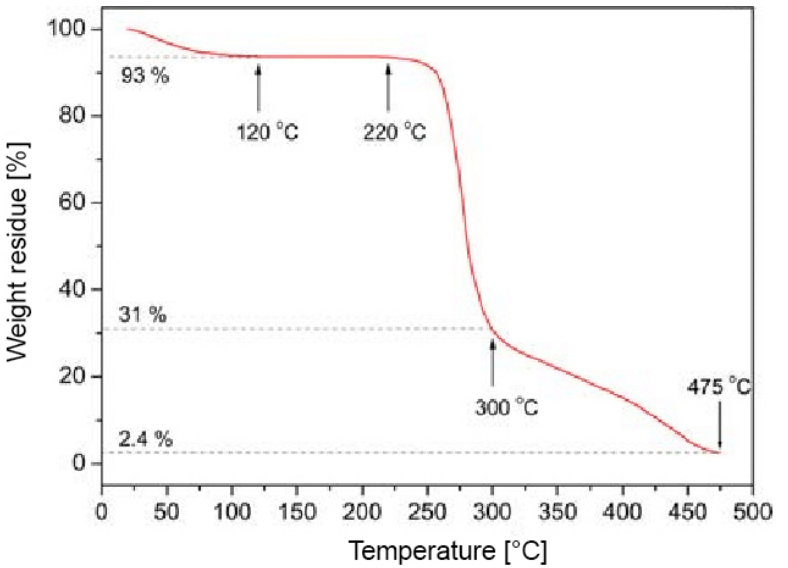
The determination of the properties of commercial (industrial) explosives is regulated by the GOSTs of the Soviet Union, by the series GOST 14839, for example [7, 8]. These standards describe methods for determining the component composition of commercial (industrial) explosives. These GOSTs distinguish the following properties of explosives:

– water resistance,
– transmission of detonation over a distance,
– charge density,
– completeness of detonation,
– particle size distribution.

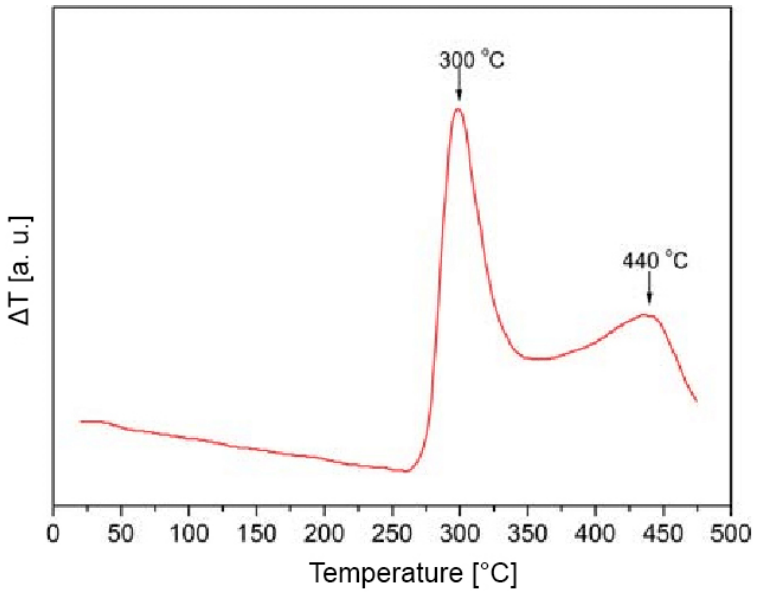
3 Thermal Sensitivity

Heat resistance is the ability of an explosive to maintain its explosive and energetic properties without significant changes, when exposed to elevated temperatures. Since most chemical transformations during heating are accompanied by a change in mass, valuable information can be obtained if the sample is weighed during a linear increase in temperature. This principle underlies the most useful analytical method that is called derivatography, which is now actively used to determine the heat resistance of explosives [1].

