Neutralization of 4,6-Dinitro-*o*-cresol Waste Pesticide by Means of Detonative Combustion

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Neutralization of 4,6-dinitro-*o*-cresol, of which the best-before date had expired and which could not be used any longer, was carried out by means of the detonative combustion method. The pesticide comprises two nitro groups and is called DNOC. Composition of the applied explosive was designed on the basis of porous ammonium nitrate as an oxidizer and the pesticide as fuel. The thermodynamic parameters of such an explosive were estimated, and then three series of experiments with detonative decomposition of the material under a shield of sand were performed: in a steel chamber, in shot-holes in soil, and in shot-holes in a quarry. The efficiency of the pesticide decomposition was examined by determination of the residual remainder of the pesticide in the environment by means of gas chromatography. It was stated that pesticide content in the analyzed samples was below the determination threshold of the applied method. Biological tests with plants were carried out as well. Suggestion was made that the energy being produced during detonative combustion can be utilized for useful work, e.g. rock mining in a quarry.

Introduction

Neutralization of pesticides, which are useless when their best-before date is expired, is a priority task that has to be solved on a global scale, as it concerns many countries from all over the world. Huge amounts of money are spent on safe neutralization methods and liquidation of old pesticides. However, well-known and commonly used approaches cannot be applied in a number of cases. Some pesticides present problems, and this text is devoted to one such "troublemaker".

Dinitrocresol is one of the oldest pesticides. It was used for the first time in 1892 as an insecticide and then in 1932 as a herbicide. It was also used for production of slimming pills (*1*). The product itself is a derivative of nitrophenol, which does not exist in the environment in a natural form. There are about 18 known variations of dinitrophenols, but one of them is the most important, namely 4,6-dinitro-*o*-cresol (DNOC) (*2−6*).

As a dry material, the product tends to be explosive, which is why the substance is moistened in order to reduce the explosion hazard (DNOC contains about 10% water). The agent is used as a herbicide, insecticide, fungicide, and acaricide. The pesticide is marketed under its commercial names, Antinonnin, Detal, and Dinitrol.

DNOC had been in use until 1991. After that time it was recalled from the market by a decision of both the European Commission and EPA and cannot be used any longer as a pesticide (*1, 7*). The mentioned decision of the European Commission caused the application of one of the oldest pesticides to be ceased within the European area.

Hence, there arose the problem of waste products and the remaining reserves that are stored in a number of locations. One of the pesticide storage methods was gathering it together with other pesticides in so-called "entombment places" (underground containers or wells made from concrete cylinders and sealed by bituminous pitch). However, as time goes by, the containers begin to leak and toxic materials penetrate ground, subterranean water and sometimes even to wells and lakes (*8, 9*). Liquidation of the "entombed" content quite frequently needs extremely sophisticated technologies, as explosion, fire, or intoxication of workers can happen even during opening and unloading of the underground containers.

Appropriate neutralization methods are adapted for every individual type of pesticide. Troubles appear if the wastes are mixed, which can occur after unsealing of packages.

A large variety of different neutralization methods for pesticide wastes have been developed and patented (*10−20*). They can be subdivided into physical, chemical, and biological methods. However, thermal degradation still remains the most efficient approach (*21−26*).
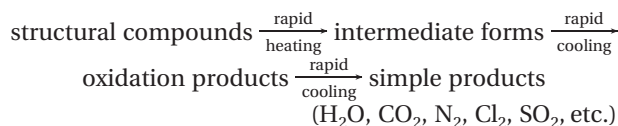
Despite numerous efforts that had been taken to find an efficient method for neutralization of various plant-protecting agents, no comprehensive technique, applicable to every agent and providing maximum efficiency, could be found. There exists even a certain group of compounds—containing nitro groups (DNOC is a representative of them)—for which combustion is not recommended. This compound contains two nitro groups and tends to be explosive. In addition, the explosion hazard even increases after drying up.

Experimental Section

Due to the explosive features of DNOC, investigation of its detonative combustion consisted of making a mixture of the pesticide with an oxidizing agent so that the mixture could be excited to detonation. It was assumed that the pesticide would be used as fuel for a heterogeneous explosive material. The properly balanced composition of that explosive, after ignition, causes commencement of a rapid reaction of deflagration. During the reaction the pesticide is combusted into its simplest products, simultaneously very quick cooling of reaction products occurs, caused by adiabatic decompression of gases (from several hundreds MPa to atmospheric pressure). The energy that is produced during detonative combustion can be utilized for useful work, e.g., rock mining in a quarry.

