

## Chromogenic Reaction of 1,1-Dimethylhydrazine with Aryltetrazolium Salts

V. M. Ostrovskaya<sup>a,b\*</sup>, D. O. Shchepilov<sup>b</sup>, and E. A. Kletter<sup>b</sup>

<sup>a</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

\*e-mail: ostr@igic.ras.ru

<sup>b</sup> The 25th State Research Institute of Chemmotology, Ministry of Defense of the Russian Federation, Moscow, Russia

Received February 15, 2018

**Abstract**—The reactions of 1,1-dimethylhydrazine with 2,3,5-triphenyl-2*H*-tetrazolium and 2,5-diphenyl-3-(4-nitrophenyl)-2*H*-tetrazolium chlorides in a solution and on a cellulose carrier have been studied by means of spectrophotometry and chromatomass spectrometry to develop new chromogenic indicators for detection of 1,1-dimethylhydrazine. 1,3,5-Triphenylformazan and 1,3-diphenyl-5-(4-nitrophenyl)formazan are formed in these reactions, respectively; deep red shifts have been observed. Other products of these reactions result from oligomerization and addition of short-living 1,1-dimethylhydrazyl and tetrazolium radicals.

**Keywords:** tetrazolium, formazan, 1,1-dimethylhydrazine, chromogenic reaction

**DOI:** 10.1134/S107036321807006X

1,1-Dimethylhydrazine is widely used as fuel in space-rocket technology and in chemical industry [1]. 1,1-Dimethylhydrazine is a toxic compound of the first class of hazard; it is a superecotoxicant [2] exhibiting high fugitiveness which can be adsorbed on different surfaces including metals, easily evaporated and desorbed, and is miscible with water in almost any ratio.

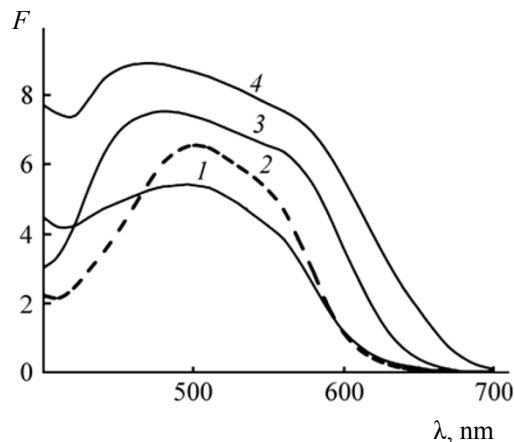
Express test methods of 1,1-dimethylhydrazine detection on solid surfaces, in air, and in water have been developed over recent decades. Such chromogenic indicators as piperidine-4-carbaldehyde [3], bromothymol blue and silver salts [4, 5], 12-molibdosilicic acid [6], 4-(dimethylamino)cinnamic aldehyde [7], indicator powder based on phosphotungstate, Safranin T, malachite green, and sulfate barium [8], 5,7-dinitro-4-chlorbenzofurazane [9, 10], 4-(dimethylamino)benzaldehyde [11], phosphomolybdic heteropoly acids [12], and cobalt salts [13] have been used. The listed indicators have some disadvantages like toxicity, limited shelf life, limited red shift in the color test reaction, sophisticated specimen preparation, high detection limit (above maximum permissible concentration). The reactions of oxygen-containing indicators with 1,1-dimethylhydrazine lead to the formation of cancerogenic nitrosodimethylamine [14]. The search

for new chromogenic reactions for detection of 1,1-dimethylhydrazine is therefore a topical issue.

