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ORIGINAL

Quantification of Transformation Products of Unsymmetrical Dimethylhydrazine in Water Using SPME and GC-MS

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Abstract Quantification of trace concentrations of transformation products of rocket fuel unsymmetrical dimethylhydrazine (UDMH) in water requires complex analytical instrumentation and tedious sample preparation. The goal of this research was to develop a simple and automated method for sensitive quantification of UDMH transformation products in water using headspace (HS) solid-phase microextraction (SPME) in combination with GC-MS and GC-MS/MS. HS SPME is based on extraction of analytes from a gas phase above samples by a micro polymer coating followed by a thermal desorption of analytes in a GC inlet. Extraction by 85 µm Carboxen/polydimethylsiloxane fiber at 50 °C during 60 min provides the best combination of sensitivity and precision. Tandem mass spectrometric detection with positive chemical ionization improves method accuracy and selectivity. Detection limits of twelve analytes by GC-MS/MS with chemical ionization are about 10 ng L^{-1}. GC-MS provides similar detection limits for five studied analytes; however, the list of analytes detected by this method can be further expanded. Accuracies determined by GC-MS were in the range of 75–125% for six analytes. Compared to other available methods based on non-SPME sample preparation approaches (e.g., liquid–liquid and solid-phase extraction), the developed method is simpler, automated and provides lower detection limits. It covers more UDMH transformation products than available SPME-based methods. The list of analytes could be further expanded if new standards become available. The developed method is recommended for assessing water quality in the territories affected by space activities and other related studies.

Keywords SPME · GC-MS · Quantification · Transformation products · Dimethylhydrazine · Water

Introduction

Despite very high toxicity of a rocket fuel based on unsymmetrical dimethylhydrazine (UDMH), it is still used in heavy rockets in Russia, Kazakhstan and China [1]. Unburned UDMH remaining in tanks is spilled into the environment [2] with formation of >50 known transformation products including nitrosoamines, tetrazenes, triazoles, pyrazoles, tetrazoles, imidazoles, pyrazines, aldehydes and other classes of compounds. Most of these transformation products are polar, have high water solubility and can accumulate in surface and ground waters used for drinking and household purposes. Despite most spilled fuel accumulates in soil [3], the greatest health risks are associated with water pollution. Ul'yanovskii et al. [4] showed that concentrations of 1-methyl-*1H*-1,2,4-triazole (MTA) and *N*,*N*-dimethylformamide (DMF) in water samples from fall regions of rockets can reach 600 µg L^{-1}.

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Available methods for quantification of UDMH transformation products in water (Table 1) are based on liquid (LC) and gas chromatography (GC) [5]. Methods based on LC [6–9] do not require complex sample preparation because samples can be directly injected to an instrument. However, these methods do not provide sufficiently low detection limits for most UDMH transformation products in real samples. Lower detection limits can be achieved using GC with tandem mass spectrometric (MS/MS) detection [4, 10]. However, such analysis requires a tedious sample preparation—liquid–liquid extraction [4] and solid-phase extraction followed by evaporative concentration [11].

In recent years, headspace (HS) solid-phase microextraction (SPME) became very popular for screening [12] and quantification of UDMH transformation products in environmental samples [13–15]. SPME is based on extraction of analytes from a gas phase above a sample to a micro polymer coating followed by a thermal desorption in a GC injection port. HS SPME is simple, fast and can be fully automated. Methods were developed for quantification of formaldehyde dimethylhydrazone [13] and *N*-nitrosodimethylamine (NDMA) [14] in water samples using SPME in combination with GC-MS with detection limits of around 1 μg L^{-1}. Grebel et al. [16] developed the SPME-based method for quantification of nitrosoamines in water samples based on SPME allowing a detection of NDMA using GC-MS with chemical ionization at the level of 30 ng L^{-1}.

The goal of this research was to develop the new multi-analyte method for a simple and sensitive quantification of main UDMH transformation products in water samples based on SPME in combination with GC-MS and GC-MS/MS.

Experimental

Standards

The list of analytes (UDMH transformation products) containing their origin and key physical properties is provided in Table 2.

Parameters of Analyses

Parameters of GC-MS Analyses

Experiments on the method development were conducted using the gas chromatograph with mass spectrometric detector 6890N/5973N (Agilent, USA) equipped with Combi-Pal (CTC Analytics, Switzerland) autosampler and split/splitless inlet. For a desorption of analytes, a SPME fiber was introduced into the GC inlet equipped with 0.75 mm i.d. SPME liner (Supelco, USA) heated to 240 °C in a splitless mode, and left there for 5 min. A septum purge at 50 mL min^{-1} was activated 1 min after the fiber was removed from the inlet followed by the activation of a gas saver at 15 mL min^{-1}. To avoid a carryover, the fiber was conditioned in the second inlet at 240 °C before and after analysis for 5 and 20 min, respectively. Separation was conducted on a 60 m × 0.25 mm DB-WAXetr (Agilent, USA) column with a 0.50 μm film of polar stationary phase based on polyethylene glycol at constant flow rate of helium (>99.995%, Tehgas, Orenburg, Russia) equal to 1 mL min^{-1}. Oven was programmed from 40 °C (held for 5 min) to 240 °C at the 3 °C/min ramp. Total time of analysis was 72 min. Detection was conducted using electron impact ionization at 70 eV in selected ion monitoring (SIM) mode. All ions were split to six groups (Table 3) with a dwell time for each quantification ion 200 and 100 ms in total for all other qualification ions. Accepted relative deviation from the target intensity ratio of quantification and qualification ions was ±5% from the values provided in the Table 3. Temperatures of ion source and quadrupole were 230 and 150 °C, respectively. Solvent delay was set to 25 min to avoid MS detection of water and to increase lifetime of a filament and an electron multiplier.