The concept of pesticide decomposition should consist of quick heating to a very high temperature, at which the energy of bond vibration leads to bond cleavage and destruction of a chemical compound. Next, by oxidation and rapid cooling of oxidation products, recombination is enabled, which leads to formation of new compounds with better thermal stability. Carrying those products through up to the form of compounds that are frequently met in nature, such as H_2O, CO_2, and N_2, would be considered as a success. The reactions should follow the equation below:

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structural compounds $\xrightarrow[\text{heating}]{\text{rapid}}$ intermediate forms $\xrightarrow[\text{cooling}]{\text{rapid}}$ oxidation products $\xrightarrow[\text{cooling}]{\text{rapid}}$ simple products

(H$_2$O, CO$_2$, N$_2$, Cl$_2$, SO$_2$, etc.)

Waste pesticides will play the role of reactants. As the reactions follow up in closed chambers, the intermediate products have not been analyzed. The experiments were focused on identification of pesticide remainders and lack of other hazardous products. It is also the reason why analyses of the gaseous mixture after explosion in the steel chamber or soil have not been carried out.

ANFO (ammonium nitrate fuel oil) was adopted as the heterogeneous explosive material, in which porous ammonium nitrate will act as oxidizer and the DNOC will act as fuel. Manufacturing of such a material, which would be able to detonate, requires meeting defined provisions. The next assumption was that the oxidation reaction should proceed under stechiometric conditions:

$$C_7H_5N_2O_5Na + 12.0NH_4NO_3 =$$
$$6.5CO_2 + 26.5H_2O + 0.5Na_2CO_3 + 13N_2 \quad (1)$$
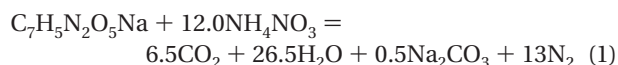
Calculations of performance parameters of the designed explosive were carried out under the assumption that DNOC had been preliminary dried prior to the experiment up to a moisture content of 0.01%; hence, for simplicity of calculation, the material was considered to be anhydrous.

Performance parameters allow making an assessment whether the obtained temperature of explosion is sufficient for pesticide decomposition and evaluating as well the concentration of energy and pressure to determine the ability to crush rock and perform certain work (it affects the so-called heap of mined rock).

The obtained results are gathered in Table 1, where parameters of classical ANFO are shown for reference. The results that are presented above were obtained in the same way as calculations for the stoichiometric conditions of the decomposition reaction in accordance with the method described in the Sector Standard (27).

Decomposition of DNOC was carried out by means of the detonative combustion method under a shield of sand in an explosion chamber located in soil and in rock (in case of decomposition failure, the molecules of DNOC are adsorbed on these materials). Efficiency of the pesticide decomposition was analyzed by means of gas chromatography (GC).

The present cycle of experiments did not include the analysis of DNOC that was contained in the investigated samples. The samples were produced by mixing a specified, predefined amount of DNOC with sand, soil, or rock. Further chromatographic analysis was handed over to the Institute of the Plant Protecting Agents from Poznań, Poland, and its affiliated branch in Sośnicowice (Upper Silesian Region). It is the research center where analyses of trace amounts of pesticides contained in soil, plants, etc. are carried out as their routine job. Effectiveness of the presented method of extraction had been estimated beforehand and was adopted by the Institute as their standard.

Detonative Decomposition in an Explosion Chamber. To examine efficiency of DNOC decomposition, an explosion chamber with capacity of 1.25 m^3 was used. The chamber was made from a horizontal drum and covered by two plates at both of its ends. One plate was welded directly to the drum, and the other one could be detached by means of bolt connections to enable access inside the chamber. The chamber had an orifice on top, through which the wires of an electric detonator were led out. The cartridge containing ANFO with DNOC, being 50 mm in diameter and 100 g in weight, was furnished with a Pentryt fuse containing 40 g of

Pentryt/m. The electric detonator was attached to the fuse and the whole unit was inserted into a plastic container filled with sand (Figure 1). The container was suspended inside the chamber, and after connecting the ignition electric circuit, the cartridge went off.