Derivatography is based on simultaneous measurement of the mass and enthalpy of the analyzed material during heating. In the course of derivatographic analysis for a single sample, three curves are recorded simultaneously: DTA, TGA, and DTG. It should be noted that this method complies with the modern methods of the EU countries, but some of these countries do not as a rule use it for the analysis of explosives. For example, other methods can be applied when compatibility is being taken into consideration [9]. An example of such an analysis is shown in Figure 1 [10].



(a)



(b)

Figure 1. TG (a) and DTA (b) thermograms of cellulose powder under air atmosphere [10]

The TGA curve is a thermogravimetric analysis curve. It involves measuring the dependence of the mass (m) of a sample on the temperature of the medium in which it is placed. The curve of mass loss has the form of a plateau, the horizontal section of which indicates the stability of the chemical compound in this temperature range and the absence of chemical transformations (while physical transformations are not excluded). A vertical step on the curve indicates chemical decomposition of the material. The TGA curve determines the mass loss of the sample upon heating (Δm), and this value allows simple chemical calculations to be used to determine the level of impurities in the analyzed material.

The DTA curve is a differential thermal analysis curve. It involves the heating or cooling of a sample at a certain velocity and the recording of the time dependence of the temperature difference between the test sample and a reference sample, which does not undergo any changes in the considered temperature range. Differential thermal analysis allows the presence or absence of phase transformations to be established, the temperature of the beginning and end of any process, accompanied by changes in the energy balance in the system, and the nature of the process over time.

The DTG curve is a derivative of the TGA curve. It allows setting the point in time or temperature at which weight change occurs most quickly. A non-standard explosive was tested as an example. Figure 2 shows the investigation of an explosive mixture of 99.5% potassium perchlorate ($KClO_4$) and 0.5% manganese dioxide (MnO_2) [11] on a "Thermoscan-2" Derivatograph (Analitpribor, St. Petersburg, 2012). "Thermoscan-2" (see Figure 3) combines two systems in one device: thermal weight and a differential thermal analyzer. The maximum temperature available is 1000 °C, however investigations of heat resistance are usually carried out in the temperature range 20-600 °C. The error in temperature determination is ±1.2 °C.

Typical results of thermal analysis obtained from "Thermoscan-2" are shown in Figure 2. The conditions were: room temperature 20 ºC, relative humidity 65%, sample mass 200 mg, heating rate 5 °C/min. The peaks on the DTA curve (red) correspond to the temperatures of the phase transition (peak 1, 300 °C) and explosive decomposition (peak 2, 520 °C) of the mixed components. The active decline of the TGA curve (black) coincides with peak 2.

