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ARTICLES

Simultaneous Determination of Hydrazine, Methylhydrazine, and 1,1-Dimethylhydrazine by High-Performance Liquid Chromatography with Pre- and Post-Column Derivatization by 5-Nitro-2-Furaldehyde

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Abstract—Approaches to the chromatographic determination of 1,1-dimethylhydrazine and two main products of its degradation (hydrazine and methylhydrazine) on their simultaneous presence are proposed using derivatization by 5-nitro-2-furaldehyde and multi-wavelength spectrophotometric detection of the formed derivatives in the visible spectral region. A combination of preliminary derivatization with separation in the reversed-phase HPLC mode and also ion-chromatographic separation with post-column derivatization allowed us to reach the limits of detection for analytes lower than 1 μg/L and to determine 1,1-dimethylhydrazine at the level of the maximum permissible concentration without preconcentration. The developed approaches were tested on an acid extract of a sample of peat bog soil collected at the place of impact of the first stage of a carrier rocket. The identity of the results obtained by different methods and the high level of soil pollution by hydrazines are shown.

Keywords: hydrazine, methylhydrazine, 1,1-dimethylhydrazine, 5-nitro-2-furaldehyde, derivatization, reaction chromatography, HPLC

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Hydrazine (H), methylhydrazine (MH) and 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) have found wide application in organic synthesis, for obtaining pharmaceutical preparations and plant protection agents, and also as high-performance rocket fuels. In addition to high toxicity, these compounds possess pronounced carcinogenic, mutagenic, and teratogenic properties [1–3]. The currently accepted standards for their concentrations in chemical products and environmental samples are very stringent and the sophistication of methods for the rapid and highly sensitive determination of hydrazine and its alkyl derivatives has not lost their importance.

Today hydrazines are separated by various versions of liquid chromatography: reversed-phase (RP) [4, 5], ion (IC) [6, 7], ion-pair [8, 9], and hydrophilic [10] in combination with spectrophotometric (SPD), fluorimetric, electrochemical, and mass-spectrometric detectors. The first two methods have found the widest application because of their high reproducibility, sensitivity, simplicity, and good compatibility with various types of chromatographic detectors.

The ion-chromatographic separation of hydrazines does not require preliminary derivatization and, in most cases, is performed on sulfocation-exchange stationary phases [6]. Its combination with direct-current amperometric detection on a glassy carbon electrode allowed the researchers to reach the sensitivity of analysis comparable with the maximum permissible concentration of 1,1-dimethylhydrazine. The limits of detection for H, MH, and UDMH are 0.2, 0.5, and 1.0 μg/L, respectively, on the injection of an extremely large sample volume (250 μL) [6]. A drawback of this method is the poor stability of the electrochemical detector in comparison with the spectrophotometric one and its sensitivity to various electroactive impurities present in complex natural matrixes.

The application of RP HPLC to the determination of hydrazines requires their preliminary derivatization for improving retention on an unpolar stationary phase, and also the introduction of chromophores or fluorophores, ensuring highly sensitive spectrophotometric or fluorimetric detection, into the structures of hydrazines. The derivatizing agents are usually carbonyl compounds, forming hydrazones with amino groups of hydrazines. Various researchers used formaldehyde [11], 4-nitrobenzaldehyde [4], *p*-dimethylaminobenzaldehyde [12], vanillin [13], and cinnamic

[14] and veratric [15] aldehydes. The highest sensitivity to MH (0.05 μg/L at the volume of injected sample 100 μL) was attained using precolumn derivatization with naphthalene-2,3-dialdehyde and spectrofluorimetric detection [16, 17]. The limit of detection (LOD) for UDMH was thus 1 μg/L.

In [18], it was proposed to use glyoxal, rapidly reacting with MH and UDMH under mild conditions with the formation of derivatives intensely absorbing at the wavelength 305 nm, as a derivatizing agent. This allowed the researchers to reach an extremely low value of LOD for 1,1-dimethylhydrazine, equal to 0.25 μg/L (sample volume 100 μL) with spectrophotometric detection. Among the drawbacks of the proposed method let us note the problematical character of the determination of hydrazine, possessing two reaction centers as a derivatizing agent, and also the necessity of detection in the UV spectral region, which slightly reduces the selectivity of analysis.