After the explosion, the sand was extracted from the chamber for analyses aimed to detect remaining pesticide. A sample of sand was taken for analysis after having the chamber aired (30 min after opening the cover). The sample was drenched with two 50-mL portions of acetone, successively, and then extraction in an ultrasonic bath was carried out (28). The extracts were filtered and evaporated dry in a vacuum evaporator. The dry remainder was standardized by dissolving it in 10 mL of acetone. After such preparation, the sample was analyzed for content of biologically active substances. The gas chromatograph was from Varian (type 3400) and equipped with an electron capture detector (ECD) and an integrator (IBDH) that enabled automatic data processing. Chromatographic separation of components was carried out in a capillary column made of silica (silicon dioxide) with a chemically connected liquid phase. The capillary column was factory-labeled as DB-5. The internal diameter of the column was 0.25 mm and thickness of the phase film 0.25 μm. The column was 30 or 60 m long. Thermal conditions of the separation were as follows: temperature of the feeder was 553 K and the temperature of the detector was 573 K. Over the first 5 min the temperature of the column was stabilized at 353 K and then gradual heating was programmed, at the rate of 10 grads/min, up to 563 K. Helium, at a flow rate of 1 mL/min, served as the carrier gas.

Identification of the determined component was carried out by comparison of retention time of a reference substance. Quantitative determining of the component was executed by means of the external calibration method. The reference substance DNOC was dissolved in dichloromethane.

Detonative Decomposition in Soil. For decomposition of DNOC by detonative combustion, plastic containers with diameter 180 mm and capacity of 5 dm^3 were used. The containers were filled with an explosive mixture, composed of 81.36% of NH$_4$NO$_3$ and 18.64% DNOC-fuel ($^1/_3 \times 5.47\%$ oil + $^2/_3 \times 18.64\%$ DNOC). Therefore, the charge of ANFO with DNOC was obtained. The 2-kg priming charge was furnished with the NONEL fuse and placed into a previously prepared shot-hole in the soil at the depth of 120 cm and then protected by stemming. The igniferous detonator was attached to the NONEL fuse and to the blasting time fuse. After such preparation the cartridge went off (Figure 2).

After detonation of the explosive, soil samples were drawn from the crater. For this purpose five boreholes were made by means of a hand-operated drill (gimlet). Each borehole was 10 cm in diameter and 140 cm in depth (with respect to the level before detonation) (Figure 3).

The soil, which was drawn from each borehole, was poured onto plastic foil and thoroughly mixed. Hence, averaged samples were taken for analyses.

Weighted samples of soil (50 g) were drenched with two 50-mL portions of chloromethane, successively, and then extraction in an ultrasonic bath was carried out. The extracts were filtered and evaporated dry in a vacuum evaporator. The dry remainder was standardized by dissolving it in 10 mL of acetone. After such a preparation, the sample was analyzed for content of biologically active substances.

Detonative Decomposition. Neutralization of DNOC in blast boreholes was carried out under conditions of real rock mining in a quarry where Jurassic limestone is excavated. One blast borehole was filled with 100 kg of ANFO with DNOC admixture. The granulated porous ammonium nitrate was used, the oil absorbing capacity of which was 7.5%. Oil was added into DNOC and ammonium nitrate was coated with the composition by mixing in accordance to the aforemen-

TABLE 1. Calculated Thermodynamic Parameters for ANFO and ANFO Modified by DNOC Admixture