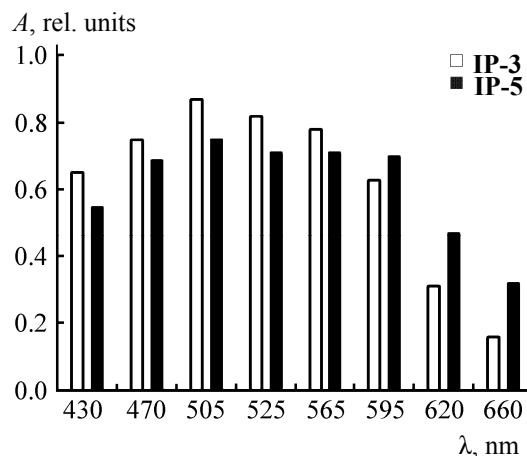
In view of the chemical properties of 1,1-dimethylhydrazine **1**, we turned to a class of widely utilized oxygen-free reduction indicators, almost colorless 2*H*-tetrazolium salts which can be reduced into strongly colored formazans. There are many compounds which react with tetrazolium salts depending on their electron acceptor properties; therefore, tetrazolium salts are used in organic, inorganic, and biochemical analysis [15]. Available 2,3,5-triphenyl-2*H*-tetrazolium chloride **2** produced in many countries on industrial scale can be reduced to 1,3,5-triphenylformazane **3** via intermediate formation of tetrazolium radical (T<sup>•</sup>). The reversible redox reaction tetrazolium **2** D formazan **3** occurs as given in Scheme 1 [16–18].

The reduction of tetrazolium salt **2** may not stop at the formation of formazan **3** but rather proceeds further to afford hydrazidine, amidrazone, and aniline, depending on the nature of the substituents in the tetrazole salt molecule and the reductant type [15].

We have investigated the chromogenic properties of the products of 1,1-dimethylhydrazine **1** reactions with two aryltetrazolium salts: 2,3,5-triphenyl-2*H*-

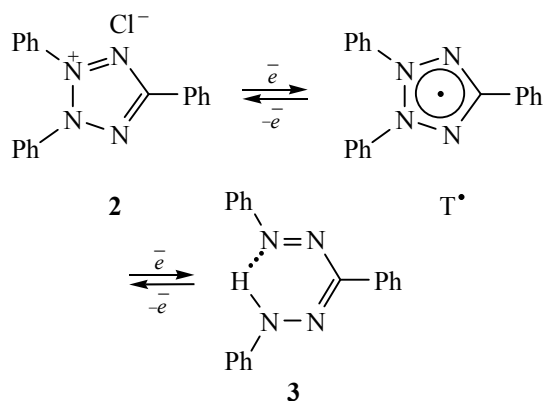


**Fig. 1.** Electronic diffuse reflection spectra of strips (1, 3) **IP-3** and (2, 4) **IP-5** formed upon reactions of **IP-2** and **IP-4** strips with 1,1-dimethylhydrazine in (1, 2) aqueous medium and (3, 4) in air.



**Fig. 2.** Histograms of optical density of **IP-3** and **IP-5** strips.

### Scheme 1.



tetrazolium chloride **2** and 3-(4-nitrophenyl)-2,5-diphenyl-2*H*-tetrazolium chloride **4** which are significantly different in the reduction potentials<sup>1</sup>. The products were identified using chromatomass spectrometry and spectrophotometry.

Indicator paper strips impregnated with salts **2** or **4** (**IP-2** and **IP-4**, respectively) upon contact with aqueous solution of 1,1-dimethylhydrazine (1 mg/cm<sup>3</sup>) demonstrated different chemical and chromogenic properties. The strip **IP-2** turned dark-red (this color is typical of compound **3**), and the coloration was stable during keeping; the final state is marked as **IP-3**, Fig. 1, curve 1). The strip **IP-4** significantly faster colored dark-red, in the color typical of 5-(4-nitrophenyl)-1,3-diphenylformazan **5**; the final state is

marked as **IP-5**, Figs. 1, curve 2). The strip became colorless after several days due to deeper reduction of the formed compound **5**.