We proposed a new derivatizing agent for the determination of hydrazines, 5-nitro-2-furaldehyde (NFA), which possesses a number of undoubted advantages [19]. Among these are, first of all, good solubility in water, intense absorbance of the formed hydrazone in the visible spectral region, and significant difference in the positions of absorption bands of hydrazine derivatives. Based on this method, we developed a method for the spectrophotometric determination of H, MH, and UDMH on their simultaneous presence with limits of detection at a level of 1.0 μg/L. A combination of this approach to the derivatization of analytes with chromatographic separation, seems highly promising, as it will ensure a substantial increase in the selectivity of analysis and the determination of hydrazines in complex matrixes. Taking into account that the optimum value of medium acidity (pH 5.5) for the reaction of hydrazines with NFA coincides with the pH of the mobile phase used in their ion-chromatographic separation, 5-nitro-2-furaldehyde can be used not only for the precolumn derivatization of hydrazines in RP HPLC, but also for post-column derivatization in IC with spectrophotometric detection.

The aims of this study were the development of corresponding approaches to the determination of H, MH, and UDMH and the assessment of their applicability to the analysis of real samples.

EXPERIMENTAL

Reagents and materials. Hydrazine dihydrochloride (>98%), methylhydrazine (>98%), and 1,1-dimethylhydrazine (98%) and also 5-nitro-2-furaldehyde (99%) were purchased from Sigma-Aldrich (Germany). The necessary pH of the medium in derivatization was created using sodium hydrogen phosphate of analytical grade (Vekton, Russia) and potassium dihydrogen phosphate of chemically pure grade (Neva-Reaktiv, Russia), and also orthophosphoric acid of analytical grade (Vekton, Russia). Grade 0 acetonitrile (Cryochrom, Russia) was used for mobile phase preparation in RP HPLC analysis. The mobile phase for the IC separations of analytes was prepared using ammonium acetate (>97%, Sigma-Aldrich, Germany) and glacial acetic acid of chemically pure grade (Neva-Reaktiv, Russia). All solutions were prepared using high-purity water with a specific resistance of 18.2 MΩ cm, obtained with a Millipore Simplicity UV system (Millipore, France). The solvent for the preparation of the stock solution of NFA was isopropyl alcohol of chemically pure grade (Komponent Reaktiv, Russia).

Preparation of solutions. Stock solutions of NFA (0.2 M) and analytes (10 mg/mL) were prepared by dissolving precisely weighed portions in 5 mL of isopropyl alcohol (for NFA) or water (for analytes) and stored in a refrigerator at 4°C for no more than one week. Working solutions of the compounds to be determined in the concentration range (0.001–1 mg/L) were obtained by consecutive dilutions of the stock solution immediately before the experiment.

Precolumn derivatization. Portions (0.5 mL) of solutions of H, MH, and UDMH with preset concentrations were placed in 10-mL volumetric flasks, 100 μL of a 0.2 M solution of a derivatizing agent was added, and the mixtures were brought to the mark with a phosphate buffer solution of pH 5.0. Mixtures from the flasks were poured in glass test tubes with tight plastic stoppers and allowed to stand within 40 min at 60°C in a Thermion laboratory thermoreactor (Lumex, Russia) [19].

Analysis by reversed-phase chromatography. Chromatographic analysis was performed in an Agilent 1220 Infinity HPLC system (Agilent, United States) equipped with a pump with a low pressure gradient system, a vacuum degasser, an autosampler, a column thermostat, and an SPD. The control of the chromatograph and data processing were carried out using the ChemStation software (Agilent, United States). Separation was performed on a Zorbax Eclipse Plus C18 column (150 × 3.0 mm, adsorbent particle size of 3.5 μm; Agilent, United States). In isocratic elution, the mobile phase was an acetonitrile mixture with water (30 : 70, v/v). In the gradient mode, the following program of changing acetonitrile concentration in the eluent, chosen in preliminary experiments, was used: 0–7 min—30%, 7–8 min—linear increase to 70%, 8–12 min—70%. The volume of the added sample was 10 μL, eluent flow rate was 0.4 mL/min, and thermostat temperature was 40°C. Detection was performed by wavelengths corresponding to absorption maxima of the obtained NFA derivatives of analytes: 385, 420, and 454 nm for H, MH, and UDMH respectively. Acetone was used as an unretained compound in the determination of the dead volume of the chromatographic system (0.41 mL).