| explosive	ANFO	ANFO + DNOC
flammable component	paraffin oil	DNOC
composition of the explosive		
flammable component (%)	5.47	18.64
NH_4NO_3 (%)	94.53	81.36
density of the explosive, d (kg/dm³)	0.900	0.900
oxygen balance B (%)	0.00	0.00
no. of moles of individual elements per 1 kg of explosive		
carbon	3.88	5.927
hydrogen	55.36	44.891
oxygen	35.45	34.727
nitrogen	23.63	22.022
others		0.848 Na
chemical composition of the explosion products (mol/kg of the explosive)		
carbon dioxide	3.88	5.503
carbon oxide	0.00	0.000
water (gaseous)	27.68	22.446
nitrogen	11.82	11.011
others		0.424 Na_2CO_3
specific volume of the explosion products, V_o (dm³/kg)	972.16	873.094
heat of combination for the explosive, Q_o (kJ/kg)	4444.64	4340.237
total heat of combination for the explosion products, Q_p (kJ/kg)	8194.82	8051.918
heat of explosion, Q_w (kJ/kg)	3750.17	3711.681
concentration of energy, E_v (kJ/dm³)	3375.16	3340.513
temperature of explosion, T_w (K)	2753	2839
average specific heat of gaseous products of explosion, c_v (J/mol K)	34.85	35.526
exponent of the adiabatic curve, k	1.24	1.23
explosion pressure, P_w (MPa)	893.76	827.631
ideal work of explosion, A (kJ/kg)	3100.00	3025.020
specific energy, f (kJ/kg)	993.06	919.590
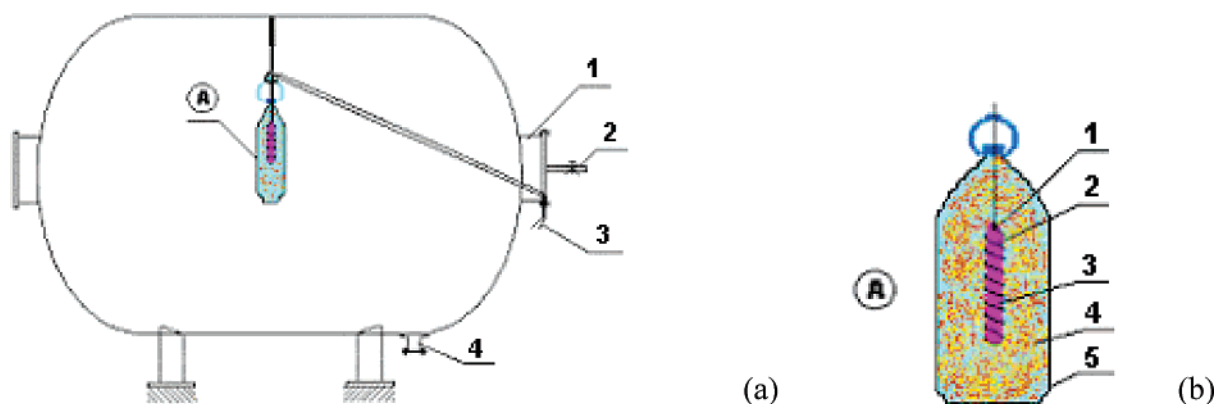
FIGURE 1. Chamber (a) and the container with the cartridge (b) for sand-shielded decomposition of DNOC. (For part a) 1, cover; 2, stub pipe; 3, wires of the electric detonator; 4, outlet stop pipe. (For part b) 1, electric detonator; 2, Pentryt fuse; 3, the cartridge (ANFO with DNOC); 4, sand; 5, container.

tioned rates. Therefore, ANFO of 0.900 kg/dm³ in density was obtained. The detonator, which was a charge of the emulsion explosive named Emulinit, furnished with the NONEL-type fuse, was inserted into the bottom of the borehole. The mixture of ANFO with DNOC was loosely poured, and for reliability of the explosion, another cartridge of Emulinit was placed in the upper part of the ANFO column. The cartridge was furnished with the NONEL fuse with longer delay time. Finally, the blast borehole was sealed with stemming. After preparation of the charges in the above manner, they were connected to the shooting line and went off. Five separate detonative decompositions of DNOC in quarry rock were carried out. The detonation rate of the explosive, measured in the blast borehole along the distance of 9.9 m, was 3600 ± 100 m/s. Measurements were taken by means of a meter to which two light pipe conductors were attached for transmission of light signals of detonation commencement and termination along the said distance.

After termination of shooting, samples were taken from several locations of the rock for further analysis.

Extraction of the crushed rock samples, having been drawn after shooting, was carried out as "direct extraction" (directly affecting the rock)—drenching with acetone and extraction in the ultrasonic bath. The extracts were filtered and evaporated dry in a vacuum evaporator. The dry remainder was standardized by dissolving it in acetone.

Biological Test. Three series of biological experiments were carried out.

First Series. Oats and white mustard were sown into the soil that had subjected to detonative decomposition. In parallel, reference tests were performed for floral soil (pure soil)

Second Series. Oats and white mustard were sown into the floral soil (pure soil). After the plants had sprouted and had gotten three leaves, they were watered with extract from the soil that had subjected to detonative decomposition of herbicides.