Parameters of GC-MS/MS Analyses

GC-MS/MS analyses were conducted on the GC-MS-TQ8040 (Shimadzu, Japan) instrument equipped with AOC-5000 Plus (Shimadzu, Japan). Separation was conducted at constant pressure of helium (>99.9999%, NII KM, Moscow, Russia) on a 60 m × 0.25 mm HP-INNOWax column with a 0.50 μm film of the polar stationary phase based on polyethylene glycol (Agilent, USA). Analytical column was protected by the 1.0 m × 0.25 mm guard column (Restek, USA) that was also used for cryo trapping of analytes. Oven temperature was programmed from 40 °C (held for 5 min) to 250 °C (held for 10 min) at the 5 °C/min ramp. Total length of the analysis was 57 min.

Desorption of analytes from SPME fiber was conducted using Optic-4 (GL Sciences BV, Japan) inlet equipped with straight 1.0 mm i.d. liner (GL Sciences BV, Japan) in splitless mode using temperature programming from 170 °C (held for 0.1 min) to 300 °C (held for 50 min) at 5 °C/s rate, which was previously optimized by Kenessov et al. [12]. After desorption, analytes were cryogenically focused at −80 °C during 5 min followed by the heating at 20 °C/s rate to 250 °C and holding the final temperature till the end of an analysis. Recording GC-MS/MS data was started after the heating of the cryotrap was started. Septum purge (10 mL min^{-1}) and gas saver (15 mL min^{-1}) were activated 1 and 2 min after the start of an analysis, respectively.

Table 1 Summary of the current analytical methods for determination of UDMH transformation products in water

Analyte	Sample preparation	Method	Limit of detection (µg L^{-1})	Results of application (measured concentrations in µg L^{-1})	References
Eight volatile UDMH transformation products (NDMA; DMF; MTA; FDMH; FurDMH; FADMH; ADMH; TMT	Extraction with acetonitrile	GC-ESI-MS/MS	0.3–2.3	MTA (680) DMF (630)	[4]
FADMH	HS-SPME	GC-EI-MS GC-NPD	1.5 0.5	n/d	[13]
DMF	SPE	GC-EI-MS	0.065	0.13	[11]
NDMA	HS-SPME	GC-EI-MS	1	–	[14]
Seven nitrosamines (NDMA)	HS-SPME	GC-PCI-MS/MS	0.005	NDMA (25)	[10]
NDMA	–	LC-UV/Vis	10	Certified method	[7]
Tetrazene	–	LC-UV/Vis	7	US EPA Method	[9]
TMT	–	LC-AD	50	Certified method	[8]
MTA	–	LC-DAD	200	n/d	[6]
Six volatile UDMH transformation products (pyrazine, 1-methyl-*1H*-pyrazole, NDMA, DMF, MTA; 1-methyl-*1H*-imidazole)	HS-SPME	GC-EI-MS	0.005–0.5	n/d	This work

n/d not detected or below detection limit, *ADMH* acetaldehyde dimethylhydrazone, *AD* amperometric detection, *CI* chemical ionization, *DAD* diode-array detection, *DMF N*,*N*-dimethylformamide, *FADMH* formaldehyde dimethylhydrazone, *FDMH* 1-formyl-2,2-dimethylhydrazine, *FurDMH* 2-furaldehyde dimethylhydrazone, *GC* gas chromatography, *HS-SPME* headspace solid-phase microextraction, *LC* liquid chromatography, *MS* mass spectrometry, *MS/MS* tandem mass spectrometry, *MTA* 1-methyl-*1H*-1,2,4-triazole, *NDMA N*-nitrosodimethylamine, *NPD* nitrogen-phosphorus detection, *SPE* solid-phase extraction, *TMT* 1,1,4,4-tetramethyl-2-tetrazene, *UV/Vis* ultraviolet and visible