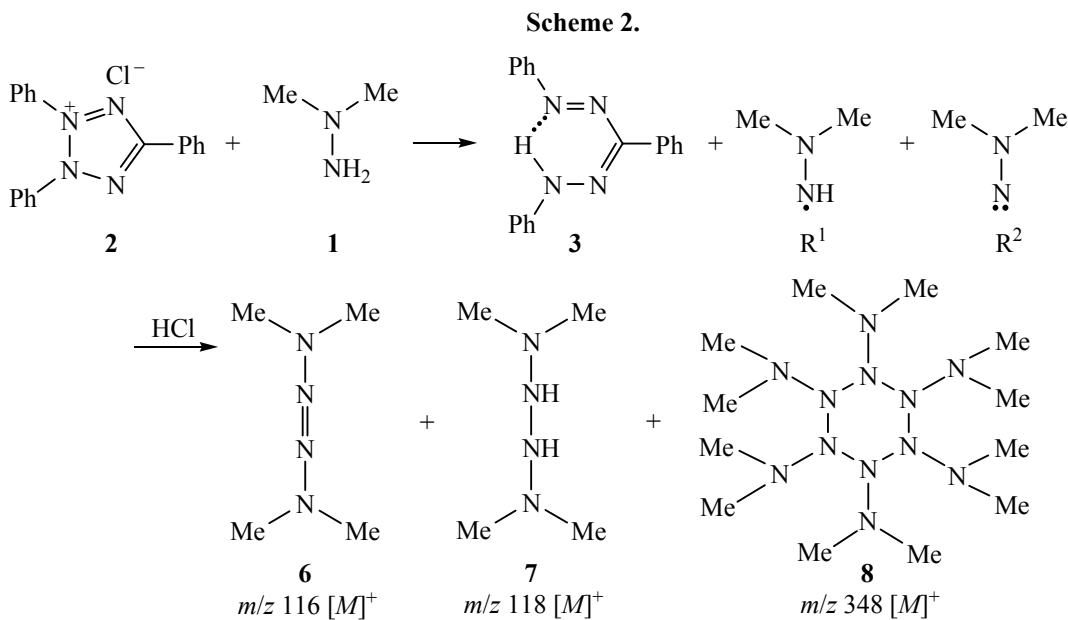
Indicator strips **IP-2** and **IP-4** were tested as chromogenic chemical reagents using an exposition in a Tishchenko flask. Air with concentration of compound **1** 1200 mg/m<sup>3</sup> was pumped through the flask at flow rate 5–6 cm<sup>3</sup>/min. The strips color was changed from white to dark-red after 17 min (dark-red strips marked as **IP-3** and **IP-5**, Figure 1, 3, 4; 2).

A dark-red suspension was formed as a result of the reaction of 1,1-dimethylhydrazine with salt **2** in ethanol; the formation of dark-red precipitate was then observed. Mass spectrum of that precipitate corresponded to that of 1,3,5-triphenylformazan **3** (according to the NIST 05 mass spectra database). The observed signals corresponded to the [M]<sup>+</sup> peaks of compound **3**, products of dimerization of radicals R<sup>1</sup> and R<sup>2</sup> into dimers **6** and **7**, cyclic hexamerization of radical R<sup>2</sup> into compound **8** (Scheme 2).

Intermediate formation of tetrazolium radical T<sup>•</sup> was indicated by the peaks with *m/z* corresponding to the products of its addition to Ph and R<sup>1</sup> radicals (Scheme 3).

Mass spectrometry data for the products of 1,1-dimethylhydrazine **1** reaction with salt **4** evidenced the formation of compound **5**, products of di- and oligomerization **6–8**, products of addition (**11**, **12**) of nitrotetrazolium radical to Ph and R<sup>1</sup> radicals, and products of deeper reduction of salt **4** into *C*-phenyl-*N*-(4-nitrophenyl)amidrazone **13** (*m/z* 256 [M]<sup>+</sup>, *M*<sub>calc</sub> 256.27)

<sup>1</sup> Polarography half-wave reduction potentials relative to saturated calomel electrode at 25°C (pH 7.2): *E*<sub>1/2</sub> –0.80 (2) and –0.43 (4) V [19].



and aniline (Scheme 4). In contrast to the behavior of salt **4**, salt **2** with lower reduction potential was not reduced into diphenylamidrazone and aniline and was more stable to the action of 1,1-dimethylhydrazine.

