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**Chemical oxidation
of unsymmetrical
dimethylhydrazine
transformation products in water**

Oxidation of unsymmetrical dimethylhydrazine (UDMH) during a water treatment has several disadvantages including formation of stable toxic byproducts. Effectiveness of treatment methods in relation to UDMH transformation products is currently poorly studied. This work considers the effectiveness of chemical oxidants in respect to main metabolites of UDMH – 1-formyl-2,2-dimethylhydrazine (FDMH), dimethylaminoacetone (DMAAN), N-nitrosodimethylamine (NDMA) and 1-methyl-1H-1,2,4-triazole (MTA). Experiments on chemical oxidation by Fenton's reagent, potassium permanganate and sodium nitrite were conducted. Quantitative determination was performed by HPLC. Oxidation products were identified by gas chromatography-mass spectrometry in combination with solid-phase microextraction. FDMH was completely oxidized by Fenton's reagent with formation of formaldehyde N-formyl-N-methyl-hydrazone, 1,4-dihydro-1,4-dimethyl-5H-tetrazol-5-one by the action of potassium permanganate and N-methyl-N-nitro-methanamine in the presence of sodium nitrite. Oxidation of FDMH also resulted in formation of NDMA. Oxidation of DMAAN proceeded with formation of hydroxyacetone, dimethylformamide and 1,2,5-trimethylpyrrole. After 30 days, DMAAN was not detected in the presence of Fenton's reagent and potassium permanganate, but its concentration in samples with sodium nitrite was 77.3 mg/L.

Key words: unsymmetrical dimethylhydrazine transformation products; 1-formyl-2,2-dimethylhydrazine; dimethylaminoacetone; N-nitrosodimethylamine; 1-methyl-1H-1,2,4-triazole; chemical oxidation.

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**Симметриялы емес
диметилгидразиннің
трансформация өнімдерінің
судағы химиялық тотығуы**

Суды залалсыздандыру процесінде симметриялы емес диметилгидразин (СЕДМГ) тотықтырудың жанама трансформация өнімдерінің түзілуімен байланысты бірқатар кемшіліктері бар. Қазір қолданылатын тазарту әдістердің СЕДМГ трансформация өнімдері тұрғысынан эффективтілігі аз зерттелінген. Берілген жұмыстың мақсаты – судағы СЕДМГ негізгі трансформация өнімдерінің – 1-формил-2,2-диметилгидразин (ФДМГ), диметиламиноацетонитрил (ДМААН), N-нитрозодиметиламин (НДМА) және 1-метил-1H-1,2,4-триазол (МТА), концентрацияларын азайтудағы әртүрлі химиялық тотықтырғыштардың эффективтілігін зерттеу. Тотықтырғыштар ретінде Фентон реактиві, калий перманганаты және натрий нитриті зерттелінген. Ластағыштардың сандық талдауы жоғары эффективті сұйық хроматография әдісімен өткізілген. Тотығу өнімдері қатты фазалы микроэкстракциямен бірлескен газды хромато-масс-спектрометрия әдісімен анықталынған.

Түйін сөздер: симметриялы емес диметилгидразин трансформация өнімдері; 1-формил-2,2-диметилгидразин; диметиламиноацетонитрил; N-нитрозодиметиламин; 1-метил-1H-1,2,4-триазол; химиялық тотығу.

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**Химическое окисление
продуктов трансформации
несимметричного
диметилгидразина в воде**

Окисление несимметричного диметилгидразина (НДМГ) при очистке воды имеет ряд недостатков, связанных с образованием побочных продуктов трансформации. Эффективность имеющихся методов очистки по отношению к продуктам трансформации НДМГ в настоящий момент мало изучена. В работе рассмотрена эффективность различных химических окислителей по отношению к основным продуктам трансформации НДМГ – 1-формил-2,2-диметилгидразина (ФДМГ), диметиламиноацетонитрила (ДМААН), N-нитрозодиметиламина (НДМА) и 1-метил-1H-1,2,4-триазола (МТА). В качестве окислителей изучены реактив Фентона, перманганат калия и нитрит натрия. Количественное определение загрязнителей проводили методом высокоэффективной жидкостной хроматографии. Продукты окисления определяли методом газовой хромато-масс-спектрометрии в сочетании с твердофазной микроэкстракцией. ФДМГ полностью окислялся, образуя различные соединения: N-формил-N-метилгидразон формальдегида в присутствии реактива Фентона, 1,4-дигидро-1,4-диметил-5H-тетразол-5-он при действии перманганата калия и N-метил-N-нитрометанамина в присутствии нитрита натрия.