Table 2 The list of studied compounds and their physicochemical properties

No	Compound	CAS no.	Molecular weight (Da)	K_H (atm m^3 mol^{-1}, 25 °C)	log K_{ow}	Boiling point (°C)	Vapor pressure (Pa, 25 °C)	MCL (µg L^{-1})
1	Pyridine (≥99.5%, Aldrich, USA)	00110-86-1	79.1	1.10E−05	0.65	115	2770	200 [17]
2	Pyrazine (≥99.5%, Aldrich, USA)	00290-37-9	80.1	2.92E−06*	−0.26	115	1440	n/a
3	Dimethylaminoacetonitrile (≥98.0%, Sigma Aldrich, USA)	00926-64-7	84.1	1.52E−08*	−0.44*	137	950*	n/a
4	1-Methyl-*1H*-pyrazole (≥98.0%, Meryer, China)	00930-36-9	82.1	7.88E−05*	0.23	127	1530*	n/a
5	*N*-Nitrosodimethylamine (≥99.5%, Supelco, USA)	00062-75-9	74.1	1.82E−06	−0.57	154	360	10 [18]
6	*N,N*-Dimethylformamide (≥99.8%, Lab-Scan, Poland)	00068-12-2	73.1	7.39E−08*	−1.01	153	516	10,000 [17]
7	1-Methyl-*1H*-1,2,4-triazole (≥98.0%, Fluorochem, UK)	06086-21-1	83.1	3.26E−05*	−0.21*	178	1410*	n/a
8	*N*-Methylformamide (≥99.5%, Meryer, China)	00123-39-7	59.1	1.97E−08*	−0.97	199	49.3*	n/a
9	1-Formyl-2,2-dimethylhydrazine (≥99.5%, CFC ‘Arktika’, Russia)	3298-49-5	88.1	3.08E−10*	−1.70*	75	18.6*	n/a
10	1-Methyl-*1H*-imidazole (≥99.5%, Meryer, China)	00616-47-7	82.1	8.01E−05*	−0.06	196	60.2*	n/a
11	Formamide (≥99.5%, Meryer, China)	00075-12-7	45.0	1.39E−09*	−1.51	220	17.5*	n/a
12	2-Furaldehyde dimethylhydrazone (97.0%, Aldrich, USA)	14064-21-2	138.2	3.58E−6*	0.99*	77	105*	n/a
13	*1H*-Pyrazole (≥98.5%, Aldrich, USA)	00288-13-1	68.1	3.69E−06*	0.26	187	32.8*	n/a
14	3-Methyl-*1H*-pyrazole (≥97.5%, Alfa Aesar, USA)	01453-58-3	82.1	4.07E−07*	0.61*	204	28.5*	n/a
15	3,5-Dimethyl-*1H*-pyrazole (≥99.0%, ABSR, Germany)	00067-51-6	96.1	4.50E−06*	1.01	218	2.79*	n/a

MCL maximum contaminant level, *CFC ‘Arktika’* Core Facility Center “Arktika” of M.V. Lomonosov Northern (Arctic) Federal University, Arkhangelsk, Russia, *n/a* not available

* Predicted values using EPI suite ver. 4.11

Detection was conducted in positive chemical ionization (PCI) mode using methane (>99.99%, Monitoring LLC, Saint Petersburg, Russia) reagent gas (240 kPa), ionization energy 30 V, emission current 150 µA, temperatures of ion source and interface 150 and 250 °C, respectively. Solvent delay was set to 20 min. Detector was working in Q1 SIM (see Electronic Supplementary Material Table S1) and multiple reaction monitoring (MRM) modes (see Electronic Supplementary Material Table S2). Pressure of argon (>99.998%, NII KM, Moscow, Russia) supplied to the collision cell was 200 kPa.

General Parameters of SPME

SPME was conducted using autosamplers and 85 µm Carboxen/polydimethylsiloxane (Car/PDMS) fibers (Supelco, USA) from headspace above samples using a periodic agitation at 250 rpm. Fibers were conditioned at 250 °C before and after an analysis during 5 and 20 min, respectively. Experiments were conducted using 20-mL screw-cap vials (Agilent, USA) and PTFE/silicone septa (Agilent, USA) preconditioned at 150 °C during 3 h. To each water sample ($V = 8.0$ mL), 2.8 g of NaCl (>99.9%,

Table 3 Program of MS detection of UDMH transformation products in SIM mode

Target compound	Retention time (min)	*m/z* of quantification ion (dwell 200 ms)	*m/z* of confirmation ion (dwell 100 ms)	Target ratio of ions' intensities (%)	Group #	Start time (min)
Pyrazine	27.84	80	53	32	1	25.0
Dimethylaminoacetonitrile	29.25	83	84	59	2	29.0
1-Methyl-*1H*-pyrazole	29.80	82	81	45		
N-Nitrosodimethylamine	33.16	74	42	37	3	33.0
N,N-Dimethylformamide	33.85	73	42	42		
1-Methyl-*1H*-1,2,4-triazole	44.97	83	56	34	4	44.0
1-Formyl-2,2-dimethylhydrazine	47.60	59	88	10	5	46.0
1-Methyl-*1H*-imidazole	49.21	82	81	20		
Formamide	52.95	45	43	25	6	51.0
1H-Pyrazole	53.66	68	42	40		

Ecros, Russia) were added to enhance the extraction [12, 16].