Third Series. Oats and white mustard were sown into the floral soil (pure soil). After the plants had sprouted and had gotten three leaves, they were sprayed with a reference
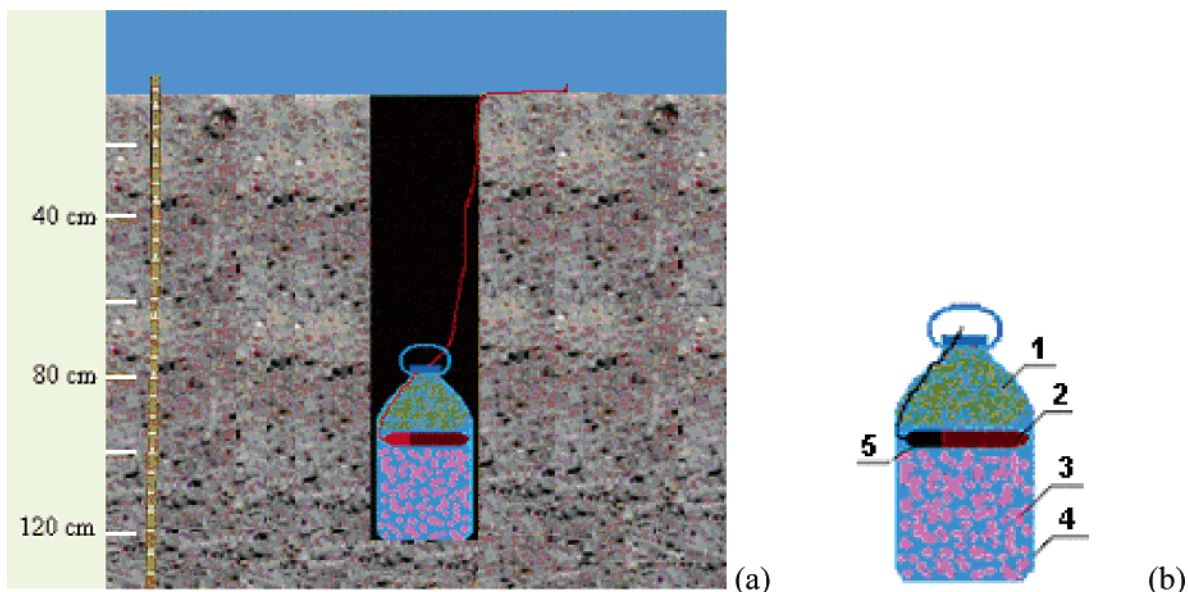
FIGURE 2. (a) Shot-hole. (b) Container with a sample of DNOC and the explosive prepared: 1, sand; 2, the Pentryt cartridge; 3, ANFO + DNOC; 4, container; 5, detonator.
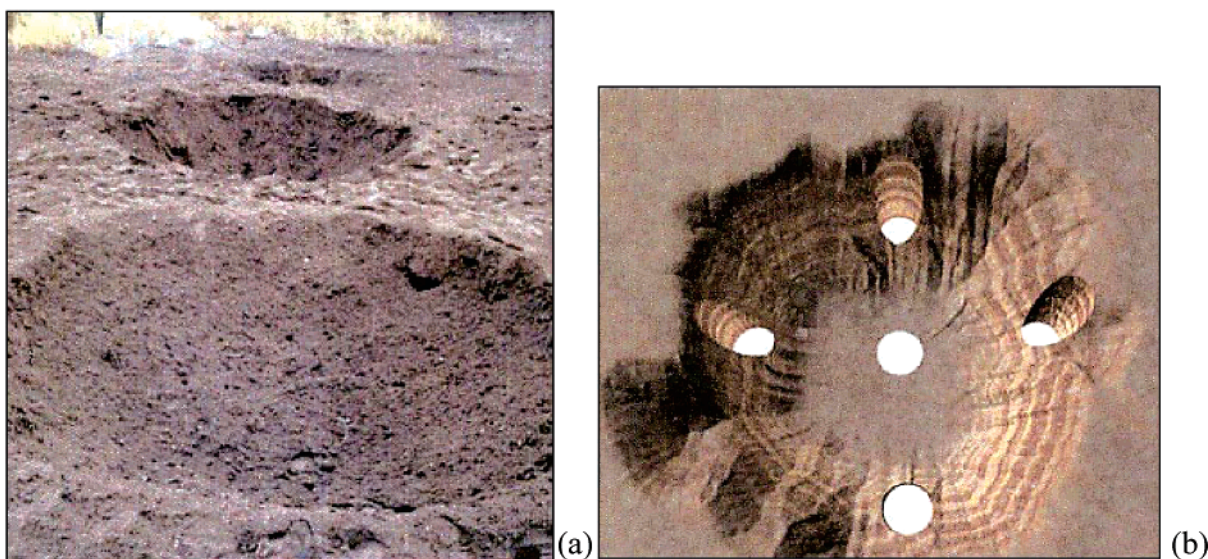

FIGURE 3. View of the craters created by the explosion (a) and the boreholes for soil sampling (b).

solution of the herbicide according to the dosage recommended by the manufacturer.

