Detection and Neutralization of Unsymmetrical Dimethylhydrazine on the Surface of Construction Materials

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Abstract—The construction materials that contacted with unsymmetrical dimethylhydrazine and the desorption solutions obtained when treating the contaminated surface of metals and alloys with water and reagents were studied by chromatography and mass spectrometry. Neutralization of unsymmetrical dimethylhydrazine was studied using ozone and shungite. Ozonation makes it possible to destroy the toxicant molecules chemically and physically adsorbed on the surface of metal constructions, due to which they can be reused and utilized. Shungite effectively adsorbs and catalytically decomposes not only unsymmetrical dimethylhydrazine and its transformation products, but also oligomer compounds formed during the storage of hydrazine fuel. Ozonation of spent shungite can increase the efficiency of destructive processes and completeness of its regeneration.

Keywords: UDMH, ozone, shungite, chromatography, mass spectrometry, construction materials

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The environment and construction materials are contaminated with various toxic compounds in the course of human economic activities, during the degradation of fuels and industrial products and when using initially poisonous compounds. For example, hydrazines, which are extremely toxic to animals and humans, are widely used as rocket propellants, in agriculture, medicine, plastics production, and other industries [1].

Unsymmetrical dimethylhydrazine (UDMH) is highly volatile and well adsorbed on various surfaces including metal ones; it mixes with water, oil products, and organic compounds, i.e., is a mobile toxicant easily migrating over various environmental objects [2]. UDMH and the majority of its transformation products are not corrosive substances for steel structures, but their dilute aqueous solutions cause increased corrosion of aluminum and its alloys [3, 4]. The high reactivity of UDMH leads to the formation of many toxic products of its oxidative transformation, many of which are rather stable and capable of accumulating in environmental objects [5–7].

Detection and neutralization of UDMH and its transformation products in air, water, and soil and on the surfaces of structural materials is a very important environmental problem that cannot be solved without developing sensitive methods for the analysis and isolation of these compounds or their transformation into nontoxic substances. Chromatography is a highly efficient analytical method that allows simultaneous determination of several target compounds. The use of mass spectrometry for detection can significantly reduce the detection limits of substances and increase the reliability and informativity of analysis. As the majority of UDMH transformation products are volatile, they are analyzed by gas chromatography-mass spectrometry (GC-MS) [7]. To identify nonvolatile substances, it is possible to use desorption mass spectrometry, for example, matrix-activated laser desorption/ionization (MALDI) or thermal desorption mass spectrometry (TDMS) [8]. Gas chromatography-mass spectrometry used for surface contamination analysis is usually based on preliminary sample preparation, wipe sampling from the surface, or sampling for pyrolysis.

The methods proposed for neutralization of UDMH include the thermal, catalytic, sorption, radi- ation, and biochemical techniques [9]. In practice, the equipment, stationary tanks, constructions, and fuel storage facilities are often neutralized by washing them with aqueous or organic solutions. This results in significant amounts of toxic wastewaters. They are environmentally hazardous because of large volume, high total toxicity, and uncontrolled spreading. To neutralize UDMH in wastewater, adsorption methods are widely used, which make it possible to concentrate the toxicants for their further destruction. For this purpose, coals, peat, aluminosilicates, shale, and lignin...
are actively used. It was proposed that the mineral shungite be used as a sorbent [7, 10]. Shungite has a rich mineral composition; it contains up to 90% carbon and impurities of catalytically active metals and oxides and has high mechanical strength and durability [11].

The destructive methods for removing UDMH are most effective; they lead to the formation of gaseous and low molecular reaction products. Ozone is a strong oxidant and environmentally friendly reagent because the reaction product is mainly oxygen [12]. Deep oxidation of organic compounds occurs at room temperature and atmospheric pressure. Metals, their oxides, catalysts, and UV and γ radiation sharply accelerate the ozonolysis [13]. The oxidation of hydrazines with ozone in gaseous and liquid media is 30 times more active than the oxidation with oxygen and leads mainly to dimethylnitramine. Only 5% of UDMH undergoes deep oxidation to CO2, nitrogen, and water during liquid-phase ozonolysis [14]. To enhance its destruction, heterophase ozonolysis of UDMH preliminarily sorbed on Al2O3 was proposed [15].