Ключевые слова: продукты трансформации несимметричного диметилгидразина; 1-формил-2,2-диметилгидразин; диметиламиноацетонитрил; N-нитрозодиметиламин; 1-метил-1H-1,2,4-триазол; химическое окисление.



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CHEMICAL OXIDATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE TRANSFORMATION PRODUCTS IN WATER

Introduction

Rocket-space technology is a source of human impact on the environment. Contamination is caused by fuel spills during regular falls of rocket-carriers, refueling, storage and transportation of rocket fuel. Most rocket fuels are toxic and lead to a detrimental effect on many aspects of living beings. Many heavy rockets use extremely toxic hydrazine, monomethylhydrazine and unsymmetrical dimethylhydrazine (UDMH) [1]. UDMH is very popular due to its physical properties and easier maintenance.

High reactivity of UDMH causes the formation of a large number of transformation products [2; 3], among which the main ones are 1-formyl-2,2-dimethylhydrazine (FDMH), dimethylaminoacetone (DMAAN), N-nitrosodimethylamine (NDMA) and 1-methyl-1H-1,2,4-triazole (MTA). Some of these metabolites are close to or even exceed UDMH in toxicity [4]. Most transformation products of 1,1-DMH have high chemical stability and solubility in water, whereby they may migrate to water sites and retain therein for approximately 30 years [3]. Water purification from transformation products of UDMH is the main way to reduce their negative impact on the environment and human health.

Microbiological, physical, chemical, electrochemical and photochemical methods are used for water cleanup from organic pollutants. Most effective chemical methods are based on oxidation, the main advantages of which are wide range of working pollutant concentrations, high efficiency of oxidation and low toxicity of most applied oxidants. Chemical methods of UDMH removal are based on strong reducing properties of the pollutant. All classic oxidants have been used to decontaminate water from UDMH (Table 1).

Table 1 – Oxidants used for removal of UDMH from environmental objects

Oxidant	Advantages	Disadvantages	Reference
Ferrates (VI) of alkali metal (E = +0.36 V)	Non-toxic, further purifies the medium due to coagulation	Poor stability	[5; 6]
Sodium nitrite (E = +0.38 V)	Produces reactive oxygen	Poor effectiveness	[7]
Chlorine oxidants (E = +1.36 V)	High effectiveness, disinfecting properties	Formation of toxic compounds	[8]
Potassium permanganate (E = +1.51 V)	Does not depend on the pH of the medium, long contact with the contaminant	Produces toxic compounds (NDMA), non-selective	[9]
Hydrogen peroxide (E = +1.77 V)	Strong oxidant, non-toxic	Ineffective in diluted form, produces toxic compounds (NDMA), inconvenient to store	[10; 11]
Ozone (E = +2.07 V)	High effectiveness	Formation of toxic compounds	[12; 13]
Fenton's reagent (E = +2.70 V)	Strong oxidant	Requires the use of acid, difficult to control the reaction, produces toxic compounds (NDMA)	[14; 15]
Peroxide or its mixture with superoxide of alkali and/or alkaline- earth metal	Strong oxidant, acts as fertilizer	Produces toxic compounds, requires large amounts of oxidant	[16]

Despite the high efficiency of oxidants presently used to neutralize UDMH, there is a number of disadvantages associated with the formation of toxic by-products such as NDMA [17]. The main drawback of the existing cleanup methods is that they target only UDMH. However, UDMH is rapidly degraded in the environment, which was confirmed by the results of monitoring [3], according to which only transformation products present in soils of fall places. The effectiveness of existing treatment methods in relation to the transformation products of UDMH is currently poorly studied. In terms of oxidation, NDMA is the most studied UDMH transformation product, as evidenced by the large number of papers devoted to its oxidation [18]. Li et al. [18] showed the main mechanisms of NDMA formation during oxidation of UDMH, methods for the determination of NDMA in water, as well as high efficiency of water purification from NDMA by sonication and oxidation with hydrogen peroxide and ozone.