Ion-chromatographic analysis with post-column derivatization. Studies by IC with spectrophotometric detection were carried out on a Nexera XR HPLC system (Shimadzu, Japan) equipped with a vacuum degasser, two LC-20AD pumps (for feeding mobile phase and derivatizing agent solution), a SIL-20AC autosampler, an CTO-20AC column thermostat, an CRB-6A flow thermoreactor with a stainless steel reaction capillary (10 m × 0.5 mm) and a cooling capillary (6 m × 0.3 mm), and also an SPD-M20A diode array spectrophotometric detector. The control of the system and data processing were performed using the LabSolution software (Shimadzu, Japan). The components were separated on a Nucleosil 100-5 SA column (125 × 4.6 mm, adsorbent particle size 5 μm) (Macherey-Nagel, Germany) at 40°C. The mobile phase was a 50 mM ammonium acetate buffer solution of pH 5.4; the reagent was a 2 mM NFA solution in isopropyl alcohol. The volume of the sample was 10 μL. The flow rate of the eluent was 1.2 mL/min, the flow rate of the derivatizing agent was 0.05 mL/min. Detection was performed under the conditions reported for RP HPLC.

Ion-chromatographic analysis with amperometric detection. We used an LC-20 HPLC system (Shimadzu, Japan), including a vacuum degasser, a SIL-20AC autosampler, an LC-20ADsp chromatographic pump, and a DECADE II electrochemical detector (Antec Leyden, Netherlands) with a three-electrode cell and a glassy-carbon working electrode. Separation was performed on a Nucleosil 100-5 SA chromatography column (125 × 4.6 mm, sorbent particle size 5 μm). The mobile phase was a 50 mM ammonium acetate buffer solution of pH 5.4. Detection was carried out in the direct-current mode at the potential of the working electrode 1.1 V. The volume of the added sample was 20 μL.

Test samples. To test the developed approaches, we chose samples of water of different origin not polluted by the rocket fuel: tap water (I); river water from Northern Dvina (II); and peat bog water selected in the place of impact of spent stages of carrier rockets in Arkhangelsk oblast (III). As a real sample of soil, we chose peat bog soil polluted by rocket fuel collected in the epicenter of the place of impact of the first stage of the "Cyclone" carrier rocket in Arkhangelsk oblast of the Russian Federation.

Extraction of hydrazines. Mobile forms of hydrazines were extracted from peat bog soil using the known approach based on the acid extraction of analytes [20]. After the careful averaging of a 50-g weighed portion of soil, hydrazines were extracted by 100 mL 0.1 M HCl within 24 h under continuous stirring. The extract was centrifuged and, after filtering through a membrane Nylon filter of the pore size 0.2 μm, injected into the chromatographic system (IC) or subjected to preliminary derivatization (RP HPLC).

Table 1. Characteristics of the separation of hydrazines derivatives with 5-nitro-2-furaldenyde by reversed-phase HPLC in isocratic and gradient elution modes

Analyte	Isocratic mode				Gradient mode			
	t_R, min	k	α	N	t_R, min	k	α	N
MH	2.96	1.89	–	3500	2.91	1.84	–	3400
UDMH	5.98	4.83	2.56	14300	5.92	4.78	2.60	14000
H	14.80	13.44	2.78	28700	9.94	8.70	1.82	40000