The mass spectra of ethanol extracts from strips **IP-2** and **IP-4** the peaks of salts **2** and **4**, respectively, were revealed. The peaks of compounds **3** and **5** and products of the 1,1-dimethylhydrazine transformations **6–8** appeared in the spectra upon the strips treatment with 1,1-dimethylhydrazine.

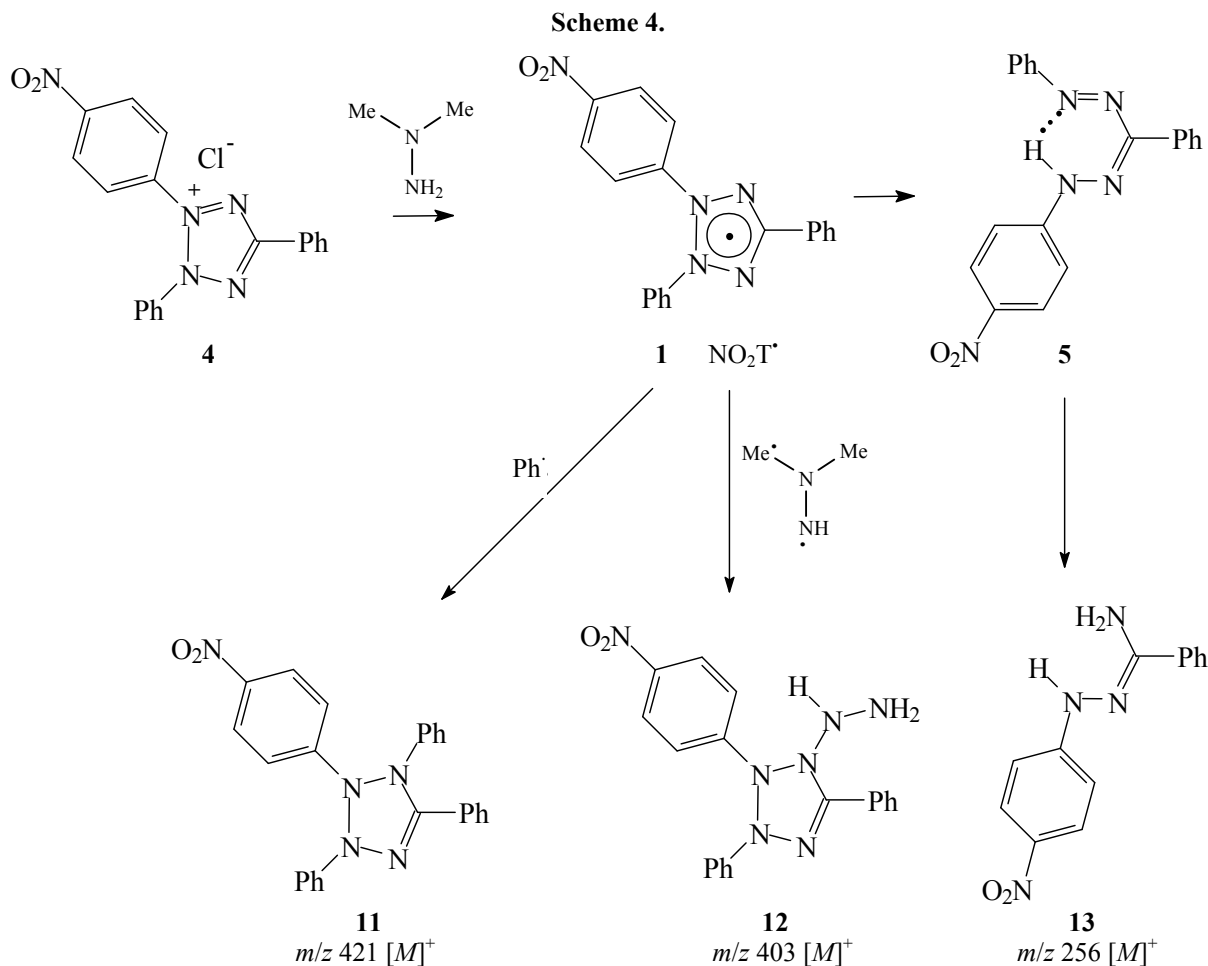
Development of the absorbance of strips **IP-3** and **IP-5** during their reduction in air containing  $0.4 \text{ mg/m}^3$  of 1,1-dimethylhydrazine (with the formation of formazans **3** and **5**, respectively) was monitored using a LED with  $\lambda$  505 nm (Fig. 3). The experiment revealed that the reduction of salt **4** was significantly faster compared to salt **2**.