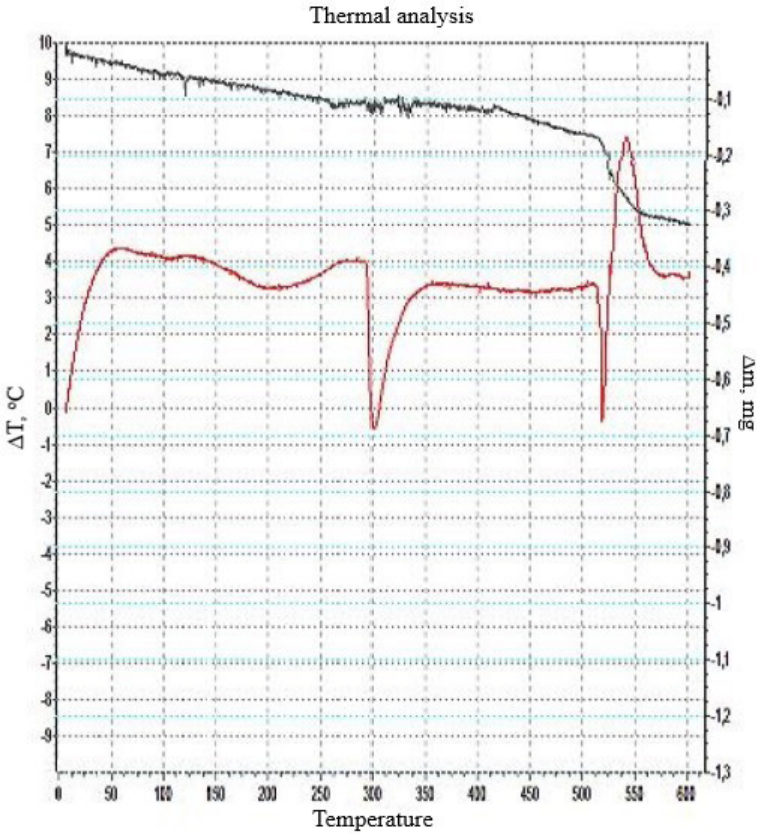


Figure 2. Derivatographic analysis (original view) of an explosive mixture of 99.5% $KClO_4$ and 0.5% MnO_2 [11]

Figure 3. Thermoscan-2 Derivatograph

4 Mechanical Sensitivity

4.1 Friction sensitivity

The sensitivity of an explosive to friction determines the probability of an explosion occurring due to external frictional effects. The sensitivity to shock friction, according to the methods, is determined using the device K-44-III [12]. The idea of the test method is presented in Figure 4 and an actual device is shown in Figure 5. Similar solutions are being known in other countries [13]. An explosive sample (20 mg) is pressed between two rollers to a certain pressure. The movement of the upper roller is initiated by the impact of the pendulum load. The drop angle of the load is determined by the pressing pressure. At each pressing pressure, 25 tests are carried out and the frequency of an explosion is determined.

The sensitivity to friction of unstressed material is determined via the device I-6-2. 30 mg of explosive is placed in the device. The pressing pressure is created and the rotation of the rubbing punch is included. The rotation time is 3 s. If no explosion is observed at the maximum pressing pressure (3000 kg/cm^2) and a rotation speed of 2040 rpm, 0.01 g of quartz sand is added.

The test results on the K-44-III and I-6-2 devices can be contradictory since the test conditions differ significantly. Therefore, an updated test procedure with the use of K-44-III is recognized in Ukraine.