According to the Agreement between the Republic of Kazakhstan and the Russian Federation on the basic principles and conditions of use of «Baikonur» cosmodrome, the Russian Federation is obliged to return the pristine falling areas. The most complex object for cleanup is soil. Methods current-

ly applied for soil cleanup are based on chemical oxidation. However, these methods have poor efficiency in respect to the transformation products of UDMH, which is caused by insufficient knowledge on their oxidation.

The goal of this work was to determine the effectiveness of different chemical oxidants for reducing the concentrations of the main transformation products of UDMH in water.

Experimental

The following reagents were used for oxidation of transformation products of UDMH:

- hydrogen peroxide, medical, 30% solution (GOST 177-88, «SKAT company» JSC, Kazakhstan);

- potassium permanganate, chemically pure (GOST 20490-75, «SKAT company» JSC, Kazakhstan);

- sodium nitrite, pure (GOST 4197-74, «SKAT company» JSC, Kazakhstan);

- sulfuric acid, pure for analysis (GOST 142262-78, «SKAT company» JSC, Kazakhstan);

- crystalline ferrous sulfate (II), chemically pure (GOST 4148-78, «SKAT company» JSC, Kazakhstan).

These reagents are the most commonly used in the purification of water samples from UDMH and NDMA.

The following transformation products were chosen as the most toxic and therefore relevant transformation products of UDMH: dimethylaminoacetonitrile, 1-methyl-1H-1,2,4-triazole, N-nitrosodimethylamine, 1-formyl-2,2-dimethylhydrazine. Experiments were performed using aqueous solutions of these compounds with concentration of 100 mg/L.

In total, 12 experimental samples were prepared: 4 transformation products x 3 oxidants (Fenton's reagent, KMnO_4 , NaNO_2). Four samples containing the individual transformation products were prepared as control samples with a volume of 250 mL.

Sample containing Fenton's reagent was prepared by introducing 2 μL of sulfuric acid, 37.5 mg of FeSO_4 and 833 μL of 30% solution of hydrogen peroxide to the solution of UDMH transformation products of 250 mL. Sulfuric acid and ferrous sulfate were used to generate an acidic medium and a catalyst, respectively. Concentration of hydrogen peroxide in the resulting solution was 1 g/L.

Potassium permanganate and sodium nitrite were added to the solutions in the dry form in the amount of 250 mg. Concentrations of oxidants in the respective solutions were 1 g/L.

Concentrations of FDMH, DMAAN, NDMA and MTA in all samples were determined by high performance liquid chromatography (HPLC) in one hour after preparation and daily during the first seven days. Final concentrations were determined 30 days after sample preparation. Analyses were performed using Agilent 1100 Series high performance liquid chromatograph with diode-array detector, quaternary pump, degasser and manual injector (Agilent, USA) according to the method described in [19-20]. Sample of 0.5 mL was injected into the manual injector with a loop of 20 μL . Separation was performed on a 75 x 4.6 mm Eclipse XDB-Phenyl column (Agilent, USA) with particle size 3.5 μm . Mobile phase was created by mixing acetonitrile and water in a ratio of 5:95. Detection was performed at 195 and 230 nm. Total analysis time was 2.5 min.

Identification of transformation products after oxidation was carried out 30 days after sample preparation using the method of gas chromatography with mass-spectrometric detection. Solid-phase microextraction was used for sample preparation. A sample of 1 mL was placed in 20-mL vial (HTA, Italy) and sealed by PTFE/silicone cap (HTA, Italy). Extraction was carried out using HT280T autosampler (HTA, Italy) and 65 μm polydimethylsiloxane/

divinylbenzene (PDMS/DVB, Supelco, USA) fiber at room temperature ($25 \pm 3^\circ\text{C}$) during 30 minutes without agitation. After extraction, the fiber was injected into inlet port of 6890N/5975C (Agilent, USA) gas chromatograph with mass spectrometric detection heated to 220°C in splitless mode. Separation was performed on a 30m x 0.25 mm HP-InnoWax column (Agilent, USA) with 0.25 μm film thickness at a constant flow of helium (Orenburg, Russia) equal to 1.0 mL/min. Oven temperature was programmed from 40°C (held for 10 min) to 100°C (held for 5 min) at a $10^\circ\text{C}/\text{min}$ ramp. Detection was carried out in Scan mode of the ions in the range of m/z 34-350 amu. Temperatures of mass spectrometer interface, ion source and quadrupole were 240, 230 and 150°C , respectively.