RESULTS AND DISCUSSION

Choice of conditions for the determination of hydrazines by RP HPLC. The retention of NFA derivatives of analytes on an octadecyl stationary phase is enhanced in the series MH < UDMH < H (Fig. 1). The unusual position of hydrazine in this series is due to the addition of two NFA residues in the derivatization with the formation of an aldazine derivative rather than a hydrazone [19]. In using elution in the isocratic mode (30 vol % of acetonitrile), we could reach an acceptable retention and separation of analytes at the duration of analysis 15 min (Table 1). Because of the strong difference in the polarity of bis[(5-nitrofuran-2-yl)methylidene]hydrazine and NFA alkylhydrazone, the retention factor for the hydrazine derivative is slightly beyond the optimum range. The use of gradient elution with a sharp increase in the concentration of acetonitrile in the mobile phase after the elution of the UDMH peak ensures the solution of this problem with reducing the duration of analysis by one and a half times and simultaneously increasing sensitivity to hydrazine because of the significant reduction of the width of the chromatographic peak (Table 1, Fig. 1).

Choice of conditions for the determination of hydrazines by IC–SPD. Among the essential drawbacks of the preliminary derivatization of analytes are the laborousness sample preparation, possibility of the introduction of additional errors, and a significant increase in the total duration of analysis of one sample in the study of small sample sets. These drawbacks can be eliminated using post-column derivatization in the real time, which is best compatible with the ion-chromatographic separation of analytes.

The most important parameters in the optimization of a procedure of post-column derivatization are the time of contact of analytes with the derivatizing reagent and also the temperature of the process. The first factor is determined by the flow rate of the mobile phase and the volume of the reaction capillary. From the viewpoint of the rapidity of analysis, the length of reaction capillary is significantly preferable compared to a decrease in the flow rate of the eluent; it is not associated with a significant loss in the system efficiency. In this connection, we used the flow rate of the

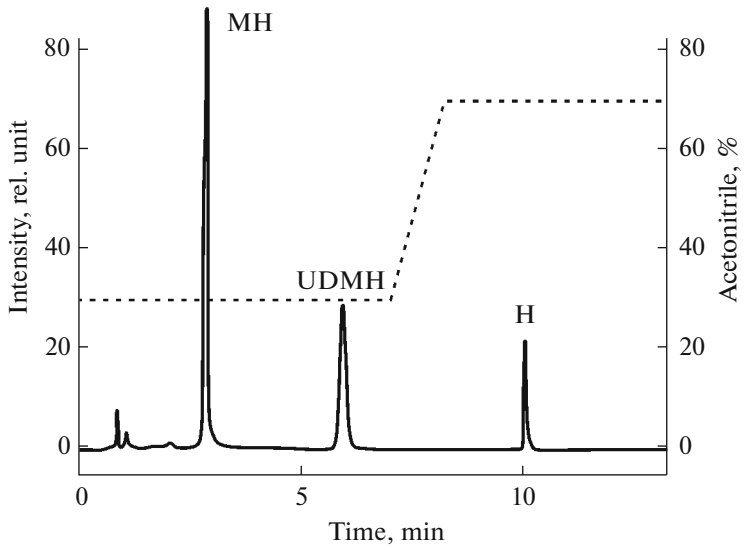

Fig. 1. A chromatogram of a model solution of products of hydrazines derivatization (1 mg/L of each component) by NFA obtained by the RP HPLC in the gradient elution mode. Dashed line demonstrates gradient profile. Detection wavelength is 454 nm.

mobile phase (1.2 mL/min.) close to the optimum rate for studied type of the chromatography column at a relatively big volume of the reactor (~2 mL) and the corresponding duration of the reaction about 1.7 min. Taking into account that, at 60°C, the rather complete proceeding of the reaction requires 30–40 min [20], post-column derivatization requires significantly higher temperatures. The dependence of the peak area of UDMH on the reactor temperature (Fig. 2) shows that the maximum degree of analyte conversion into NFA derivative is attained at 140–150°C. Heating to higher temperatures did not allow us to reduce the duration of transformation because of a noticeable decomposition of the derivatizing agent. The chromatogram obtained under the chosen conditions (Fig. 3) demonstrates a good separation of analytes: for the H–MH pair, the coefficient of selectivity was 1.15 and resolution was 2.4.