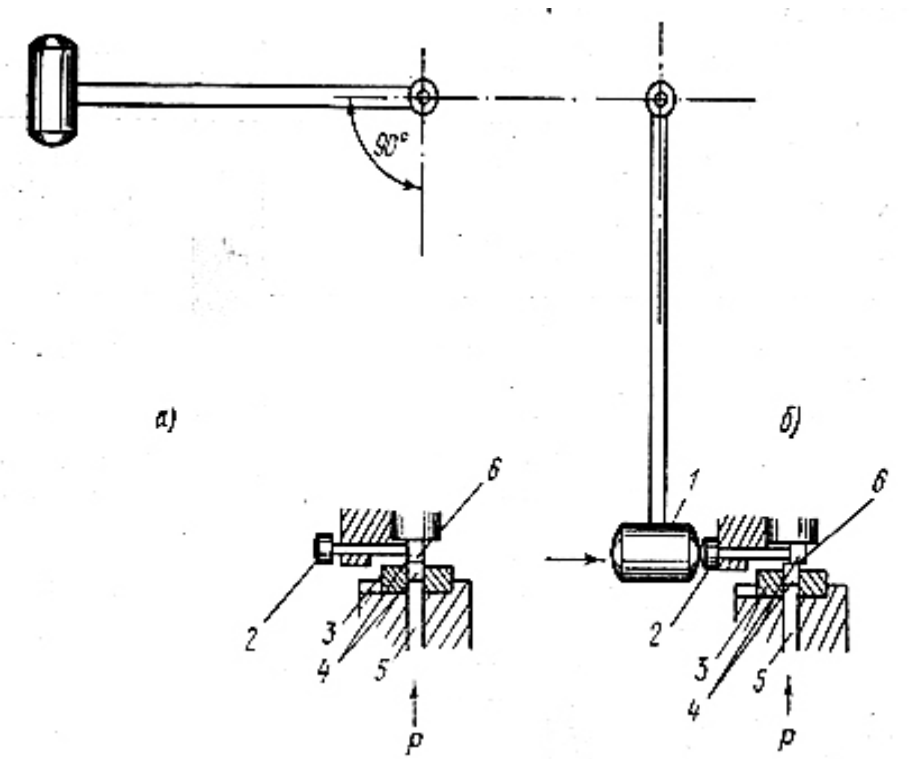


Figure 4. The principle of operation of the pendulum pile driver (pendulum copra) K-44-III: the position of the pile parts before dropping the load (a) and the position of the pile parts after dropping the load (b), where: 1 – cargo, 2 – hammer, 3 – clutch of the stamping device, 4 – rollers, 5– plunger of the oil press, 6 – explosive

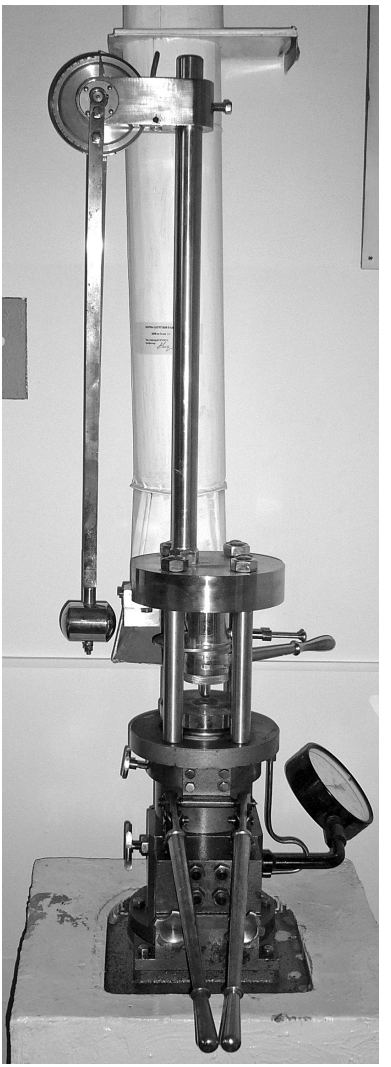


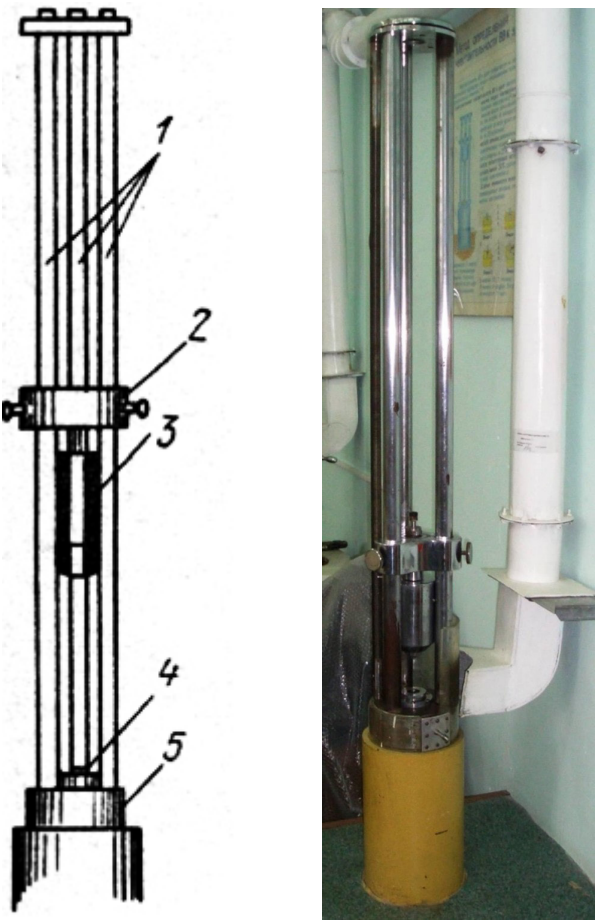
Figure 5. Image of pendulum pile driver (pendulum copra) K-44-III