Unlike other carbon sorbents, shungite is capable of catalytically decomposing UDMH [10]. It can hardly be oxidized with ozone, and there are no noticeable changes in the structure of shungite carbon as a result of low-temperature ozonation [15]. The nonsteady-state character of the vibrational kinetics of shungite ozonation and the absence of CO2 in reaction products are the distinctions of shungite from the majority of carbon materials [16]. As a result of ozonation, the characteristics of shungite such as the specific surface area, volume of micropores, their number, adsorption activity, and the number of oxygen-containing surface groups increase [17].

The goal of this work was a physicochemical study of neutralization of UDMH and the products of its oxidative transformation that contaminate the surfaces of construction materials using ozone and shungite. As so far there are no methods for effective neutralization of UDMH-contaminated objects that would meet modern environmental safety requirements, the search for new ways for neutralization of UDMH using available and environmentally friendly technologies is an important problem.

EXPERIMENTAL

The standard fuel containing 98% UDMH (Salavatnefteorgsintez, GOST (State Standard) R ISO 15859-7-2010) was used. The real samples of construction materials in contact with UDMH were the containers of rocket vehicles and the fragments of fuel tanks in which hydrazine fuel had been stored for a long time, as well as the aluminum-magnesium alloy AMg6 (GOST (State Standard) 4784-2019) containing up to 93.7% Al and the samples of construction materials fixed in plates on the casing of the International Space Station.

The powder of the mineral shungite-III from Zazhoginskoe deposit (Karbonshunig company, TU (Specifications) 5714-007-12862296-2016) with a specific surface area \( S_{sp} \approx 2 \text{ m}^2 \text{ g}^{-1} \) and a pore volume of 0.046 cm3 g\(^{-1}\) was studied.

Acetone (Baker, the Netherlands), m-nitrobenzoic acid (Vekton, Russia), and deionized water were used as reagents to remove UDMH and the products of its transformation from the surface of construction materials.

The 0.05–0.1% aqueous solutions of UDMH and UDMH-contaminated steel structures were ozonated under dynamic conditions at 20°C in a specially designed device for cleaning metal surfaces and equipment [18]. The ozone concentration in the ozone–oxygen mixture was 60 mg L\(^{-1}\); the gas flow rate was 0.5 L h\(^{-1}\). The steel surfaces were treated in a tank with circulating ozonized water (ozone concentration 3.4 mg L\(^{-1}\), flow rate 0.5–0.6 L h\(^{-1}\)).

The composition of the liquid phase was analyzed by GC–MS and TDMS using a JMS-D300 mass spectrometer (Jeol, Japan). The thermal desorption of the compounds was studied by directly introducing an ampule with a sample and heater in the zone of the ion source. The heating rate of the sample was 10°C min\(^{-1}\), accelerating voltage 3 kV, ionizing electron energy 70 eV, range of recording of mass numbers 40–800 Da. The substances were separated on a quartz capillary column (30 m × 0.5 mm) with a DB-5 liquid stationary phase (J&W Scientific, United States) using an HP 5890 gas chromatograph (Hewlett-Packard, United States). The injector temperature was 280°C, carrier gas (helium) velocity 1 mL min\(^{-1}\).

For simultaneous determination of UDMH and the products of its transformation in solutions, the acetone derivatization technique was used [7]. Qualitative identification of substances was performed using the library search programs based on the tendencies in the transformation reactions of UDMH and the properties and reactivities of intermediate and final reaction products [8]. For quantitative analysis, we used an approach based on the assumption that the responses of the mass spectrometric detector to all substances were equal. Deuteronaphthalene (Sigma–Aldrich, United States) with \( m/z = 136 \) served as an internal standard.