Performance characteristics of the developed procedures. A study of the dependences of peak area on the concentration of analytes demonstrated the strict linearity of the calibration graphs ($r^2 > 0.999$) in the range of analyte concentrations up to 1 mg/L. Using the 3σ-test (signal-to-noise ratio equal to 3 : 1), we determined limits of detection for each analyte both in RP HPLC and IC with post-column derivatization (Table 2). To calculate the lower limits of quantitation (c_{low}), we used the 10σ-test. The obtained calculated

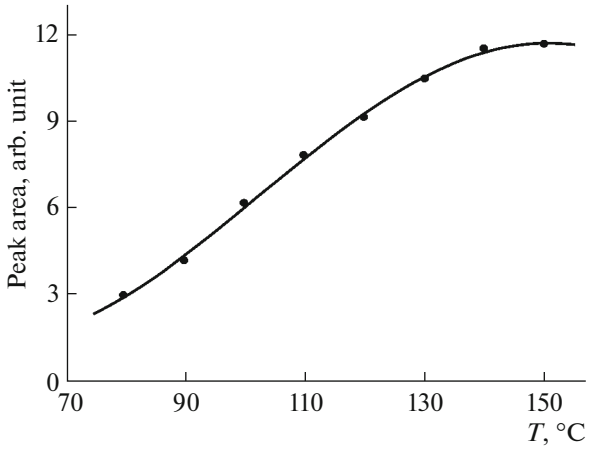

Fig. 2. Chromatographic peak area of UDMH as a function of reactor temperature in post-column derivatization by NFA. Detection wavelength is 454 nm.

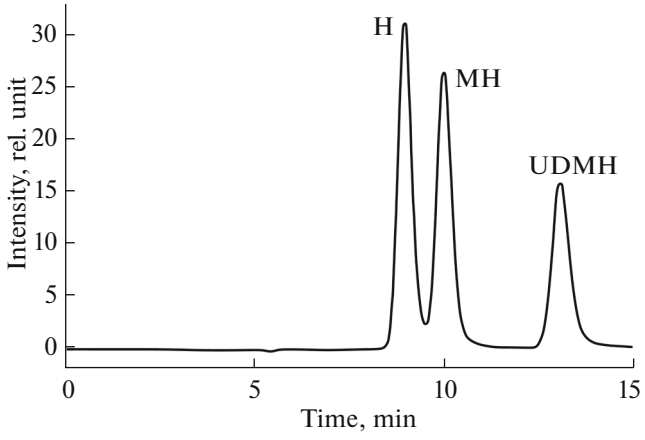

Fig. 3. A chromatogram of a model solution of hydrazines (1 mg/L of each component) obtained by IC with post-column derivatization by NFA. Detection wavelength is 454 nm.

Table 2. Slopes of calibration dependences (a) of peak areas vs. concentration ($y = ax$), LOD, and c_{low} of analytes for reversed-phase HPLC with precolumn derivatization (I) and ion chromatography with post-column derivatization (II) by 5-nitro-2-furaldehyde

Analyte	Method I				Method II			
	a	R^2	LOD, μg/L	c_{low}, μg/L	a	R^2	LOD, μg/L	c_{low}, μg/L
H	34	0.999	1.0	3.4	15	0.999	0.9	3.2
MH	89	0.999	0.6	2.0	24	0.999	0.4	1.4
UDMH	141	0.999	0.3	0.9	88	0.999	0.2	0.7

values of LOD and c_{low} were confirmed experimentally in the analysis of model solutions with concentrations of H, MH, and UDMH close to c_{low}.

In RP HPLC with precolumn derivatization, the attained limits of detection for H, MH, and UDMH are significantly lower in comparison with those in the procedures based on derivatization with 4-nitrobenzaldehyde aldehyde and other aromatic aldehydes in combination with SPD. The sensitivity of the proposed procedure to UDMH virtually does not differ from that attained in [18] using glyoxal as a derivatizing agent and ensures the detection of the pollutant at the concentration level equal to MPC for fishery reservoirs without using additional preconcentration steps. Note that the used sample volume (10 μL) is tenfold smaller than that in the procedure described in [18]. This ensures the reliable determination of UDMH in concentrations lower than MPC on increasing sample volume to 20–40 μL without a noticeable loss in the efficiency of separation and selectivity of analysis. An important advantage of the developed approach is also in a possibility of the simultaneous determination of not only MH and UDMH, but also H, which significantly improves the reliability of results of analysis of real samples polluted by rocket fuels.