Samples

Experiments were conducted on model samples prepared by spiking distilled (**A**) and lake (**B**) (Sakisor lake, 54°4′26″N, 75°36′34″E) water. Model samples were prepared by mixing 8.0 mL of water with 120 µL of a standard solution of analytes in a 20-mL vial followed by sealing a vial and agitation during 30 min. For experiments on optimization of SPME, model samples were prepared by injecting 10 µL of a standard solution into the vial using Combi-Pal autosampler. All used solutions were stored at 5–7 °C for the maximum of one week. Sample **B** was kept frozen and melted only 10 h before starting an experiment.

Methodology of Experiments

Optimization of the Extraction Temperature

Experiments were conducted on model samples **A** with concentrations of analytes **3–7, 9–13** (Table 2) 3000 µg L^{-1}, and pyrazine (**2**)—500 µg L^{-1}. Preincubation (5 min) and extraction (5 min) were conducted in the agitator of Combi-Pal autosampler at 30, 50, 70 and 85 °C.

Optimization of the Extraction Time

Experiment was conducted on model samples **A** with concentrations of analyte **3–7, 9–13**—30 µg L^{-1} and pyrazine (**2**)—5 µg L^{-1} in three replicates. SPME was conducted in the agitator of Combi-Pal autosampler heated to 70 °C during 10, 20, 30 and 60 min.

Determination of Linearity, LODs and LOQs of the Developed Method Based on SPME-GC-MS

Experiment was conducted on model samples **A** and **B** prepared 1 h before analyses in two replicates. SPME was conducted in the agitator of Combi-Pal autosampler heated to 50 °C during 60 min followed by a GC-MS analysis.

Improvement of the Method Accuracy and Detection Limits Using Tandem Mass Spectrometry with Chemical Ionization

Experiments were conducted on model samples **A** spiked with standard solution containing 13 transformation products of UDMH 1 h before an analysis in duplicates. SPME was conducted in the agitator of AOC-500 autosampler heated to 50 °C during 60 min followed by GC-MS/MS analysis.

Results and Discussion

Optimization of Extraction Temperature

The increase of extraction temperature from 30 to 85 °C resulted in a 4.4-, 4.5-, 9.7- and 4.2-fold increase of peak areas of MTA, 1-formyl-2,2-dimethylhydrazine (FDMH), 1-methyl-*1H*-imidazole and *1H*-pyrazole, respectively (Fig. 1). Greatest responses of DMF, formamide and 1-methyl-*1H*-1,2,4-triazole were observed at 70 °C, NDMA—at 50 °C. The increase of extraction temperature led to the decrease of the response of dimethylaminoacetonitrile

(DMAAN). Thus, temperatures of 50–70 °C are optimal for the extraction of all analytes. In addition to the decrease of fiber effectiveness, a higher temperature can potentially lead to a decomposition of UDMH and its unstable transformation products. However, extraction temperature can be increased if pollution of sampled water occurred long time ago, and less volatile analytes are of a greater importance.

Optimization of Extraction Time

For most analytes, the increase of an extraction time from 10 to 60 min resulted in the two to threefold increase of responses (Fig. 2). For MTA and *1H*-pyrazole, responses increased 3.4 and 3.2 times. The increase in the response of formamide was in the range of standard deviations. Peak area of DMAAN decreased with time: signal-to-noise ratio decreased from 20:1 at 10 min to 5:1 at 30-min long extraction, most probably due to decomposition of this analyte. Thus, a decision was made to withdraw this analyte from the method being developed because of substantial difference of its physicochemical properties from other analytes.

Effect of SPME Parameters on Precision of the Developed Method

Lowest relative standard deviations (RSDs) were observed at extraction temperature 85 °C and made up less than 18% for all analytes (Fig. 3a). Highest RSDs at 85 °C were observed for FDMH and DMF, minimal (3%)—for NDMA and 1-methyl-*1H*-imidazole. At 30 °C, RSDs of responses of FDMH, MTA and formamide were 50, 48 and 32%, respectively. At 50 °C, RSDs were <20% for all analytes except formamide.

The increase of extraction time from 10 to 60 min resulted in the decrease of RSDs from 8–30% to 3–18% (Fig. 3b). The increase of extraction time mostly affected RSDs of responses of DMF and NDMA, which decreased nine and seven times, respectively. For FDMH and 1-methyl-*1H*-imidazole, RSDs decreased from 20 to 18 and 16%, respectively. Thus, SPME at 50 °C during 60 min provides best combination of precision and sensitivity for the quantification of UDMH transformation products in water samples.

Method Detection Limits, Linearity and Accuracy

Linearity of external standard calibration plots obtained on distilled and lake water were 0.85–0.99 and 0.35–0.99, respectively (Table 4). Coefficients of determination >0.99 were observed for pyrazine, 1-methyl-*1H*-pyrazole, NDMA and MTA. Calibration plots for FDMH and formamide had poor linearity (<0.90). Compared to other analytes, these analytes are detected at lower *m/z* (59 and 45, respectively), where high level of background and matrix noise are observed (Fig. 4). For these analytes in lake sample, r^2 decreased to 0.73 and 0.74, respectively. Worst linearity ($r^2 = 0.35$) was observed for *1H*-pyrazole.

