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Bulat N. Kenessov
al-Farabi Kazakh National University

Jacek A. Koziel
Iowa State University, koziel@iastate.edu

Tim Grotenhuis
Wageningen University

Lars Carlsen
Awareness Center

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Abstract
The paper describes a novel SPME-based approach for sampling and analysis of transformation products of highly reactive and toxic unsymmetrical dimethylhydrazine (UDMH) which is used as a fuel in many Russian, European, Indian, and Chinese heavy cargo carrier rockets. The effects of several parameters were studied to optimize analyte recovery. It was found that the 85 μm Carboxen/polydimethylsiloxane fiber coating provides the highest selectivity for selected UDMH transformation products. Optimal sampling/sample preparation parameters were determined to be 1-h soil headspace sampling time at 40 °C. The GC inlet temperature was optimized to 170 °C held for 0.1 min, then 1 °C s−1 ramp to 250 °C where it was held for 40 min. Temperature programing resulted in a fast desorption along with minimal chemical transformation in the GC inlet. SPME was very effective extracting UDMH transformation products from soil samples contaminated with rocket fuel. The use of SPME resulted in high sensitivity, speed, small labor consumption due to an automation and simplicity of use. It was shown that water addition to soil leads to a significant decrease of recovery of almost all target transformation products of UDMH. The use of SPME for sampling and sample preparation resulted in detection of the total of 21 new compounds that are relevant to the UDMH transformation in soils. In addition, the number of confirmed transformation products of UDMH increased from 15 to 27. This sampling/sample preparation approach can be recommended for environmental assessment of soil samples from areas affected by space rocket activity.

Keywords
Unsymmetrical dimethylhydrazine, Solid phase microextraction, Soil, Rocket fuel, Sampling, Sample preparation

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Sampling and Analysis of Volatile Transformation Products in Soils Contaminated with Unsymmetrical Dimethylhydrazine

Bulat N. Kenessov[1,2*], Jacek A. Koziel[1,3], Tim Grotenhuis[4], Lars Carlsen[5]

[1] - Agrotechnology & Food Sciences Group, Wageningen University and Research Centre (PO Box 17, 6700 AA Wageningen, The Netherlands);

[2] – Center of Physicochemical Methods of Research and Analysis, al-Farabi Kazakh National University (050012 Almaty, 95a Karassai batyr Str., Kazakhstan);

[3] – Iowa State University, Department of Agricultural and Biosystems Engineering, Department of Civil, Construction and Environmental Engineering, Department of Food Science and Human Nutrition, Iowa State University (Ames, Iowa, 50011, USA);

[4] – Section Environmental Technology, Wageningen University (P.O. Box 8129, 6700 EV Wageningen, The Netherlands);

[5] – Awareness Center, Linkøpingvej 35, Trekroner (DK-4000 Roskilde, Denmark);

* - Corresponding author, 050012 Almaty, 95a Karassai batyr Str., Kazakhstan, tel: 7 727 2613844; fax: 7 727 2923731; e-mail: bkenesov@gmail.com.

Abstract

The paper describes novel approach for sampling and analysis of transformation products of highly reactive and toxic unsymmetrical dimethylhydrazine (UDMH) which is used as a fuel in many Russian, European, Indian, and Chinese heavy cargo carrier rockets. The effects of several sampling and sample preparation parameters were studied to optimize sample recovery. It was found that the 85 μm Carboxen/polydimethylsiloxane fiber coating provides the highest

selectivity for detection of selected UDMH transformation products. Optimal sampling and sample preparation parameters were determined to be 1-hr soil headspace sampling time at incubation temperature of 40°C. The GC inlet temperature was optimized to 170ºC hold for 0.1 min, then 1ºC sec^{-1} ramp to 250ºC where it was held for 40 min. Temperature programming resulted in a fast desorption along with minimal chemical transformation in the GC inlet. SPME was very effective extracting UDMH transformation products from soil samples contaminated with rocket fuel. The use of SPME resulted in high sensitivity, speed, small labor consumption due to an automation and simplicity of use. It was shown that water addition to soil leads to a significant decrease of recovery of almost all target transformation products of UDMH. The use of SPME for sampling and sample preparation resulted in detection of the total of 55 new compounds that are relevant to the UDMH transformation in soils. In addition, the number of confirmed transformation products of UDMH increased from 15 to 27. This sampling/sample preparation approach can be recommended for environmental assessment of soil samples from areas affected by space rocket activity.