In summary, spectral study of the chromogenic reactions of 1,1-dimethylhydrazine with 2,3,5-tri-

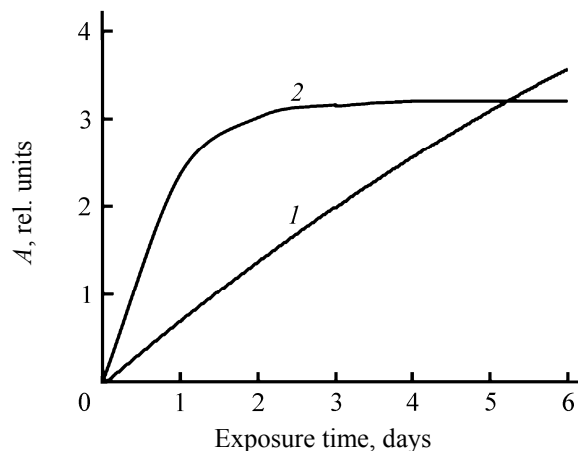
phenyl-2*H*-tetrazolium and 3-(4-nitrophenyl)-2,5-diphenyl-2*H*-tetrazolium chlorides in a solution and on a cellulose paper carrier revealed the formation of the corresponding formazan (via the tetrazolium radical), cyclohexamer of 1,1-dimethylhydrazyl biradical, product of 1,1-dimethylhydrazyl radical addition to the tetrazolium radical, and dimers of both radicals. Aryltetrazolium salts are promising sensitive chromogenic reagents for detection of 1,1-dimethylhydrazine.

## EXPERIMENTAL

Diffuse reflection spectra of indicator strips were recorded using an ilPro (Gretag Mackbet, Switzerland) minispectrophotometer and processed using Kubelka–Munk function [ $F = (1 - R)^2/2R$ ,  $R$  being reflection coefficient]. Absorbance of indicator strips was measured with an EKOTEST 20-40 reflectometer equipped with 8 LEDs and outboard exchangeable cartridges [20] (EKONIKS). Mass spectra were registered using a Khromatek-Kristall 5000 (Khromatek)



gas-liquid chromatograph equipped with a mass spectroscopic detector and direct injection system (electron ionization, frequency 50 Hz, carrier gas helium; resolution  $R = M/\Delta M = 300$ ). The components were identified using NIST 05 mass-spectra database.



**Fig. 3.** Developing of absorbance ( $\lambda$  505 nm) of (1) IP-2 and (2) IP-4 strips during exposure in air with 1,1-dimethylhydrazine concentration  $0.40 \pm 0.05 \text{ mg/m}^3$ .

Concentration of 1,1-dimethylhydrazine in air was determined using an ITM-8 indicator tube (Servek).

The used chemicals and solvents were of “pure” or “chemically pure” grade.

Indicator strips **IP-2** and **IP-4** were obtained by soaking the express test paper strips (TU OP 13-7310005-20-83) in a solution of tetrazolium salt **2** or **4** [19] (0.1% in a DMF–ethanol mixture, 1 : 1 by volume), respectively. The obtained pieces were dried and cut using a precise cutter [21]. White  $9.5 \times 50 \text{ mm}$  indicator strips were thus prepared.