Differences between slope factors for distilled and lake water varied from 5 to 21%. Lowest differences were observed for pyrazine (5%), 1-methyl-*1H*-pyrazole (7%) and DMF (8%), the greatest—for 1-methyl-*1H*-imidazole (21%) and FDMH (16%). Despite high RSDs observed for *1H*-pyrazole and formamide, differences between

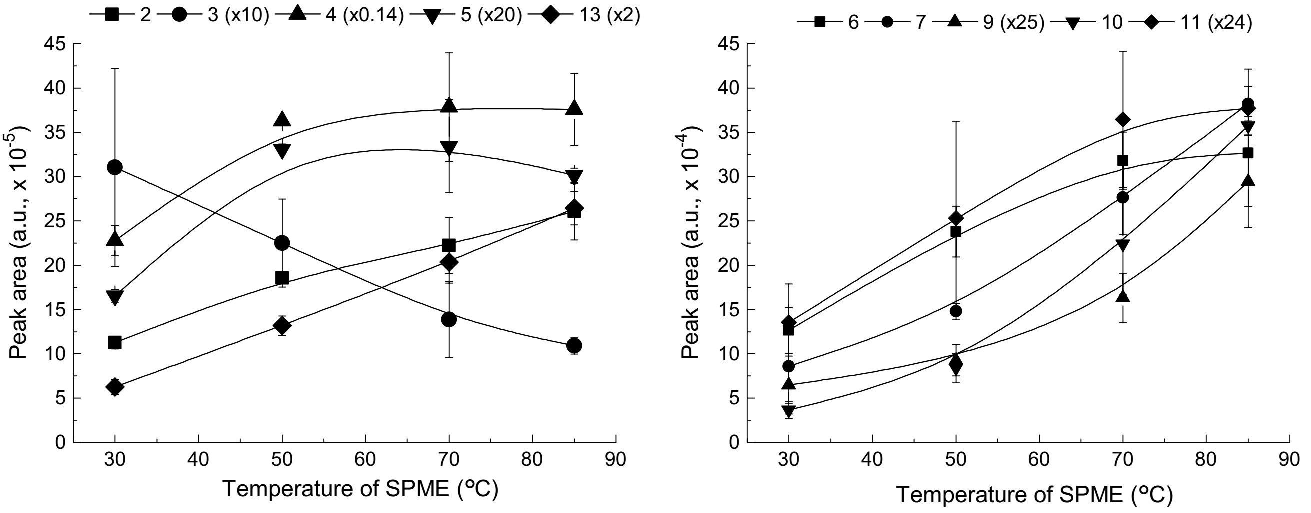

Fig. 1 Effect of extraction temperature on peak areas of UDMH transformation products by headspace SPME. Sample volume = 8.0 mL, m(NaCl) = 2.8 g; extraction time = 5 min; 85 µm Car/PDMS fiber; model samples A with concentrations of analytes **3–7, 9–13**—3000 µg L^{-1}, pyrazine (**2**)—500 µg L^{-1}