Keywords: Unsymmetrical Dimethylhydrazine, Solid Phase Microextraction, Soil, Rocket Fuel, Sampling, Sample Preparation.

1. Introduction

1.1. Environmental problem statement

At present, many European, Russian, Indian, and Chinese heavy cargo carrier rocket use unsymmetrical dimethylhydrazine (UDMH), also known as heptyl, as a relatively inexpensive fuel [1]. Up to 2 metric tons of residual fuel may remain in fuel tanks and engines of a stage after

separation of the burned-out rocket stages. A part of the residual fuel is evaporated during the fall process. However, remaining fuel is eventually spilled to the environment during the crash landing of the burned out rocket stage in a so-called fall, or drop zone [2].

UDMH is a highly toxic compound displaying, among other effects, carcinogenic and mutagenic properties [3,4]. The use of UDMH as a fuel can cause negative effect to the environment and human health [4,5]. It is known that UDMH is highly reactive displaying strong reducing properties. Recent studies showed that UDMH spilled to the environment is transformed with formation of a number of compounds such as formaldehyde dimethylhydrazone (FADMH), tetramethyltetrazene (TMT), N-nitrosodimethylamine (NDMA), 1-methyl-*1H*-1,2,4-triazole (MTA), dimethylaminoacetonitrile (DMAACN), 1-formyl-2,2-dimethylhydrazine (FDMH) and 10 other compounds [6,7,8,9].

The toxicity of most known transformation products of UDMH is not known. However, some of them are known to be very toxic, e.g., NDMA. Carlsen et al [4,5,10] studied environmental and human health impact of UDMH and its transformation products using modeling and calculations based on QSAR/QSTR methods. As a result, most known toxic compounds originating from UDMH transformations were ranked by their toxicity using partial order ranking technique. Using this method, NDMA, TMT, tetramethylhydrazine (TMH), FADMH, FDMH were ranked as the most toxic UDMH transformation products, respectively [4].

Studies of soil samples from fall regions of rockets, launched from the Baikonur Cosmodrome, located in Central Kazakhstan showed the presence of UDMH and its transformation products even 30 years after landing of a rocket stage [11,12]. The presence of few pollutants for which the chemical analysis methods exist was only reported in the epicenter (crater) of a fall place. To date, however, no comprehensive environmental assessment of fall zones was completed. More

research is warranted towards full assessment of rocket fuel impact on environment and its cleanup options.

1.2. Current analytical methods for analysis of UDMH transformation products

Scientists and engineers are challenged with a lack of robust analytical methods and sampling techniques for analysis of environmental samples for the content of UDMH and its transformation products. Determination of UDMH and its transformation products in environmental samples is a quite complex task primarily due to reactivity and on-going chemical and biological processes in samples. Such analytical methods are especially needed, since UDMH is considered to be very reactive and readily converting to transformation products upon contact with air, water and soil. Environmental factors driving these processes are only little known. Analytical methods should consider and minimize chemical transformations especially during sample preparation. Research during the last 15 years was mainly focused on the methods for determination of UDMH [13,14,15,16,17,18,19]. However, to date, there are no robust methods for determination of its transformation products.

A summary of currently available methods for determination of UDMH and its transformation products is presented in Table 1.

Table 1.

The majority of current methods for determination of UDMH transformation products are available only for water samples (For references see Table 1 below). These methods require complex equipment and sample preparation to achieve sufficient sensitivity and selectivity. In addition, it should be noted that all of the currently available methods target typically one

compound (cf. Table 1). These methods are not necessarily optimized and comprehensive, i.e., they tend to separately target different compounds and use different sample preparation techniques and analytical equipment [31].

1.3. SPME uses for environmental sampling and analyses

Solid phase microextraction (SPME) combines sampling and sample preparation into one step. It conveniently reduces the sampling/sample preparation time, and it eliminates the use of solvents for sample preparation or the use of special equipment if it is used for field sampling and the fibers are reusable [32]. Extractions with SPME are facilitated on a thin polymeric coating that has a high affinity for organic compounds. SPME is very useful for qualitative characterization of complex environments such as organic gases emitted from swine manure [33], gases emitted from rumen [34], gases adsorbed to dust [35], or gases emitted from live insects [36]. Quantitative sampling and analysis of organic gases in complex environment is also possible [37,38].