**Products of the reaction of 1,1-dimethylhydrazine 1 with 2,3,5-triphenyl-2H-tetrazolium chloride 2 in liquid medium.** 0.33 g (5.5 mmol) of 1,1-dimethylhydrazine was added to a solution of 1.50 g (5 mmol) of compound **2** in 50 mL of ethanol. The reaction mixture was kept for 2 days until the formation of a dark-red suspension. The precipitate (0.9 g) was filtered off and dried. **Triphenyl formazan (3)**,  $t_R$  0.40 min. Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 300 (43)

$[M]^+$  (calculated for  $C_{19}H_{16}N_4$ : 300.37). Mass spectrum of the filtrate,  $m/z$  ( $I_{rel}$ , %): 300 (40)  $[M]^+$ , 376 (12)  $[T^+ + Ph]^+$ , 358 (2)  $[T^+ + Me_2N_2H]^+$ , 348 (2)  $[Me_{12}N_{12}]^+$ , 223 (15)  $[M - Ph]^+$ , 195 (90)  $[PhC=NNHPh]^+$ , 116 (7)  $[Me_4N_4]^+$ , 118 (12)  $[Me_4N_4H_2]^+$ , 92 (98)  $[HNPh]^+$ , 77 (20)  $[Ph]$ .

**Products of the reaction of 1,1-dimethylhydrazine 1 with 3-(4-nitrophenyl)-2,5-diphenyl-2H-tetrazolium chloride 2 in liquid medium.** 0.33 g (5.5 mmol) of 1,1-dimethylhydrazine was added to a solution of 1.60 g (5 mmol) of salt 4 in 50 mL of ethanol. The obtained dark-red suspension was filtered. 0.8 g of formazan 5 was obtained,  $t_R$  0.64 min. Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 345 (50)  $[M]^+$  (calculated for  $C_{19}H_{15}N_5O_2$ : 345.36). Mass spectrum of the solution,  $m/z$  ( $I_{rel}$ , %): 345 (16)  $[M]^+$ , 421 (6)  $[NO_2T^+ + Ph]^+$ , 403 (1)  $[NO_2T^+ + Me_2N_2H]^+$ , 348 (2)  $[Me_{12}N_{12}]^+$ , 268 (6)  $[M - Ph]^+$ , 256 (2)  $[Ph(NH)NNHC_6H_4NO_2]^+$ , 223 (3)  $[M - PhNO_2]^+$ , 195 (62)  $[PhC=NNHPh]^+$ , 240 (19)  $[PhC=NNHNO_2]^+$ , 137 (10)  $[HNPhNO_2]^+$ , 116 (4)  $[Me_4N_4]^+$ , 118 (4)  $[Me_4N_4H_2]^+$ , 92 (58)  $[HNPh]^+$ , 77 (55)  $[Ph]$ .

**Products of the reactions of 1,1-dimethylhydrazine 1 with 2,3,5-triphenyl-2H-tetrazolium chloride 2 and 3-(4-nitrophenyl)-2,5-diphenyl-2H-tetrazolium chloride 2 immobilized on a cellulose carrier.** Colorless strips IP-2 and IP-4 were placed into an air chamber with 1,1-dimethylhydrazine 1 concentration 1200 mg/m<sup>3</sup> and kept until appearance of strong coloration. The obtained dark-red strips were marked IP-3 and IP-5. Their absorbance ( $A$ ) was measured (Fig. 2).

**Extracts of tetrazolium salts and formazans from indicator strips.** Indicator strip (1×1 cm) was placed into a test tube; 0.5 mL of ethanol was added, and the mixture was kept for 15 min. 1  $\mu$ L of the ethanol extract was tested using a chromatograph. Mass spectrum,  $m/z$  ( $I_{rel}$ , %): before reaction, 299 (38) (salt 2), 344 (10) (salt 4); after reaction, 300 (98) (formazan 3), 345 (40) (formazan 5).

#### CONFLICT OF INTERESTS

No conflict of interest was declared by the authors.