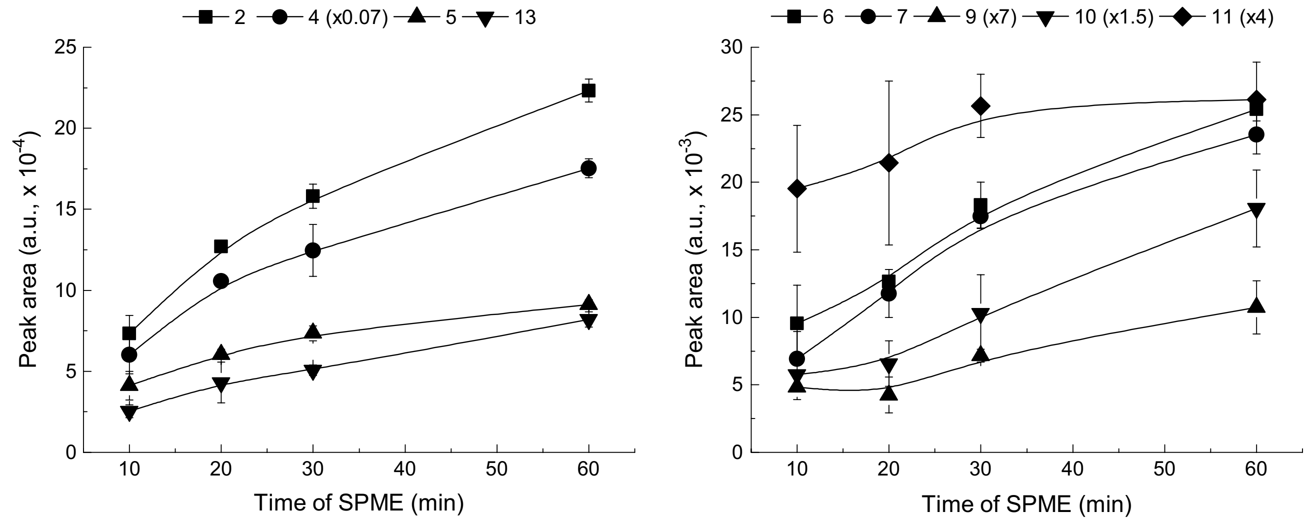

Fig. 2 Effect of extraction time on peak areas of UDMH transformation products by HS SPME. Sample volume = 8.0 mL; m(NaCl) = 2.8 g; extraction temperature 70 °C; 85 µm Car/PDMS fiber; model samples A with concentrations of analytes **3–7, 9–13**—30 µg L^{-1} and pyrazine (**2**)—5 µg L^{-1}

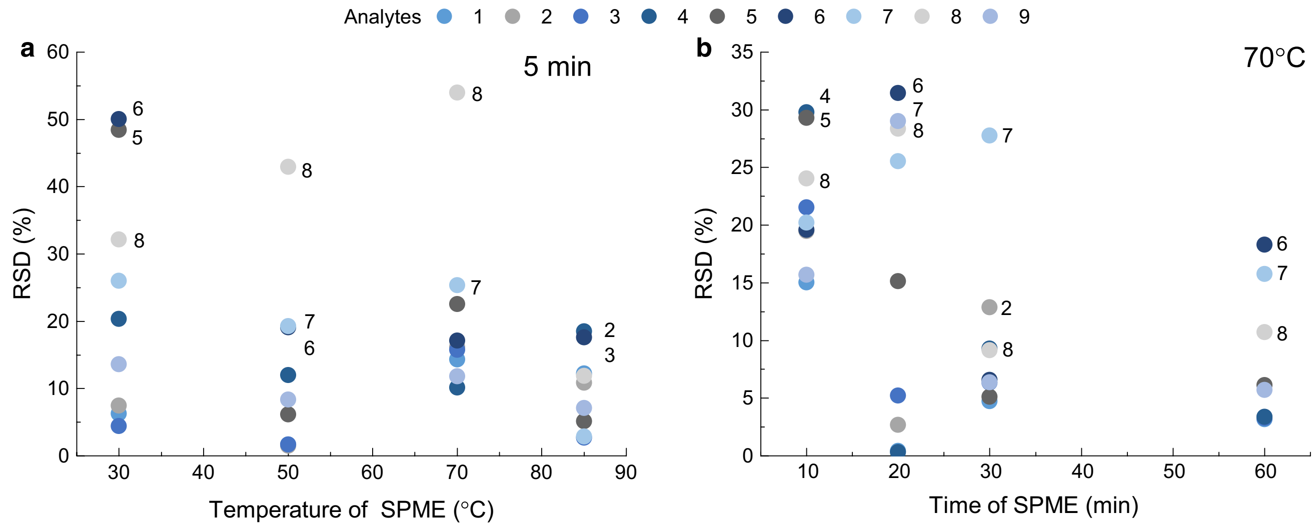

Fig. 3 Effects of extraction temperature and time on relative standard deviations of UDMH transformation products. Analytes: *1* pyrazine; *3* 1-methyl-*1H*-pyrazole; *4* *N*-nitrosodimethylamine; *5* *N*,*N*-dimethylformamide; *6* 1-methyl-*1H*-1,2,4-triazole; *7* 1-formyl-2,2-dimethylhydrazine; *8* 1-methyl-*1H*-imidazole; *9* formamide; *10* *1H*-pyrazole

slope factors of their calibration plots for both types of calibration samples were 15 and 12%, respectively.

Detection limits for analytes providing RSDs of slope factors less than 15% were calculated on calibration samples prepared using lake water with lowest concentrations of analytes. For other analytes, data obtained for samples based on distilled water were used. For most analytes, detection limits were less than 1 µg L^{-1}. Detection limits for FDMH and formamide are 68 and 10 µg L^{-1}, respectively.

Thus, the developed method based on SPME-GC-MS provides simultaneous determination of six main transformation products of UDMH (pyrazine, 1-methyl-*1H*-pyrazole, NDMA, DMF, MTA and 1-methyl-*1H*-imidazole) in water using external standard calibration at the accuracy of 75–125%. Quantification of three other analytes (1-formyl-2,2-dimethylhydrazine, formamide and *1H*-pyrazole) does not provide the required precision and accuracy due to matrix effects. Accuracy of their quantification by the developed method can be improved using standard addition