The materials and swipes from the surface of contaminated metals were analyzed by the MALDI–MS method on a Bruker Daltonics Ultraflex II mass spectrometer (Bruker, Germany) equipped with a time-of-flight mass analyzer with a nitrogen laser (\( \lambda = 337 \text{ nm} \), maximum energy 110 μJ, pulse frequency 20 and 50 Hz). 2,5-Dihydroxybenzoic acid (Bruker Dalton-
ics, Germany) was used as a matrix and target of stainless steel. The positive ions were detected in the range of \( m/z = 20–800 \) Da. The mass spectra were processed using the FlexControl 3.4 and FlexAnalysis 3.4 software.

RESULTS AND DISCUSSION

Some part of UDMH on the surface of construction materials slowly evaporates at a rate of 5% per day; the remaining UDMH undergoes oxidative transformation and is gradually converted into dimethylmethylenedihydrazone, dimethylamidine, trimethylhydrazone, tetramethyldiazene, diazomethane, formaldehyde, and nitrous oxide. Under the influence of sunlight and heat, UDMH is oxidized to hydrogen cyanide, ammonia, nitrogen, methane, carbon oxides, and water [2, 6].

Figure 1 shows the MALDI mass spectrum of an aqueous solution (wipe sample) obtained by washing the fuel tank from hydrazine fuel stored in it.

The wipe sample from the walls of the fuel tank is a complex mixture of compounds. Its mass spectrum contains the signals of the protonated molecules of UDMH (\( m/z = 61 \)); trimethylamine (\( m/z = 60 \)); dimethylenethylenedihydrazone (\( m/z = 73 \)); dimethylformamide and dimethyltriazone (\( m/z = 74 \)); dimethyl-N-nitrosamine (\( m/z = 75 \)); 1,1-dimethylmethylenetetrazene (\( m/z = 101 \)); 1,1,4,4-tetramethyl-2-tetrazene (\( m/z = 117 \)); N1,N1-dimethyl-N2-(dimethylamino)formamidine (\( m/z = 116 \)); dimethylaminocetaldehyde dimethylhydrazone (\( m/z = 130 \)); ethanediol and propanediol bis(dimethylhydrazone) (\( m/z = 142 \) and 157); and bis(dimethylhydrazone)-3,4-diaza-1,3,5-hexatriene (\( m/z = 197 \)). Other N-containing compounds with a molecular mass of 200–600 Da are the components of black tar formed during long-term storage of hydrazine fuel as a result of oxidation, addition, cyclization, condensation, and oligomerization of UDMH.

The products of UDMH transformation were found in large amounts in the wipe samples from the casing materials of the International Space Station (Table 1), which uses hydrazine-fuel engines. Treatment of the wipe samples with acetone provides favorable conditions for the separation and detection of these compounds in the form of hydrazones [7]. It was found that the qualitative composition of the wipe samples from materials after the space flight is very similar to the composition of the products of oxidative transformation of UDMH under land environment conditions. Similar results were later obtained when analyzing the case and solar cells of the Mir space station. The components of the rocket propellant oxidized on earth are evidently those that were chemisorbed and retained for a long time on the case and materials of space stations under high space vacuum conditions.

The contents of these toxic substances in the wipe samples from construction materials is tens of times higher than the maximum permissible concentrations according to health standards [19]. Hydrogen cyanide, hydrazine, methylhydrazine, UDMH, and dimethylnitrosamine belong to class 1 of highly hazardous compounds; dimethylamine and formaldehyde, to class 2; and tetramethyldiazene and dimethylformamide, to class 3. Moreover, this mixture contains alkyltriazole derivatives, whose cytotoxicity proved higher than that of UDMH [20]. The contamination
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of space stations with hydrazine fuel and toxic products of UDMH transformation is an important practical problem, whose solution is critical to the life support of the station and the safety of the crew.

Using the GC-MS and TDMS methods, it is possible to analyze not only the wipe samples from the surfaces of materials, but also from the materials themselves, for example, from the AMg6 alloy that contacted with hydrazine fuel. The electronic ionization mass spectrum of the products of thermal desorption from the surface of a contaminated material (Fig. 2) contains characteristic ions of both UDMH itself and the products of its oxidative transformation [5–7].