Results and discussion

FDMH was not detected in water samples taken one hour after addition of Fenton's reagent and potassium permanganate. In the presence of sodium nitrite, FDMH concentration decreased with time reaching 0.5 mg/L 30 days after addition of oxidant. In the control sample, concentration of FDMH decreased significantly slower. After 30 days, FDMH concentration in the solution was 83.7 mg/L (Table 2). Low stability of FDMH in the presence of oxidants is apparently due to its strong reducing properties.

Concentration of dimethylaminoacetonitrile decreased rapidly under the influence of Fenton's reagent and KMnO_4 . In the sample with Fenton's reagent, DMAAN was not detected 1 day after mixing. During 7 days, KMnO_4 decreased the concentration of DMAAN to only 2% of the initial. In the presence of sodium nitrite, concentration of DMAAN decreased to 78 mg/L after 30 days (Table 2). During the first 7 days, sodium nitrite did not affect DMAAN concentration.

In 30 days, NDMA concentration in the presence of Fenton's reagent, potassium permanganate and sodium nitrite decreased by 85, 80 and 50%, respectively. In the control sample, NDMA concentration decreased by 50%, indicating that no effect of sodium nitrite on NDMA content in water was observed. Decrease of NDMA concentration in the presence of Fenton's reagent and KMnO_4 relative to the control sample was 70 and 60%, respectively. Higher efficiency of Fenton's reagent correlates with the literature data [17, 18].

Only Fenton's reagent allowed to reduce the concentration of MTA. In 30 days, concentration of MTA decreased by 50% relative to the initial concentration and by 35% relative to the control

sample. In the presence of KMnO_4 and NaNO_2 , concentration of MTA was similar to the control one during experiment, which can be explained by its

high chemical stability. MTA was found in soils of falling places of rockets in 10 years after the spillage of UDMH [3].

Table 2 – Concentrations of transformation products after oxidation ($C_0 = 100$ mg/L)

Time after introduction of oxidant, days	Concentration (mg/L)			
	Fenton's reagent	KMnO_4	NaNO_2	Control
<i>FDMH solutions</i>				
1	n.a.	n.a.	68.7	93.4
2	n.a.	n.a.	42.1	91.1
3	n.a.	n.a.	20.3	90.7
4	n.a.	n.a.	15.4	89.4
5	n.a.	n.a.	10.2	88.2
6	n.a.	n.a.	4.3	88.0
7	n.a.	n.a.	1.7	87.6
30	n.a.	n.a.	0.5	83.7
<i>DMAAN solutions</i>				
1	n.a.	2.5	99.3	99.5
2	n.a.	2.3	99.1	99.6
3	n.a.	2.1	99.2	99.4
4	n.a.	2.0	99.4	99.5
5	n.a.	1.5	98.8	99.3
6	n.a.	1.3	99.1	99.7
7	n.a.	1.2	99.3	99.6
30	n.a.	n.a.	77.3	86.4
<i>NDMA solutions</i>				
1	40.5	53.2	93.8	95.1
2	37.6	52.7	93.1	94.7
3	36.7	52.2	92.8	94.4
4	35.7	51.8	92.6	94.0
5	34.9	51.6	92.7	93.7
6	33.1	51.1	92.1	93.5
7	32.0	50.8	91.8	92.8
30	15.2	20.6	51.4	53.9
<i>MTA solutions</i>				
1	94.5	99.1	99.8	99.9
2	90.9	99.0	99.8	99.7
3	88.1	98.7	99.7	99.5
4	85.2	98.5	99.4	99.4
5	84.3	97.6	99.3	99.3
6	83.5	97.3	98.6	99.1
7	82.9	97.1	98.4	98.6
30	53.1	83.7	80.3	85.4

The oxidation of FDMH by KMnO_4 led to the formation of DMAAN and NDMA (Figures 1-2) followed by their subsequent oxidation. Concentration of DMAAN was decreasing during 10 days reaching values below detection limit. In 30 days, concentration of NDMA was 0.1 mg/L. Highest concentration of NDMA (5.6 mg/L) was determined 2 days after addition of Fenton's reagent to a solution with FDMH. During 30 days, NDMA concentration in this sample was gradually decreasing reaching 0.1 mg/L.