All the experiments were carried out simultaneously, under the same conditions, and the plants were kept in such an environment that assured favorable vegetation. To ensure the best sprouting, the seeds that were used for tests had been carefully selected (only robust and shapely seeds had been chosen).

Thirty white mustard seeds were sown into soil in plastic plates with diameter of 14 and 3 cm deep. Seven plates were used for each series (two for reference). After the seeds had sprouted (the second cotyledon phase), the weakest specimens were removed and 25 robust plants were left, which was the amount of seeds that were sown in the first series.

Eighteen oat seeds were sown in a similar way as the white mustard. After the seeds had sprouted, the weakest specimens were removed and 15 robust plants were left for further experiments, which was the amount of seeds that were sown in the first series.

Results and Discussion

Extracts of the pesticide residues from the sand contain, beside the determined component, some contamination at extremely low concentration. Such content of admixtures does not disturb the chromatographic separation and the quantitative determination of the pesticide content.

The DNOC elutes at $t_R = 24.135$, before slight contamination of the sand. The corresponding peak and the printout of the detector signal are shown on the chromatogram (Figure 4).

The result that was obtained for DNOC decomposition by means of a heterogeneous explosive, being the result of explosion of the cartridge inside a sand shield, revealed some remaining pesticide that failed to decompose (90.5 mg of the pesticide per 1 kg of sand). This can be explained by unfavorable detonation conditions (low resistance of the explosive shield, which was sand) as well as by the small diameter of the cartridge.

Upon detonation of an explosive material in soil, three zones affected by the blast can be distinguished: (i) a
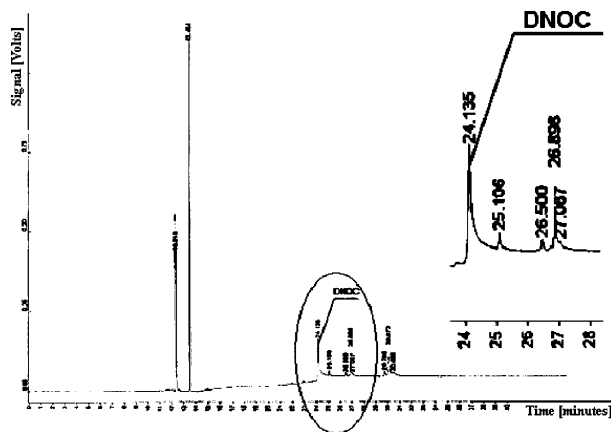
FIGURE 4. Chromatogram obtained for determining DNOC content in the sand; $t_R = 24.135$ (column length, 60 m).
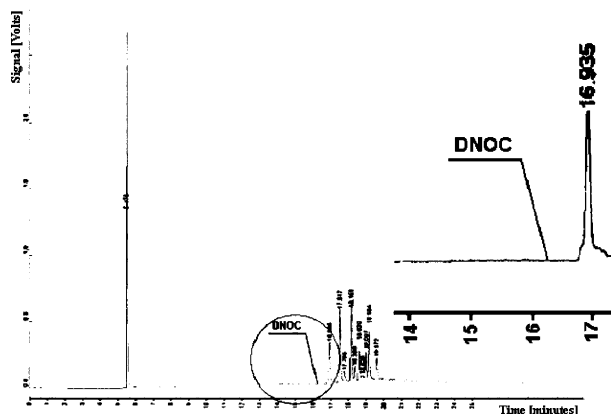

FIGURE 5. Chromatogram obtained for determining DNOC content in the sample extracted from soil; $t_R = 16.104$.

FIGURE 6. Chromatogram for DNOC reference solution; $t_R = 24.095$.

FIGURE 7. Chromatogram obtained for determining DNOC content in the sample extracted from rock, $t_R = 24.095$.

compression zone caused by compression of the ground by detonation products (results in thickening of the ground); (ii) demolition that occurs outside the compression zone, characterized by destruction of connections between the ground particles (results is crumbling of the ground and formation of cracks; and (iii) shock that upsets the ground structure. The calculations were carried out under the assumption that the disturbed ground would be thrown upward and fall back into the crater created. It was assumed that the crater diameter is $r = 1.25-1.50$ m and the depth where the examined samples are taken from is 1.40 m. The weight of the explosive cartridge (ANFO) was estimated as 2 kg.