An analysis of the kinetics of release of thermal desorption products from the surface of AMg6 contaminated with UDMH made it possible to establish that the maximum amount of compounds is desorbed at 150–250°C; i.e., they are rather tightly bound to the surface. After the high-temperature treatment of the aluminum alloy with water and re-contamination of the material with UDMH, the amount of desorbed compounds increases substantially (Fig. 3). On the mass thermogram of one of the main fragment ions of UDMH with \( m/z = 58 \), a new, poorly separated peak appears in the range 200–220°C in addition to the peak with a maximum at 180°C (Fig. 3b). This indicates that adsorption of UDMH on the hydroxylated surface of AMg6 increased, and more stable surface compounds formed. Thus, high-temperature treatment of the surface of construction materials contaminated with UDMH, water, and steam increases the adsorption and chemisorption of UDMH during the subsequent use of such materials based on aluminum alloys and lowers the probability of their successful regeneration.

A study of stainless steel materials that contacted with hydrazine fuel revealed that the physically adsorbed molecules of toxicants are desorbed below 150°C, while their chemically adsorbed molecules are desorbed above 180 up to 250°C. The chromatogram of the water wipe sample obtained from the surface of contaminated steel (Fig. 4a) contains the peaks of UDMH, its transformation products, and a small amount of hydrocarbons in the range 3–20 min. Ozone treatment of this solution for 5 h leads to a decrease in the UDMH concentration from 0.05 wt % to 0. As shown by the analysis of ozonized solutions, the concentrations of dimethylnitrosamine and other products of UDMH transformation increase simultaneously within 3 h. They decrease to a safe level only after 7 h of ozonation of aqueous solutions. As a result, only insignificant impurities of hydrocarbons from water remain in solution (Fig. 4b).

However, with water we can wash off only the toxicant molecules weakly bound to the steel surface. The part of toxicant that is more tightly bound to the surface and penetrated deep into the metal can desorb

| Substance | \( \tau \), min | \( m/z \) | \( m, \mu g \) |
|-----------|----------------|------|-------------|
| Cyanate derivative | 1.8 | 56 | 5.43 |
| 1,3,5-Triazine | 2.4 | 81 | 5.80 |
| Acetone dimethylhydrazone | 2.9 | 100 | 0.63 |
| Dimethylnitrosamine | 3.6 | 74 | 4.23 |
| Dimethylaminoacetonitrile | 3.7 | 83 | 25.02 |
| N-Methylformamide | 4.4 | 59 | 2.06 |
| N,N-Dimethylformamide | 4.6 | 73 | 2.23 |
| 4,5-Dihydro-5,5-dimethyl-1H-pyrazole | 5.0 | 83 | 4.52 |
| Isocyanate derivative | 5.3 | 56 | 7.06 |
| 3-Amino-N-methyl-1H-1,2,4-triazole | 5.4 | 97 | 0.99 |
| 4-Methylpyrimidine | 6.0 | 94 | 1.01 |
| 4,5-Dihydro-1,5-dimethyl-1H-pyrazole | 6.1 | 98 | 1.53 |
| 1-Methyl-1H-1,2,4-triazole | 6.4 | 83 | 31.45 |
| 4,5-Dihydro-3,5,5-trimethyl-1H-pyrazole | 6.6 | 97 | 6.92 |
| 2,5-Dimethylpyrrole | 6.8 | 94 | 0.58 |
| Guanidine | 7.2 | 59 | 6.83 |
| 2,6-Dimethylpyridine | 7.4 | 107 | 0.29 |
| Tetramethylamidrazine | 7.5 | 115 | 24.33 |
| N,N-Diethylacetamide | 7.7 | 58 | 6.98 |
| Oxyethyltriazole | 7.9 | 42 | 24.03 |
| 3,5-Diamino-1H-1,2,4-triazole | 8.2 | 99 | 3.22 |
| Dimethylpyridine | 8.8 | 107 | 1.30 |
| Methylimidazole | 9.1 | 82 | 0.73 |
| Dimethyltriazole | 9.4 | 97 | 7.73 |
| Tetramethylurea | 12.9 | 44 | 4.86 |
| Aminotriazole | 13.3 | 127 | 0.76 |
| 4-Nitro-1H-pyrazole | 14.9 | 113 | 0.71 |
| Dimethylbenzamide | 16.3 | 120 | 0.83 |