The sensitivity of analysis in the IC version with post-column derivatization (LOD values were 1.1–1.5 times lower) is close to that in RP HPLC, despite the weak smearing of chromatographic peaks in the reaction capillary and also a possible incomplete proceeding of the reaction or the decomposition of analytes at high temperature in the reactor, which was expressed in smaller slope of calibration dependences (Table 2). This is explained by a considerable dilution of the analyzed solution in the course of precolumn derivatization with the aim to create the optimum pH the solution and the necessary concentration of NFA.

A combination of the ion-chromatographic separation of hydrazines with post-column derivatization by NFA allowed us to gain a significant increase in the sensitivity of UDMH determination even in comparison with the most sensitive procedures based on derivatization by glyoxal and naphthalene-2,3-dialdehyde and also by IC with amperometric detection. A drawback of the proposed approach is in a little higher values of the limits of detection for H and MH, which, being recalculated to a comparable sample volume, are nevertheless at the level of highly sensitive procedures of analysis mentioned above.

To check the accuracy of the developed procedures for the determination of hydrazines in water (RP HPLC–SPD, IC–SPD) and natural surface water (IC–SPD), we used the added–found method for three levels of analyte concentration. The results obtained confirm the absence of noticeable matrix effects even at the concentration of hydrazines below 100 μg/L and in the analysis of water samples II and III with high concentrations of the dissolved organic matter (Tables 3, 4). The determination error virtually does not change for different waters and does not exceed 20% at the minimum concentration level. Unfortunately, similar experiments at the concentration of analytes close to c_{low} could not be performed because of the rapid covalent binding of hydrazines with lignohumic substances [10].

Soil analysis. Of the greatest interest was a possibility of using the developed procedures for the determination of rocket fuel components in such complex samples as peat bog soils, characteristic for areas of the impact of the spent stages of carrier rockets in the north of the Russian Federation. We analyzed an acid extract of a peat bog sample collected directly in the

Table 3. Results (mg/L) of check of the accuracy of hydrazine determination in a sample of tap water I by reversed-phase HPLC with preliminary derivatization by 5-nitro-2-furaldehyde ($n = 5$, $P = 0.95$)

Analyte	Added	Found	Accuracy, %
UDMH	3.0	3.0 ± 0.1	100 ± 3
MH	3.0	2.9 ± 0.1	97 ± 3
H	2.5	2.4 ± 0.2	96 ± 8
UDMH	0.50	0.49 ± 0.03	98 ± 6
MH	0.50	0.49 ± 0.03	98 ± 6
H	0.20	0.20 ± 0.02	100 ± 10
UDMH	0.050	0.044 ± 0.006	88 ± 12
MH	0.050	0.040 ± 0.010	80 ± 20
H	0.030	0.027 ± 0.007	90 ± 23

Table 4. Results (mg/L) of check of the accuracy of hydrazine determination by ion chromatography with post-column derivatization by 5-nitro-2-furaldehyde on examples of samples of tap (I) and river (II) water and peat bog surface water (III) ($n = 5$, $P = 0.95$)

Analyte	Added	Found	Accuracy, %	Added	Found	Accuracy, %	Added	Found	Accuracy, %
				Tap water					
UDMH	57	52 ± 4	91 ± 7	2.8	2.6 ± 0.2	93 ± 7	0.14	0.13 ± 0.02	93 ± 14
MH	59	55 ± 4	93 ± 7	3.0	2.7 ± 0.3	90 ± 10	0.15	0.13 ± 0.02	87 ± 13
H	34	32 ± 2	94 ± 6	1.7	1.5 ± 0.1	88 ± 6	0.09	0.07 ± 0.01	78 ± 11
				River water					
UDMH	57	56 ± 1	98 ± 2	2.8	2.8 ± 0.1	100 ± 6	0.14	0.13 ± 0.01	93 ± 7
MH	59	57 ± 2	97 ± 3	3.0	2.8 ± 0.2	93 ± 7	0.15	0.14 ± 0.01	93 ± 7
H	34	33 ± 2	97 ± 6	1.7	1.6 ± 0.1	94 ± 6	0.09	0.08 ± 0.01	89 ± 11
				Peat bog surface water					
UDMH	57	53 ± 4	93 ± 7	2.8	2.6 ± 0.2	93 ± 7	0.14	0.13 ± 0.01	93 ± 7
MH	59	57 ± 2	97 ± 3	3.0	2.8 ± 0.2	93 ± 7	0.15	0.14 ± 0.01	93 ± 7
H	34	33 ± 1	97 ± 3	1.7	1.6 ± 0.1	94 ± 6	0.09	0.08 ± 0.01	89 ± 11