#### REFERENCES

1. *Ullmann's Encyclopedia of Industrial Chemistry*, Elvers, B., ed., Weinheim: KGaA, 2007, vol. H, p. 615. doi 10.1021/op970020u
2. *Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens*, Pohanish, R.P., Ed., Amsterdam; Sydney; Tokyo: Elsevier, 2012, p. 1057.
3. Kolesnikov, S.V., Stepanov, N.D., Boldakova, I.P., and Stukolova, E.V., RF Patent 2305835, 2007; *Byull. Izobret.*, 2007, no. 25.
4. Litvinenko, A.N, Avzalov, A.F., Litvinenko, A.A., and Litvinenko, N.A., RF Patent 2084872, 1997.
5. *Drager-Tubes & CMS Handbook Soil, Water, and Air Investigations as Well as Technical Gas Analysis*, Lubeck: KGaA, 2011, p. 173.
6. Ostrovskaya, V.M., Vinogradov, Yu.V., and Korolev, Yu.S., RF Patent 2088916, 1997; *Byull. Izobret.*, 1997, no. 24.
7. Chernova, R.K., Kozlova, L.M., Shestopalova, N.B., and R'yanova, Yu.O., *Izv. Saratovsk. Univ., Ser. Khim., Biol., Ekol.*, 2008, vol. 8, no. 2, p. 15.
8. Farmakovskaya, T.A., Veksler, K.V., and Kalinin, D.S., RF Patent 2562990, 2015; *Byull. Izobret.*, 2015, no. 22.
9. Evgen'ev, M.I., Goryunova, S.M., and Evgen'eva I.I., *Vestn. Kazan. Tekhnol. Univ.*, 2015, vol. 18, no. 21, p. 27.
10. Evgen'ev, M.I. and Levinson, F.S., *Khim. Geterotsikl. Soedin*, 1991, no. 11, p. 1565.
11. Khamrakulov, T.K. and Kondrat'ev, O.T., *Zav. Lab. Diagnost. Mater.*, 2002, vol. 68, no. 10, p. 24.
12. Morosanova, E.I., *Talanta*, 2012, no. 102, p. 114. doi 10.1016/j.talanta.2012.07.043
13. Posokhov, N.N., Pashinin, V.A., Kosyrev, P.N., Semin, A.A., and Khalimova A.S., RF Patent 2563839, 2015; *Byull. Izobret.*, 2015, no. 26.
14. Ostrovskaya, V.M., Man'shev, D.A., Lyamina, O.I., Popov, O.V., and Kupriyanova, T.A., *Membrany. Ser. Krit. Tekhnol.*, 2002, no. 15, p. 29.
15. Buzykin, B.I., Lipunova, G.N., Pervova, I.G., Ostrovskaya, V.M., Lipunov, I.N., Maslakova, T.I., Stozhko, N.Yu., Barachevskii, V.A., and Sigeikin, G.I., *Progress v khimii formazanov. Sintez-svoistva-primenenie* (Advanced in Chemistry of Farmazones. Synthesis, Properties, and Application), Moscow: Nauchnyi Mir, 2009.
16. Rapta, P., Brezova, V., Ceppan, M., Melnik, M., Bustin, D., and Stasko, A., *Free Rad. Res.*, 1994, vol. 20, no. 2, p. 71.
17. Pikaev, A.K. and Kriminskaya, Z.K., *Russ. Chem. Rev.*, 1998, vol. 67, no. 8, p. 671. doi 10.1070/RC1998v067n08ABEH000392
18. Tezcan, H., Ekmekci, G., and Aksu, L., *Turk. J. Chem.*, 2013, vol. 37, p. 57.
19. Ostrovskaya, V.M., Davydovskaya, Yu.A., Pryanishnikov, A.A., Vainshtein, Yu.I., and Dziomko, V.M., *Zh. Obshch. Khim.*, 1965, vol. 35, no. 2, p. 230.
20. Ostrovskaya, V.M., Man'shev, D.A., and Terekhov, V.N., RF Patent 2188403, 2002; *Byull. Izobret.*, 2002, no. 24.
21. Ostrovskaya, V.M., RF Patent 117853, 2012; *Byull. Izobret.*, 2012, no. 19.