\( \tau \) is the elution time of the chromatographic peak maximum, \( m \) is the mass, and \( m/z \) is the ratio of the mass to the charge of the characteristic ion that is most intense in the mass spectrum.
with time due to changes in the temperature, pressure, and other external conditions, creating a dangerous \textit{on}flow effect of UDMH already after neutralization of the bulk of it. Therefore, additional treatment of steel structures with circulating ozonized water was performed for 3 h (ozone concentration in water 3.4 mg L\textsuperscript{–1}, flow rate 0.5–1 L h\textsuperscript{–1}) in a specially designed device [18]. An analysis of the composition of gases that contacted with metal structures performed in 3 h and 10 days after ozonation showed that there was no UDMH \textit{on}flow effect; i.e., the toxicant molecules both physically and chemically adsorbed on the metal were oxidized within 10 h of ozonation. The absence of chemisorbed UDMH molecules on the steel surface was also confirmed by a TDMS study of the thermal desorption products. The proposed method for neutralization of UDMH with ozonized water is effective when treating large metal structures, storage tanks, fuel tanks of launch vehicles, and transport and refueling systems, when other methods of UDMH neutralization are impossible or dangerous. Ozonation of UDMH-contaminated metal structures allows their recycling or safe utilization.

The washing of UDMH-contaminated metal structures with aqueous or organic solutions often leads to the appearance of corrosion inhibitors in the wipe samples used for preliminary treatment of the products. The \textit{m}-nitrobenzoic acid (MNBA) salts are widely used as corrosion inhibitors [4] and are also part of detergent solutions. The presence of up to 5\% of these reagents in the wipe samples from contaminated metals [4] can negatively affect the results of neutralization of UDMH and leads to wastewater pollution. An analysis of the wipe samples containing 0.5\% MNBA and not containing it (Fig. 5) showed that UDMH, its transformation products, and MNBA decomposed to a safe level after 10 h of treatment of solutions with ozone in both cases. The concentration of substances in a neutralized solution after 10 h of ozonation did not exceed their MPC for household water [19].

The composition of the products remaining in the wipe sample containing UDMH and MNBA after 3 and 10 h of ozone treatment is given in Table 2.

According to [13, 14], ozonation of UDMH adsorbed on Al\textsubscript{2}O\textsubscript{3} significantly increases the efficiency of the destruction of this toxicant. We studied shungite as a sorbent for UDMH. It was found that shungite adsorbed UDMH well from aqueous solutions; after 1 h of sorption contact of shungite with a 10\% UDMH solution, the signals of toxic UDMH (\textit{m/z} = 61), dimethylnitrosamine (\textit{m/z} = 75), and tetramethyltetrazene (\textit{m/z} = 117) vanished from the mass spectrum of solution (Fig. 6); the peak intensity of stable dimethylformamide (\textit{m/z} = 74) relative to
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Fig. 4. Chromatograms of the water wipe sample from the surface of stainless steel contaminated with UDMH (a) before and (b) after 7 h of ozonation of the solution (the peak of the standard is at 21 min).

Fig. 5. Chromatograms of the water wipe sample from the tank wall contaminated with UDMH and containing 0.5% MNBA after (a) 3 and (b) 10 h of ozonation.

Fig. 6. MALDI mass spectrum of 10% sample washed with water from the walls of the fuel tank in which hydrazine fuel was stored, after its contact with shungite.
that of dimethylaminoacetaldehyde dimethylhydrazone ($m/z = 130$) slightly increased; and the peaks of compounds with $m/z > 200$ significantly decreased or disappeared.