Solid phase microextraction has been proven very useful for determination of VOCs in air and water [32,37]. Soil samples present a special problem for quantitative SPME of most analytes because of strong differences in soil matrix properties [39]. Llompart et al. [40] developed headspace (HS) SPME method for determination of VOCs in soil samples, which showed much higher sensitivity than conventional HS sampling followed by direct injection of gas samples for analysis. The proposed methodology did not work well for determination of semivolatiles in soil. Poor sensitivity was observed due to apparent slow kinetics of soil-gas partitioning processes.

Grebel et al., used SPME to characterize *N*-nitrosamines in water, i.e., a class of compounds closely related to those discussed in the present research. Brown et al. [41] developed a SPME-GC-MS method for analysis of soils contaminated with kerosene-based jet propellant JP-8. This

129 method was then used to determine 34 marker compounds which were hydrocarbons of different
130 structure. Solid phase microextraction was also used for determination of JP-8 ingredients in
131 liver and blood of rats [42]. The paper of Jaraula et al. [43] describes a SPME-based method
132 used to study the natural attenuation of aviation-grade diesel spilled on the perennial ice cover of
133 Lake Fryxell, Antarctica. In all cases related to fuels and their fate in environment, SPME
134 showed usability, enabled good detection limits and facilitated simplicity in use.
135
136 To date, there is no published research describing the use SPME for determination of hydrazine-
137 based rocket fuels or its transformation products. However, it appears that SPME would be an
138 appropriate technology for both qualitative and qualitative rapid assessment of UDMH and its
139 transformation products in soil samples.
140
141 **1.4. Objectives and scope**
142
143 The objective of the present research was to develop a GC-MS-based method for screening of
144 UDMH and its transformation products in soil samples using a novel SPME-based technique for
145 sampling and sample preparation. The effects of several sampling and sample preparation
146 parameters were studied. These involved SPME fiber coating type, SPME sampling temperature
147 and time, effects of added water and optimization of GC injection/desorption temperature
148 program to minimize thermal oxidation of target analytes.

149 # 2. Methods

150

151 **2.1. Soil sample preparation**

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All experiments were carried out in 20 mL crimp vials (InterScience, Breda, Netherlands) which were cleaned and conditioned by washing with ultrapure-grade water with subsequent baking in an oven with convection at 180 ºC overnight. Soil sample weight was always constant and equal to 1±0.02 g. Soil samples used for studies were unpolluted soils from Kazakhstan rocket drop zones spiked with UDMH (15 g of blank soil spiked with 10 µL of UDMH). All the spiked samples were 6 months old when analyzed.

2.2. Solid phase microextraction

Solid phase microextraction was performed manually using manual holder (Supelco, Bellefonte, PA). Sampling temperature for SPME was controlled using the agitator well of Thermo Tri-Plus autosampler samples during experiments with above-room temperatures. Vial penetration was set to 14 mm using SPME manual holder. All SPME fibers (for discussion of studied fibers, see section 3.2) were conditioned in GC inlet at 250 °C before first use. SPME-based sample desorption was carried out at GC inlet temperature of 250 °C for 30 min in splitless mode. One mm injector liner was used to obtain sufficient linear flow rate during desorption stage in the GC inlet.

2.3. Chemicals

UDMH (1,1-dimethylhydrazine; 99% purity) and common solvents were purchased from Sigma-Aldrich (Zwijndrecht, Netherlands). UDMH contained the following impurities: dimethylamine, formaldehyde dimethylhydrazone and water. Millipore water was used for dilutions and UHP-grade helium was used as carrier gas for GC work. All work with chemicals was performed in vented fume hood using protective gloves and established waste disposal routines.

2.4. Gas Chromatography- Mass Spectrometry

The Trace Ultra GC was equipped with PTV-type injector. The optimal injector temperature was determined experimentally. The injector was operated in splitless mode and was connected to the Rtx-Wax column (60 m × 0.32 mm × 0.25 µm) (Restek, Bellefonte, PA). The column was maintained at constant flow of UHP-grade helium at 1 mL min^{-1}. GC oven program was as follows: 40 ºC for the first 10 min, followed by 8 ºC min^{-1} ramping to 240 ºC, where the column was held for 15 min before cooling. Each run was 50 min. The GC column was interfaced with a DSQII MS via transfer line maintained at 250 ºC. The MS was operated in full scan mode from 34 to 150 m/z. The ion source was held at 250 ºC and the electron multiplier was set at 1300 V. The MS scan rate was 3.94 scan sec^{-1}. Analytical instrument was controlled with Xcalibur software (from InterScience, Breda, Netherlands).