As is seen from the obtained results, addition of oxidizing agents has different effects on the studied transformation products of UDMH. The least stable transformation product was FDMH while the most stable was MTA. The most effective oxidant is a Fenton's reagent, and the least efficient – sodium nitrite.

Determination of the qualitative composition of the investigated samples

According to the results of qualitative analysis, FDMH oxidation in all samples resulted in the formation of NDMA, the highest response of which was detected in the presence of potassium permanganate, which confirmed the data obtained by HPLC. Oxidation by Fenton's reagent proceeded with formation of formaldehyde N-formyl-N-methylhydrazone. In the presence of potassium permanganate, 1,4-dihydro-1,4-dimethyl-5H-tetrazol-5-one was formed. In the presence of NaNO_2 , methylnitrate and N-methyl-N-nitro-methanamine were formed (Table 3).

In DMAAN solution, 30 days after introduction of Fenton's reagent, N,N-dimethylformamide and 1,2,5-trimethylpyrrole were detected. In the presence of potassium permanganate, N,N-dimethylformamide was identified. Hydroxyacetonitrile and dimethylformamide were present in the sample containing sodium nitrite. In the control sample hydroxyacetonitrile and dimethylformamide were found. Absence of hydroxyacetonitrile in samples with Fenton's reagent and KMnO_4 may apparently indicate that this compound is an intermediate in the formation of N,N-dimethylformamide and 1,2,5-trimethylpyrrole.

Oxidation of NDMA in all samples including the control one led to the formation of MTA, the highest response of which was detected in the sample with sodium nitrite. Dimethylpropanediol dinitrate was formed as a result of NDMA oxidation by Fenton's reagent.

Control sample with MTA contained NDMA. In the presence of oxidants, volatile transformation products were not detected.

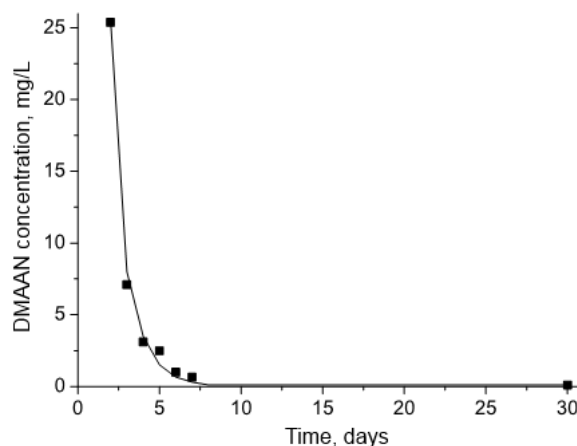


Figure 1 – Concentration of DMAAN during oxidation of FDMH by potassium permanganate

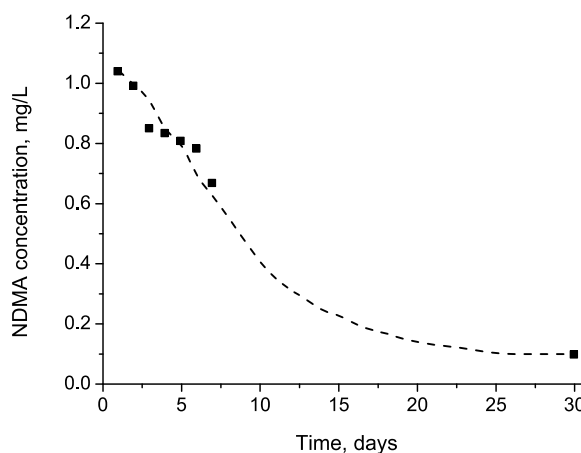


Figure 2 – Concentration of NDMA during oxidation of FDMH by potassium permanganate