In a friction shock sensitivity test, the following parameters are determined:

– the lower limit of sensitivity to shock friction, which is the maximum compression pressure (P_o) of the explosive sample between the rollers, in which explosion does not occur in any of 25 tests ;
– the upper limit of sensitivity to shock friction, which is the minimum compression pressure (P_{100}) of the explosive sample between the rollers, in which explosion occurs at all cases in 25 tests.

4.2 Impact sensitivity

Sensitivity to impact (shock) is the characteristic of explosives that determines the probability of an explosion with an external impact. To determine the characteristics of the sensitivity of explosives to mechanical stress, tests using the pile driver K-44-II are carried out [14]. A brass cap from the capsule of a pistol cartridge containing a pressurized (50-100 MPa) explosive (usually 0.02 g) is mounted under the hammer. This method has been updated in Ukraine (see Figure 6).



(a) (b)

Figure 6. Vertical pile driver K-44-II: 1 – guide pieces, 2 – holder, 3 – cargo, 4 – stamping device, 5 – anvil

The shock sensitivity test measures parameters such as:

– the lower limit of shock sensitivity, which means the maximum height (H_0) of the load (2 or 10 kg) dropped onto the explosive, at which no explosions occur in 25 tests;
– the upper limit of shock sensitivity, which means the minimum height (H_{100}) of the load (2 or 10 kg) dropped onto the explosive, at which explosion occurs in all cases in 25 tests s;
– the frequency of explosions is the number of explosions from 25 tests when a load of 2 or 10 kg weight is dropped onto an explosive [15].

5 Water-resistance

Water-resistance is the ability of an explosive to retain its basic properties for some time or change them in a small degree during contact with water. The water-resistance of explosives during testing is usually characterized by maintaining the explosive's ability to transmit detonation to a distance after holding cartridges in water for a certain time [16].

The test conditions are considered standard, under which cartridges with a diameter of 32 mm and a mass of 200 g are placed in a vertical position in a water tank so that a water column 1 m high is above their upper end. The cartridges are kept in this position for 1 h. Cartridges extracted from water should then transmit detonation according to a standard sample to a distance only slightly different from the distance established for dry cartridges. At the same time, the minimum distance over which detonation should be transmitted must be at least 2 m.

Water-resistant charges of increased density and large size (for wells) are checked for completeness of detonation after holding without protection in water in a vertical position for 4 h. The completeness of detonation is judged by the formation of a funnel after the explosion and by the absence of explosive remnants.

6 Density

The density of an explosive is determined by the ratio of its mass to its volume without taking into account the shell. There is the actual density of the explosive, and its loading density. Actually, the density of liquid explosives (emulsion, suspension) is a constant, while the density of a bulk explosive is increased when a load is applied [17].

The density of bulk explosives (powdered, granular) in their natural state is called the bulk or gravimetric density. The charge density is defined as the ratio of the mass of explosive to the part of the volume of the charging chamber occupied by it, limited by the length (height) of the charge, including voids that are not filled with explosive. For liquid and bulk explosives, charged by the free-filling method, the charge density coincides with the density of the explosive. During pneumatic loading, the loading density is higher than the gravimetric density, while when loading cartridges the explosive density is lower.

In Ukraine, the density of cartridges and blocks is usually determined by hydrostatic weighing or measurement; the bulk density of explosives is determined by measuring the volume of the explosive mass freely poured into a measuring cylinder., The volumetric energy and detonation parameters increase with an increase in the density of the explosive. However for explosive mixtures, the dependence is extreme. At a certain low critical density of an explosive, the detonation parameters fall, leading eventually to the complete loss of detonation ability.