2.5. Data Analysis

The following strategy was used for analysis of all the obtained chromatograms:

1) identification of UDMH transformation products was based on comparison of the obtained mass spectra with available spectra in the MS libraries (Wiley 7th edition, NIST'05);
2) building the extract (selected) ion chromatograms for each detected UDMH transformation product using the ions with the highest response at mass spectra;
3) integration of the obtained selected ion chromatograms for calculation of the peak area for each analyte (using the built-in ChemStation integrator).

MS data collected using Xcalibur software were converted to AIA format (*.cdf) and imported to Agilent MSD ChemStation software (ver. E.01.01.335) for treatment.

205 **2.5. Quality control**

206 Repeatability of the applied method was confirmed by analysis of selected samples in triplicate.
207 RSDs for replicates did not exceed 15%.

208

209 # 3. Results

210

211 **3.1. Comparison of SPME to headspace sampling**

212

213 The efficiency of headspace SPME sampling for analysis of soil spiked with UDMH was
214 compared to conventional soil headspace sampling technique as reported earlier [9]. In this
215 research, sampling was carried out at the same temperature (20 ºC) and the same GC PTV inlet
216 program was used. It was apparent that SPME-based sampling was a more sensitive technique
217 for sampling and sample preparation of gases in soil headspace. The SPME-based samples
218 contained more relevant information about the UDMH transformation products in soil. Some
219 important transformation products could not be detected using conventional headspace sampling.
220 The use of SPME to collect gases in soil headspace resulted in 20× to 30× higher sensitivity even
221 for such a short SPME sampling time (15 sec exposure to headspace of soil) for the majority of
222 identified compounds. Eleven UDMH transformation products were identified with conventional
223 headspace gas sampling. All these compounds were identified when HS SPME was used and
224 additional 5 transformation products were also detected. It should be noted that one of the most
225 toxic UDMH transformation products, i.e., FDMH was not detected using conventional
226 headspace sampling probably due to its very low volatility whereas a sufficient MS response for
227 FDMH identification was obtained when HS SPME was used. Considering this apparent increase
228 in analytical sensitivity, SPME was used as sampling/sample preparation technique for
229 contaminated soil samples in this research.

230

3.2. Selection of SPME fiber coating

Polymeric coatings used in SPME vary in their physicochemical properties which affect SPME sensitivity towards specific chemical groups of compounds [32]. Development of sampling method with SPME involves testing of various coating types for a specific application. The most suitable SPME fiber coating for sampling of UDMH and its transformation products from soil spiked with UDMH was selected from the 65 μm PDMS/DVB, 85 μm Carboxen (CAR)/PDMS, 85 μm PA and 100 μm PDMS tested for recovery of main UDMH transformation products. Extractions with SPME were carried out from the headspace of soils using two different sampling times: 1 min and 1 hr. Results are shown in Figure 1.

Figure 1

The use of 65 μm PDMS/DVB resulted in highest recoveries for all the analytes for relatively short HS SPME sampling times of 1 min. On the other hand, the 85 μm CAR/PDMS was the most efficient fiber for almost all the analytes (except for FDMH) at a longer HS SPME sampling time of 1 hr. The use of CAR/PDMS fiber resulted in at least two times higher sample recoveries compared with sample recoveries associated with the PDMS/DVB fiber for the majority of target analytes considered in this research. Thus, 85 μm CAR/PDMS fiber was selected for development of analytical method.

3.3. Effects of SPME sampling time

The 85 μm CAR/PDMS SPME coating was selected for characterization of transformation products of UDMH. Several sampling times (1 min, 1 hr and 18 hrs) were studied to determine practical SPME sampling time for soil headspace samples. Mass detector responses versus

SPME sampling time are presented in Figure 2. The increase of extracted mass with the increase of sampling time is observed for all the analytes. One hr sampling was chosen as a practical and optimal sampling time for further work. This was due to sufficiently high detector response for target analytes collected with 1 hr HS SPME that could be accomplished simultaneously with a practical sample analysis run time of 1 hr. This information is also useful for considerations to automate sampling and analysis of UDMH transformation products in the future. It should further be noted that the possibility of SPME fiber coating saturation and sample losses during sample preparation will be minimized with 1 hr HS SPME compared with longer sampling times.

Figure 2.

3.4. Effects of water and salt addition on sample recovery

Addition of a small amount of water has often been used for acceleration of analytes extraction from solid phase samples [39]. Headspace SPME was carried out without/with addition of 0.3, 0.5, 1, 5 mL of water to 1 g of soil spiked with UDMH with measured initial water content of 21%. The results are presented in Figure 3.