The samples extracted from denotative decomposition of soil contained, beside possible reminders of the pesticide, some organic compounds, which become volatile under the thermal condition of the chromatography. Therefore, peaks for both organic components of soil and pesticides under determination are visible in chromatographs. The extracted samples of neutral type as well as acid ones were analyzed.

There are also two large peaks on the left-hand side of the chromatogram that have not been identified, although they are likely to be produced by the solvent used. Apart from DNOC, 20 other pesticides were investigated. Although characteristic groups of the pesticides were different, a similar peak occurred on every occasion for the same retention time. As the peak did not superpose with retention time of any investigated substance, the attempt to identify it was abandoned.

The DNOC elutes at $t_R = 16.104$, before admixtures of the soil (column length, 30 m) (Figure 5); therefore, its determination is effortless.
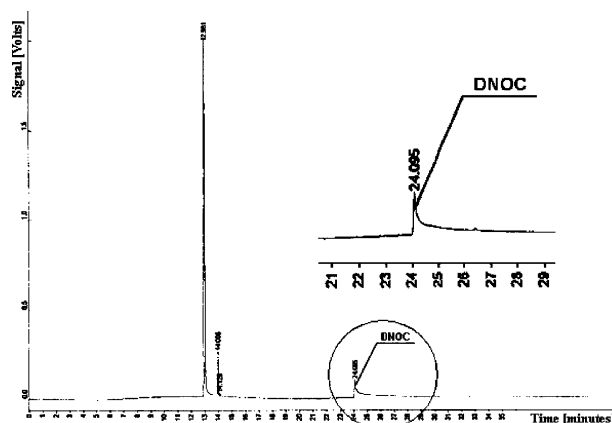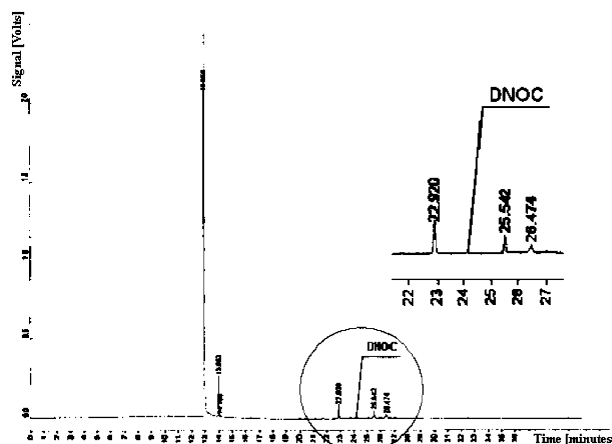
The content of biologically active substances in the extracted samples after the explosive decomposition was below the determination threshold. It follows that the decomposition degree of that compound was very high.

In strip mines shooting of blast boreholes is applied—it is the method for detonative mining of rock that involves placing explosive charges in blast boreholes of diameter > 60 mm and length not less than 10 m. The blast boreholes, where the explosive is located, are mechanically drilled by means of a rotating and picking drilling rig. The charges are lined up in one or two rows in parallel to the wall of the uncovered body of the mined rock. Every blast hole should be filled with the explosive mixture up to two-thirds of its depth, and the upper one-third of the borehole depth should be filled and sealed by means of the stemming. All the boreholes in a single row go off at the same time.

No remainder of DNOC was detected for any extracted sample.

Figure 6 presents the chromatograph of the reference solution. DNOC elutes at $t_R = 24.095$. In this case, the detector signal that refers to the related peak would correspond to the compound ratio of 48 mg/kg.

Figure 7 presents one of the chromatographs proving that no traces of DNOC were found in samples extracted from rock. Possible content of the pesticide could have been below the determination threshold, which was 1.5 mg/kg.

Assessment of the degree to which the herbicide had affected both white mustard and oats was carried out according to the nine-grade scale (Table 2).

Observation of the plant was carried out every day, but assessment of their constitution was scheduled differently. For the first series, judgments were made in five steps (the

TABLE 2. Stand Quality Classification for the Influence of Herbicides on Crop Plants According to the Nine-Grade Scale

symptoms of toxic effect on crop plants	stand quality class
no symptoms	1
slight symptoms, growth retarded insignificantly	2
symptoms weak but clearly visible	3
stronger symptoms, e.g. chlorosis	4
plants thinned out, strong chlorosis or plants muffled	5
large scale of damages, plants are withered and dying.	6
	7
	8
total destruction	9

FIGURE 8. Oats on day 21 after spraying with extract from the soil that had subjected to detonative decomposition of DNOC.