7 Detonation Velocity

Methods for determining the detonation velocity, including allowing it to be measured with accuracy, can be divided into two groups:

– methods that make it possible to determine the average speed in a certain section of the charge length,
– methods fixing the entire process of detonation along the length of the charge and making it possible to determine the speed of detonation at any point on its length [17].

The first group includes the oldest Dautriche method, which is still often used due to its simplicity and accessibility, as well as oscillographic methods. The latter is also suitable for continuous speed measurement along the length of a charge, if special resistance sensors are placed in it.

The second group includes:

– Photographic methods in which photo-registers record on a photographic film a luminescence coincident with the propagation of a detonation wave over a charge in a transparent shell.
– The rheostatic method, in which the change in resistance is measured along the length of the charge section.
– The oscillographic method with variable resistance sensors.
– Radio interferometric method, which is based on the Doppler Effect. It includes the measurement of the Doppler frequency shift of a centimeter

or millimeter radio wave, reflected from the detonation wave.
– OTDR method (reflected impulse method or location method), which is based on the propagation of impulse signals.

The Dautriche method is the most often used in Ukraine, as the simplest, most effective, and least material-intensive method.

8 Thermodynamic Properties

8.1 Temperature of explosion

At present, the determination of the temperature of an explosion is possible using optical colour methods or using combustible thermocouples. It is difficult to determine the temperature of the explosion experimentally due to the short duration of the process and the high pressure of the explosion.

The most accurate optical colour method is based on determining the energy from a continuous spectrum characteristic of detonation, or on determining the ratio of brightness values at two wavelengths, called the "red-blue comparison" method. Measuring the detonation temperature of condensed explosives by optical methods does not have a universally recognized solution. This is due to additional glow effects at the interface between the explosive and the optically transparent medium. Due to the high cost of sensors and data research methods, the determination of detonation pressure and explosion temperature using experimental methods seems to be a difficult task. Therefore such data are determined theoretically in Ukraine [18, 19].

For a rough estimate, if it is assumed that the detonation pressure acting on the walls of the charging cavity is approximately equal to the pressure at the Chapman-Jouguet point $P \sim P_{\text{Ch-J}}$, then the temperature of the explosion (T) in K, is determined according to Equation 1.

$$T = \frac{273 \cdot P \cdot (V - 0{,}0006 \cdot V_{PE})}{1{,}01 \cdot 10^5 \cdot V_{PE}} \tag{1}$$

where V_{PE} is a volume of the products of the explosion in m^3. V_{PE} is determined theoretically according to the formula for thermal decomposition of the explosive.

8.2 Evolution of heat

To determine the evolution of heat during the explosion, a calorimetric bomb is used, originally made to study the explosion products [20]. The strength of the bomb allows charges up to 5-10 g to be exploded, and, in particular, charges in shells. The heat released during the explosion of such charges, per unit weight,

for all explosives used must certainly be close to the heat released during the explosion of large charges under practical conditions.

In conventional calorimetric measurements, a bomb is placed in a calorimeter with water and mixers. The base of this bomb is a steel block with three thermometers. The general scheme of a bomb with a suspended charge is shown in Figure 7. Two main thermometers are located in the upper and lower parts of the bomb. This arrangement is required because the lower and upper parts of the bomb are heated unevenly, especially during explosions in shells, when the heated parts of the shell provide slightly greater heating. Temperature equalization of the bottom and top of the bomb is relatively slow, and therefore two thermometers are used. The time for which averaging the temperature is carried out is rather long, but the temperatures are close. In addition to the two main thermometers, a third one, located in the lid, is also used.