Table 4 Linearity, LODs and LOQs of the developed method based on GC-MS

Compound	Linear range (µg L^{-1})	Distilled water		Lake water		LOD (µg L^{-1})	LOQ (µg L^{-1})	RSD at LOQ (%)
		Slope (RSD in %)	r^2	Slope (RSD in %)	r^2			
Pyrazine	0.5–75	55,273 (1)	0.9998	51,670 (1)	0.9971	0.01	0.03	7
1-Methyl-*1H*-pyrazole	0.5–60	101,855 (2)	0.9985	112,594 (5)	0.9894	0.005	0.01	3
N-Nitrosodimethylamine	1–150	6710 (1)	0.9998	5445 (2)	0.9915	0.05	0.15	4
N,N-Dimethylformamide	1–150	1231 (8)	0.9702	1113 (13)	0.9269	0.05	0.15	5
1-Methyl-*1H*-1,2,4-triazole	1–150	681 (4)	0.9915	572 (2)	0.9977	0.3	0.9	34
1-Formyl-2,2-dimethylhydrazine*	70–900	11 (18)	0.8536	9 (27)	0.7336	70	200	9
1-Methyl-*1H*-imidazole	1–150	315 (4)	0.9936	231 (3)	0.9971	0.5	1.3	4
Formamide*	50–700	29 (15)	0.8969	34 (26)	0.7392	10	30	55
1H-Pyrazole*	2–200	2670 (9)	0.9628	3301 (61)	0.3499	0.03	0.08	77

LOD limit of detection, 3.3·C_a/signal/noise, *LOQ* limit of quantification, 10·C_a/signal/noise, *RSD* relative standard deviation

* Quantification of these analytes by the developed method has low accuracy and/or precision

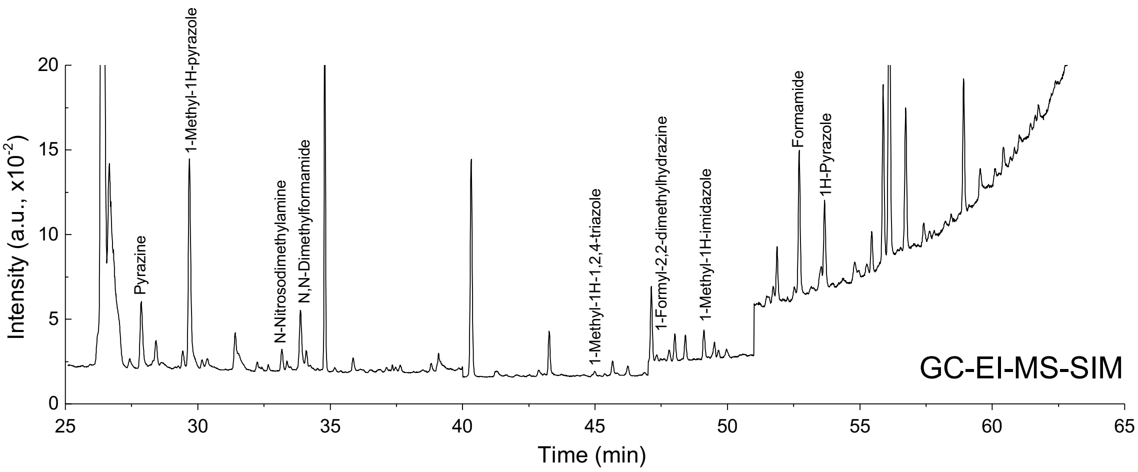

Fig. 4 Chromatogram of lake water sample (**B**) spiked with trace concentrations of UDMH transformation products. Sample volume 8.0 mL; m(NaCl) = 2.8 g; extraction temperature 50 °C; extraction time 60 min, 85 µm Car/PDMS fiber

or matrix-matched calibration. Internal standard calibration can also be used for improving accuracy; however, selection of a suitable internal standard could be complicated because it should have similar physicochemical properties as analytes including volatility, polarity and dissociation constant. Isotopically labeled internal standards should provide greatest accuracies, but they are very expensive or unavailable.

Improvement of the Method Accuracy and Detection Limits Using Tandem Mass Spectrometry with Chemical Ionization

As was shown in the previous section, the quantification of several analytes by GC-MS is limited by a poor accuracy, precision and linearity. The goal of this experiment was to check whether the more selective tandem mass spectrometric detection with positive chemical ionization could provide better quantification of UDMH transformation products using SPME. It is known [10] that soft chemical ionization provides significant gain in sensitivity for analytes, which produce ions with low *m/z* in EI ionization. The list of analytes was expanded to 13 compounds. New analytes have similar volatility and polarity and can be efficiently analyzed using the optimized method parameters.

Chemical ionization allowed decreasing LODs of formamide and FDMH to 1 µg L^{-1}, MTA and 1-methyl-*1H*-imidazole—to 0.05 and 0.1 µg L^{-1}, respectively (Table 5). LODs of pyrazine, *1H*-pyrazole, NDMA and DMF increased 3, 5, 1.4 and 2 times, respectively, which could be caused by a greater effectiveness of EI ionization of these analytes compared to PCI. Coefficients of determination (r^2) and RSDs of slope factors for most analytes were better using chemical ionization (Table 5) compared to EI ionization (Table 4), particularly for formamide and *1H*-pyrazole. Detection limits of most analytes in MRM detection mode were higher than in SIM mode (Table 5) due to losses of ions in the collision cell, but it can be used to increase selectivity when analyzing complex samples.