Complete neutralization of UDMH and its transformation products lasted 24 h in a 10% solution and 4 days in a 90% solution (hydrazine fuel) with the same amount of shungite. An analysis of the wipe samples from the shungite samples that adsorbed UDMH from solutions showed that they had no toxic compounds. Toxic compounds were also not found in the products of thermal desorption from their surface.

The deposition of shungite on the surface of stainless steel with adsorbed UDMH also effectively leads
to the destruction of UDMH molecules and the products of its transformation (Fig. 7).

An analysis of the wipe sample from the surface of Al$_2$O$_3$ that contacted with the same UDMH solution, performed for the sake of comparison, revealed the presence of both UDMH itself and its transformation products (dimethylnitrosamine, tetrazene, toxic triazole, tetramethylimidrazone, and ethanedial bis(dimethylhydrazone). Thus, in contrast to Al$_2$O$_3$, shungite not only adsorbed UDMH and other toxicants from solution, but also catalytically decomposed them to low-molecular products [11]. A comparison of the efficiency of UDMH neutralization in 10 and 90% UDMH solutions showed that at a high toxic load, neutralization of UDMH requires an increased amount shungite or its additional activation. The adsorption and catalytic properties of shungite can be enhanced by its mechanochemical and thermal oxidative modification and by doping with transition metal salts [11, 21]. According to [15, 16], low-temperature ozonation of shungite leads to an increase in its specific surface area, pore volume, and number of oxygen-containing surface compounds and to the appearance of micropores, resulting in increased adsorption and catalytic activity of this mineral [17]. On the other hand, ozonation of shungite already contaminated with UDMH will accelerate the oxidation of toxic compounds and lead to environmentally safe sorbent regeneration. This sorbent will be safe for recycling.

Thus, construction materials that contacted with UDMH and desorption solutions obtained by treating the contaminated surface of metals and alloys with reagent solutions and water were studied by chromatography and mass spectrometry. It was shown that neutralization of UDMH by high-temperature treatment of metal structures made of an aluminum-magnesium alloy with water or steam increases the subsequent adsorption and chemisorption of UDMH on

#### Table 2
Concentrations of substances in the sample washed off with water from the tank wall contaminated with UDMH and containing 0.5% MNBA after 3 and 10 h of ozonation (UDMH concentration in the wipe sample before ozonation is 500 mg L$^{-1}$)

| Substance                      | $\tau$, min | $C$, mg L$^{-1}$ |
|-------------------------------|-------------|-----------------|
|                               |             | 3 h  | 10 h  |
| Nitromethane                  | 3.4         | 0.008| —     |
| Dimethylnitrosamine           | 9.9         | 1.7  | 0.0045|
| Dinitrobenzene                | 28.8        | 0.51 | 0.2   |
| MNBA methyl ester             | 29.1        | 0.062| 0.0006|
| MNBA                          | 32.0        | 3.6  | 0.004 |
| Trinitrobenzoic acid          | 32.1        | 0.005| 0.008 |

$\tau$ is the elution time of the chromatographic peak maximum, and $C$ is the concentration after ozonation.
their surface, which will complicate further use of materials and their disposal. Neutralization of UDMH with ozone and shungite has been investigated. As a result of 7–10 h treatment with ozonized water, the level of toxic contamination of the steel surface decreased to safe values. At the same time, wastewater is purified from toxic and chemically active reagents. Ozonation destroys the UDMH molecules chemically and physically adsorbed on the surface of metal structures, making it possible to reuse and utilize them. The use of shungite allows efficient sorption and catalytic decomposition of not only UDMH and the products of its transformation, but also of oligomeric compounds formed during the storage of hydrazine fuel. Ozonation of spent shungite can increase the efficiency of destructive processes and completeness of its regeneration.

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CONFLICTS OF INTEREST

The authors have no conflicts of interest to declare that are relevant to the contents of this article.

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