Figure 3.

Figure 3 shows that addition of even small amounts of water to the soil samples significantly decreases the response of target UDMH transformation products except for 1,3-dimethyl-*1H*-1,2,4-triazole. This could be explained by considering high polarity and high water solubility of target analytes. The increased extraction of 1,3-dmethyl-*1H*-1,2,4-triazole after addition of 0.3 mL and 0.5 mL of water could, on the other hand, be explained by the increase of its mobility

and increase of mass transfer to headspace with added water. In addition, it is also reasonable to assume that the decrease of the recovery of other target analytes was likely caused by high initial water content in test soil sample (21%). Thus, it was shown that water content in soil plays significant role on recoveries of all UDMH transformation products and makes quantification process difficult or even impossible without significant error.

Considering that even small changes in the water content result in significant changes in compound recovery, it was proposed to add the excess amount of water (5 mL) to all soil samples to minimize variability. In this case, the resulting differences in water content between all the samples would be minimal. It was observed that adding 5 mL of water to 1 g of soil resulted in decreased recovery of analytes (consistent with the trend illustrated in Figure 3). Thus, increased temperatures and addition of salt were used to compensate for this apparent loss of sensitivity. The effect of temperature on sample recovery of soil-water mixture was analyzed at SPME sampling temperatures 20 ºC and 40 ºC. The effect of salt addition was tested using the same soil-water mixture, i.e., 1.5 g of NaCl (concentration was chosen to prepare saturated solution of NaCl) was added, and the prepared mixture was analyzed using SPME sampling temperature of 40 ºC. The results are shown in Figure 4.

Figure 4.

The temperature increase (see next section) as well as addition of salt resulted in increased concentration of analytes in headspace and responses of all the compounds except dimethylaminoacetonitrile and N,N-dimethylformamide. It can be concluded, that increase of temperature and addition of salt increases recoveries of UDMH transformation products. Also, it should be considered that the presence of water in contaminated soils combined with elevated sample preparation temperatures could affect sample recovery and chemical analysis. This is

due to possible chemical interactions between compounds especially the dimethylhydrazones of formaldehyde and acetaldehyde which are known to be hydrolyzed by water especially at lower pH.

3.5. Effects of SPME sampling temperature on recovery of UDMH transformation products

Temperature plays significant role in compound distribution between headspace and solid (or liquid) phase and its increase usually leads to the increase of the recoveries of analytes from headspace. Effect of temperature was studied at 20 ºC (room temperature), 40 ºC and 50 ºC. The results are presented in Figure 5.

Figure 5.

The increase of soil incubation and SPME sampling temperature resulted in increased recovery of almost all analytes, especially those with higher boiling points. The strongest effect of temperature was observed for N,N-dimethylformamide and 1-formyl-2,2-dimethylhydrazine where a ~5× higher of recovery was observed when temperature increased from 20 ºC to 50 ºC. Increased sample recovery with increased temperature could be offset when SPME sampling is too long. This effect was observed when 18 hr sampling of analytes at temperatures 20 ºC and 50 ºC was completed. The results are shown in Figure 6.

Figure 6.

A decrease of recovery with an increase of temperature was observed for volatile analytes when relatively long sampling time was used. This could be caused by (a) on-going compound

transformations, (b) competition and displacement of compounds on SPME fiber [44], and (c) decrease of SPME sorptive capacity with an increase of temperature [45].

3.6. Optimization of SPME desorption temperature

It is generally recommended that desorption temperature should be no less than 250 ºC for fast thermal desorption of analytes from CAR/PDMS fibers onto GC injector. However, UDMH and some of its transformation products could be very unstable at elevated temperatures. This is apparently one of the main reasons why the UDMH peak could not be observed in chromatograms of even highly contaminated soil samples when the samples were introduced to GC injector at 250 ºC. Also, it is known [46] that one of the main transformation products, i.e., TMT, can be degraded in the GC inlet at temperatures higher than 180 ºC. Thus, the effects of desorption temperature on responses of UDMH transformation products were studied. Headspaces of pure UDMH (5 µL spiked into pre-cleaned 20 mL vial) and 1 g of soil spiked with ~0.67 µL UDMH were analyzed using different GC inlet temperatures. A 15 sec HS SPME sampling time was chosen during all the experiments due to the high concentration of analytes in soils and to avoid MS detector overload.