Application of the Developed Method

The developed method based on SPME-GC-MS was used for the analysis of three samples of snow taken on 12/03/2015 at Toretam railway station (Kyzyl-Orda oblast, Kazakhstan; coordinates: N45°39′10.4″, E63°19′11.9″) located on the way of rocket fuel transportation to Baikonur cosmodrome. One control sample of snow was taken near the railroad at the distance of 5 km east from the Toretam railway station (N45°39′58.3″, E63°22′48.0″). The control point was located out of the route used for transportation of the rocket fuel. UDMH transformation products were not detected in the analyzed samples, most probably, due to their lower concentrations than LODs of the developed method.

Conclusion

Thus, the new simple and automated method for sensitive quantification of main transformation products of rocket fuel dimethylhydrazine in water samples was developed using solid-phase microextraction and GC-MS. Highest precision of the method was achieved at extraction temperature 50 °C and time 60 min. These parameters also provide greatest peak areas of most transformation products. Accuracies of quantification of pyrazine, 1-methyl-*1H*-pyrazole, *N*-nitrosodimethylamine, *N,N*-dimethylformamide, 1-methyl-*1H*-1,2,4-triazole and 1-methyl-*1H*-imidazole in water using external standard calibration are in the range of 75–125%. LODs of these analytes are below 1 µg L^{-1}. Determination of formamide and *1H*-pyrazole at the target accuracy and detection limits was possible by the more selective triple quadrupole detection with positive chemical ionization. Using GC-PCI-MS/MS, the list of analytes was also expanded by pyridine, 2-furaldehyde dimethylhydrazone, 3-methyl-*1H*-pyrazole and 3,5-dimethyl-*1H*-pyrazole. Dimethylaminoacetonitrile could not be quantified using the developed method because of its poor stability in water during an extraction. The determination of 1-formyl-2,2-dimethylhydrazine was associated with poor detection limits, accuracy and precision. The developed method was used for the analysis of four snow samples taken near the route of rocket fuel transportation. UDMH transformation products were not detected in the analyzed samples.

Compared to other methods based on GC-MS, the developed method is simpler, automated and provides lower detection limits. In addition, it covers the greater number of analytes, the range of which could be further expanded if standards become available. The method can be recommended for assessing water quality on the territories affected by space activities and other related studies.

Table 5 Linearity, LODs and LOQs of the developed method in combination with GC-MS/MS

Compound	Linear range (µg L^{-1})	GC-PCI-MS/MS (Q1 SIM)				GC-PCI-MS/MS (MRM)			
		Slope (RSD in %)	r^2	LOD (µg L^{-1})	LOQ (µg L^{-1}	Slope (RSD in %)	r^2	LOD (µg L^{-1})	LOQ (µg L^{-1})
Pyridine	0.06–7.5	3202 (7)	0.9873	0.001	0.002	351.0 (5)	0.9915	0.01	0.02
Pyrazine	0.3–75	339 (8)	0.9722	0.03	0.07	100.0 (2)	0.9981	0.09	0.26
N-Nitrosodimethylamine	0.3–75	102.7 (9)	0.9688	0.07	0.22	102.4 (3)	0.9963	0.08	0.25
N,N-Dimethylformamide	0.3–75	26.9 (20)	0.8584	0.08	0.20	27.5 (26)	0.7830	0.02	0.05
1-Methyl-*1H*-1,2,4-triazole	0.6–750	7.48 (9)	0.9628	0.05	0.14	2.06 (10)	0.9481	0.14	0.41
N-Methylformamide	0.6–750	4.25 (14)	0.9296	0.03	0.09	0.92 (28)	0.7152	0.14	0.41
1-Formyl-2,2-dimethylhydrazine	30–3000	–	–	–	–	0.33 (11)	0.9548	0.9	2.8
1-Methyl-*1H*-imidazole	15–1500	8.07 (5)	0.9935	0.09	0.27	1.42 (3)	0.9952	3	10
Formamide	30–3000	59.3 (7)	0.9914	0.13	0.40	3.00 (2)	0.9981	0.8	2.4
2-Furaldehyde dimethylhydrazone	30–7500	1283 (2)	0.9981	0.01	0.03	81.0 (6)	0.9813	0.5	1.5
1H-Pyrazole	3–750	24.0 (1)	0.9995	0.14	0.42	3.85 (1)	0.9993	1.2	3.5
3-Methyl-*1H*-pyrazole	3–750	44.4 (2)	0.9981	0.09	0.26	4.43 (1)	0.9994	1.6	5.0
3,5-Dimethyl-*1H*-pyrazole	6–1500	68.3 (3)	0.9974	0.05	0.16	4.75 (1)	0.9996	1.6	4.7

LOD limit of detection, *LOQ* limit of quantification, *RSD* relative standard deviation, *PCI* positive chemical ionization, *MRM* multiple reaction monitoring, *Q1 SIM* selected ion monitoring using the first quadrupole for separation of ions

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Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest in relation to this research.

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