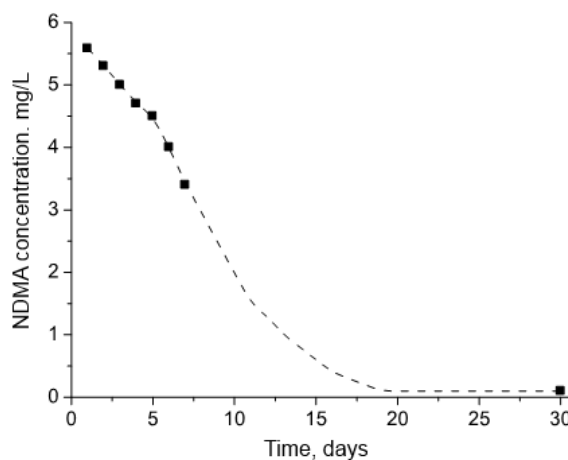


Figure 3 – Concentration of NDMA during oxidation of FDMH by Fenton's reagent

Table 3 – Compounds detected in studied samples

Compound	CAS number	Retention time, min	Peak area, x10 ⁻³			
			Fenton's reagent	KMnO ₄	NaNO ₂	Control
<i>Compounds found in FDMH solutions</i>						
Methylnitrate	598-58-3	3.3	-	-	7990	-
NDMA	55-18-5	18.9	1485	7370	5000	-
Formaldehyde N-formyl-N-methylhydrazone	61748-05-8	21.8	1820	-	-	-
N-Methyl-N-nitro-methanamine	4164-28-7	25.6	-	-	2782	-
1,4-Dihydro-1,4-dimethyl-5H-tetrazol-5-one	16486-74-1	29.6	-	8280	-	-
<i>Compounds found in DMAAN solutions</i>						
Dimethylformamide	68-12-2	19.4	619	2920	643	515
Hydroxyacetonitrile	107-16-4	36.0	-	-	877	1020
1,2,5-Trimethylpyrrole	930-87-0	38.0	2770	-	-	-
<i>Compounds found in NDMA solutions</i>						
MTA	6086-21-1	26.5	396	538	908	514
Dimethylpropanediol dinitrate	26482-65-5	32.1	394	-	-	-
<i>Compounds found in MTA solutions</i>						
NDMA	55-18-5	18.9	-	-	-	81

Conclusion

FDMH quickly reacts with all studied oxidants, forming different compounds: formaldehyde N-formyl-N-methyl-hydrazone in the presence of Fenton's reagent, 1,4-dihydro-1,4-dimethyl-5H-tetrazol-5-one by the action of potassium permanganate and N-methyl-N-nitro-methanamine in the presence of sodium nitrite. Addition of any oxidant resulted in the formation of NDMA. Oxidation by potassium permanganate resulted in the formation of the highest NDMA concentrations during the oxidation of FDMH. This reagent is unsuitable for the use in the presence of FDMH and UDMH because it leads to elevated concentrations of NDMA.

Fenton's reagent has the highest efficiency for oxidation of DMAAN, which was not detected 1 hour after mixing. Oxidation of DMAAN proceeded in two steps with formation of hydroxyacetonitrile as an intermediate product followed by the formation of dimethylformamide and 1,2,5-trimethylpyrrole.

In the presence of Fenton's reagent, potassium permanganate and sodium nitrite after 30 days NDMA concentration in water decreased by 85, 80 and 50%, respectively. In the control sample, NDMA concentration decreased by 50%, indicating that sodium nitrite has no effect on NDMA content in water.

Among the studied oxidants, only Fenton's reagent allowed to reduce the concentration of MTA in water by 50% in 30 days. In the presence of other oxidants MTA concentration decreased by 15-20%, which corresponds to MTA concentration reduction in the control sample.

In general, Fenton's reagent proved to be the most efficient and environmentally friendly oxidant for water purification from metabolites of UDMH. However, development of the effective method of chemical treatment of water requires more in-depth study and optimization of the oxidation process. Special attention should be paid to the reduction in the concentration of NDMA during oxidation of FDMH.

The least effective oxidizing agent is sodium nitrite, which allowed to oxidize only FDMH. This oxidizing agent can not be recommended for the treatment of water samples contaminated by transformation products of UDMH.

The methodology used for the experiment and based on the combination of HPLC and SPME-GC-MS showed high efficiency for the study of the processes occurring during the oxidation of transformation products of UDMH. However, the sensitivity of the method based on SPME-GC-MS can be improved by addition of strong electrolyte. In future experiments, the method of SPME-GC-MS is desirable to use for daily analysis of experimental samples.

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