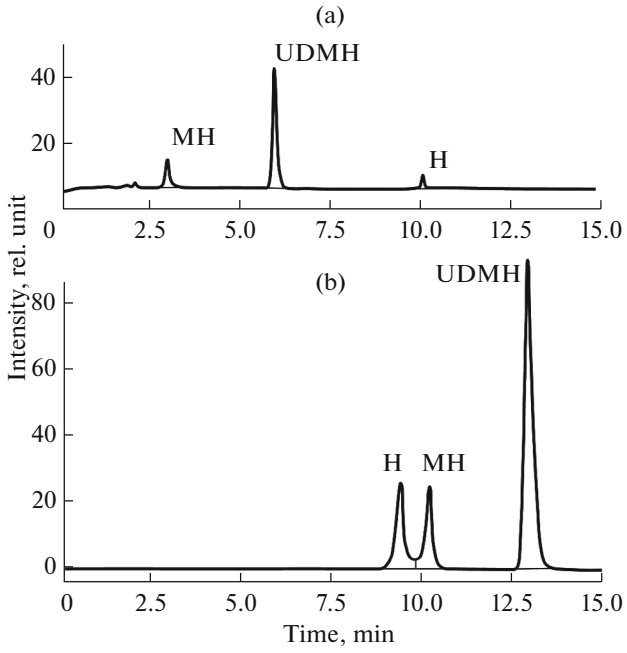

Fig. 4. Chromatograms of an acid extract of a peat bog soil from the place of impact of the first stage of a carrier rocket obtained by (a) RP HPLC–SPD with precolumn derivatization by NFA and (b) IC–SPD method with post-column derivatization by NFA. Detection wavelength is 454 nm.

place of impact of the first rocket stage. The amount of acid used in the extraction ensures the limit of detection for UDMH in soil at a level of 0.4–0.6 μg/kg, being recalculated to an absolutely dry sample (at a typical humidity of 90–95%), the mobile form of UDMH can be detected at its concentration in the peat from 4 to 12 μg/kg, which is tenfold lower than the established MPC value (0.1 mg/kg). As an independent method for comparison with the results obtained, we used IC with amperometric detection [6]. The obtained chromatograms (Fig. 4) clearly demonstrate the absence of peaks of foreign components for both modes of analysis, despite the presence of significant amounts of organic soil substance in extract. The concentrations of analytes found in the soil by different methods (Table 5) are almost identical (taking into account the determination error), which points to the adequacy and high reliability of the used procedures. Note that, in the real sample of soil from the place of impact of the first stage of the carrier rocket, we observed the high level of pollution by hydrazines (more than 500 MPC for UDMH) even after a long time (more than 5 years) after the ingress of the pollutant. This is due to the strong binding of hydrazines with lignohumic substances, favoring both the weak distribution of pollutants and long preservation of the dangerous level of pollution on local sites.

Table 5. Comparison of the results (mg/kg) of analysis of an acid extract of peat bog soil polluted by rocket fuel by different methods ($n = 5$, $P = 0.95$)

Component	RP HPLC–SPD with precolumn derivatization	IC–SPD with post-column derivatization	IC–AD*
UDMH	55 ± 1	55.8 ± 0.9	55 ± 1
MH	11.9 ± 0.4	12.2 ± 0.4	12.4 ± 0.5
H	7.7 ± 0.4	7.2 ± 0.3	7.1 ± 0.4

* Amperometric detector.

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