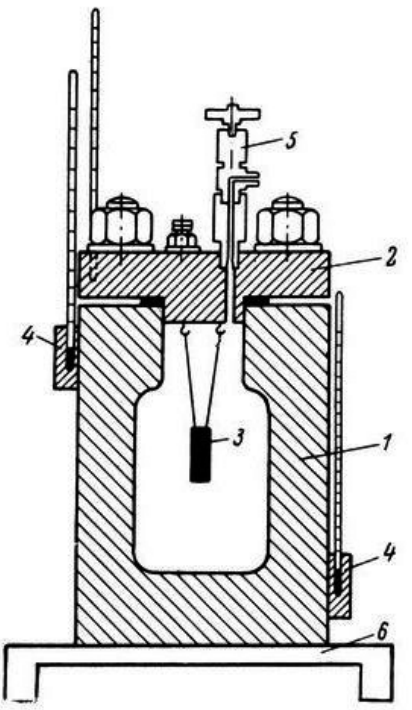


Figure 7. Scheme of the calorimetric bomb for measuring the evolution of heat: 1 – bomb body, 2 – lid, 3 – suspended charge, 4 – holders for thermometers, 5 – valve for gas discharge and pumping, and 6 – a wooden stand on which a bomb is mounted

During an explosion, the lid receives relatively little heat and then begins to slowly heat up. Knowing the rise in the temperature of the lid, it is possible to calculate the amount of heat that has gone into the lid and introduce the corresponding correction. The holders are made of red copper. Their inner surface has a curvature corresponding to the curvature of the surface of the bomb. In this way, good contact is maintained between the bomb and the thermometer holder. Fundamentally, the possibility that during the explosion there is a loss of a certain amount of energy carried away by the shock wave is not excluded. However, the shape and material (wood) of the stand are such that the loss is inconsequential.

8.3 Liberation of gases

Toxic gases generated during the detonation of explosive charges pose a great danger when conducting explosive work in underground conditions or poor ventilation. The most dangerous detonation products are nitrogen oxides, sulfur compounds, and carbon monoxide. One of the main reasons for the formation of toxic gases is the incompleteness of the chemical reactions of explosive transformation, which should end with the complete oxidation of combustible elements [21]. This can be caused by the incomplete balance of the explosive mixture in terms of oxygen balance, insufficient manufacturing quality or deterioration of the detonation ability during storage, as well as adverse conditions of use. In Ukraine, this property of an explosive is determined theoretically, but there is also an empirical technique. The standards for an explosive's toxicity is regulated by [4].

In theoretical calculations, the reaction of explosive decomposition of an explosive is used, according to which one calculates the volume (V), in dm^3 per 1 kg of an analyzed explosive material, of products that were formed during the explosion, mostly:

- carbon oxides, that were formed during the explosion ($V(CO)$),
- nitrogen oxides ($V(NO_2)$),
- sulfur dioxide and hydrogen sulfide ($V(SO_2 + H_2S)$).

Then, the total amount of toxic gases (Y), in dm^3 per 1 kg of an analyzed explosive material, per conventional carbon monoxide, can be calculated according to Equation 2.

$$Y = V(CO) + 6.5V(NO_2) + 2.5V(SO_2 + H_2S) \quad (2)$$

9 Conclusions

- This paper discusses the methods used in Ukraine for determining the properties of energy-saturated materials. The emphasis is on standard and innovative methods for determining the following characteristics of explosives:
  - heat resistance: by derivatographic methods,
  - friction sensitivity: via the K-44-III and I-6-2 devices,
  - impact sensitivity: via the K-44-II device,
  - water-resistance,
  - real density: by hydrostatic weighing or measurement,
  - bulk density: by measuring the volume of mass freely poured into a measuring cylinder,
  - detonation velocity: by photographic, rheostatic, oscillographic with sensors of variable resistance, radio-interferometry according to the Doppler effect, OTDR methods and the classical Dautriche method,
  - temperature of the explosion: by optical methods,
  - evolution of heat during the explosion: by a calorimetric bomb,
  - calculation of the volume of toxic gases after the explosion.
- It is concluded that innovative methods, in spite of their obvious progressiveness, do not always exceed the qualitatively standard methods of testing for energy-saturated materials. All of the considered methods can be applied under certain conditions, depending on the initial requirements for the tested explosive.

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