FIGURE 9. White mustard on day 21 after spraying with extract from the soil that had subjected to detonative decomposition of DNOC.
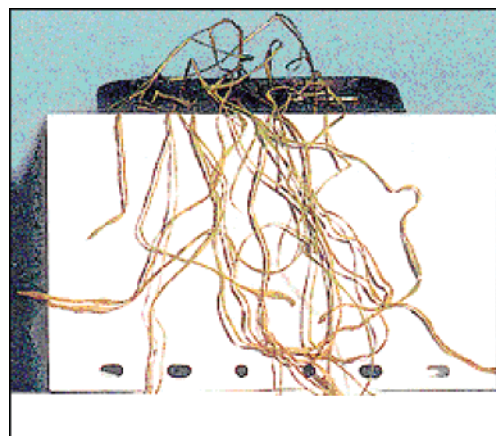

FIGURE 10. Oats on day 21 after spraying with a water solution of DNOC.

FIGURE 11. White mustard on day 21 after spraying with water solution of DNOC.

first appraisal was on day 4 after sprouting had begun, the second one 3 days later, the third one 7 days after the first one, the fourth one on day 14 after the first observation, and the last one 21 days after the first one). Series 2 and 3 involved four milestone observations (the first appraisal was on day 3 after spraying, the second one 7 days later, the third one on day 14 after the first assessment, and the fourth one 21 days after the first one). Obtained results are shown in Figures 8–11and in Tables 3–5.

None of the experiments showed a toxic effect on the crop plants. That confirms the absence of any remainder (or vestigial amounts) of herbicide in soil that had been sampled from a place where detonative combustion of herbicides was carried out.

Incomplete sprouting resulted from a lack of full effectiveness of sprouting of the seeds under experiment, despite the preliminary selection of the seeds. The only criteria that governed selection of the seeds for experiments was their appearance, but that could fail ensuring full effectiveness of sprouting.

No toxic effect on a crop plant was observed. Test results confirm the absence of any remainder (or vestigial amounts) of a herbicide in a soil that had been sampled from a place where detonative combustion was carried out.

In conclusion, one should state that the method of detonative combustion revealed parameters that were favorable for final DNOC neutralization: high rates of reaction zone dislocation, which was 3600 m/s; high reaction temperature up to 2900 K; and fast cooling of reaction products.

Application of the developed method is extremely preferred for compounds with the nitrate group. The practical aspect of the presented method is also its advantage—the rock-crushing capability of the ANFO that had the pesticide

TABLE 3. Results of Experiments for the First Series of Biological Tests

plant	sample	sown	sprouted	efficiency of sprouting (%)	stand quality class	symptoms
white mustard	1	25	25	100	1	none
	2	25	21	84	1	none
	3	25	21	84	1	none
	4	25	21	84	1	none
	5	25	23	92	1	none
oats	1	15	15	100	1	none
	2	15	15	100	1	none
	3	15	15	100	1	none
	4	15	15	100	1	none
	5	15	15	100	1	none

TABLE 4. Results of Experiments for the Second Series of Biological Tests

plant	sample	stand quality class			
		step I	step II	step III	step IV
white mustard	1	1	1	1	1
	2	1	1	1	1
	3	1	1	1	1
	4	1	1	1	1
	5	1	1	1	1
oats	1	1	1	1	1
	2	1	1	1	1
	3	1	1	1	1
	4	1	1	1	1
	5	1	1	1	1

TABLE 5. Results of Experiments for the Third Series of Biological Tests

plant	sample	stand quality class			
		step I	step II	step III	step IV
white mustard	1	6	9		
	2	7	9		
	3	7	9	observation terminated[a]	observation terminated[a]
	4	6	9		
	5	6	9		
oats	1	1	3	7	9
	2	1	3	8	9
	3	1	2	7	9
	4	1	2	8	9
	5	1	3	8	9

[a] Observation was terminated because of the total destruction of the plants after treatment by the aforementioned herbicides.

admixed as fuel was no worse than traditional ANFO, when the fining degree was analyzed.

Therefore, further experiments should be followed up, where the detonative combustion should be executed in soil or real rock rather than in a chamber. This method not only can solve the environmental problem posed by pesticide waste but also can simultaneously provide the required energy for rock mining.

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