Several transformation products were detected in vials spiked with UDMH as expected. Highest responses were observed for dimethylamine and formaldehyde dimethylhydrazone. However, analysis of the obtained chromatograms showed that responses of UDMH and formaldehyde dimethylhydrazone strongly depended on GC inlet temperature, which. This was likely caused by chemical transformation at high temperatures during desorption phase on the surface of SPME fiber or in the GC inlet. The MS detector response to TMT significantly decreased (i.e., by nearly an order of magnitude) with the increase of desorption temperatures from 180 ºC to 250 ºC. However, an incomplete sample desorption occurred, resulting in eventual carry-over of

samples when GC injector temperatures were relatively low. To address this problem, a programmable temperature vaporizing (PTV) inlet function to program (and to rise) GC inject temperature after injection was used. The following temperature program was used: 170 ºC hold for 0.1 min, than 1 ºC sec^{-1} ramp to 250 ºC, hold for 40 min (length of entire run). The effects of SPME desorption temperature were tested by comparing sample recoveries of UDMH transformation products associated with the use of variable and constant injector temperature using HS SPME sample collected over 1 g of soil spiked with ~0.67 µL of UDMH. Significant differences were observed (see chromatograms in Figure 7). Several additional compounds such as tetramethylhydrazine; methanediamine, N,N,N',N'-tetramethyl-; dimethylamine, 1,1-dimethyl-2-(dimethylamino)formamidine were detected when desorption temperature was 250 ºC. However, UDMH was only detected using the PTV program. UDMH coeluted with FADMH (peak #4 on Figure 7) and was identified by the characteristic m/z=60 ion. In addition, the TMT recovery decreased about 40% compared to the program utilizing constant GC injector temperature.

Figure 7.

3.7. Identification of UDMH transformation products in soil samples

The number (15) of known transformation products of UDMH [6, 7, 8, 9] is limited by the efficiency of analytical methods. SPME was used to improve characterization of UDMH transformation products. Relatively long sampling time of soil headspace of 18 h was used to increase the number of compounds that could be recovered and identified. A moderate temperature of 50 °C was used to encourage gas transfer from soil to headspace and recovery of compounds with higher boiling points. Approximately 70 compounds were identified in the contaminated soil headspace. This result is rather remarkable, considering that sampling of headspace was done on relatively old (6 months after spiking with UDMH) soil samples. This

finding has implications for environmental assessment in the field, i.e., that a number of toxic compound could be found long after the initial spill. These findings are consistent with the data obtained earlier [11,12] reporting that UDMH could be still detected in fall zones which are 30 years old. The list of compounds recovered from contaminated soil headspace and their preliminary identification is presented in Table 2.

Table 2.

Comparison of the results on identification of UDMH transformation products using SPME with the previously published data [1, 6, 8, 9] provided additional information on the transformation processes in soil. The use of SPME for sampling and sample preparation resulted in detection of the total of 55 new compounds, i.e., 12 new transformation products of UDMH (compounds No. 6, 7, 10, 12, 14, 16, 17, 18, 19, 23, 25, 26, 27); 9 compounds with lower MS match (and therefore lower degree of confidence in proper identification) and 34 compounds which can potentially be transformation products of UDMH (Table 2). This represents 80% increase of confirmed compounds known to be products of UDMH transformation in soil. Taken together, SPME coupled to GC-MS allowed to obtain more comprehensive data on identification of UDMH transformation products in soils contaminated with hydrazine-based rocket fuel. In comparison with the other methods, SPME showed to be the more powerful tool for extraction, detection and identification of a broader range of metabolites.

Quantitative determination of UDMH transformation products using HS SPME as sampling and sample preparation is challenging due to significant effects of soil type, composition and moisture content on recovery of analytes. Development of a quantitative method was not a part of this research. However, the results of this research provide useful strategies for development

of SPME-based methods for characterization and quantification of UDMH transformation products in contaminated soils and possibly water.

4. Conclusion

The objective of this research was to characterize UDMH and its transformation products in soil using novel approach, i.e., SPME for sampling and sample preparation. The effects of several sampling and sample preparation parameters were studied. These involved SPME fiber type, sampling temperature and time, amount of water and salt addition, and GC injector/desorption temperature. It was determined that the 85 μm CAR/PDMS SPME fiber coating provides the highest selectivity for detection of UDMH transformation products. Optimal sampling parameters were determined to be 1-hr sampling time at 40 °C. The following temperature program: 170 ºC hold for 0.1 min, than 1 ºC sec^{-1} ramp to 250 ºC, hold for 40 min was resulted in fast sample desorption from SPME along with minimal chemical transformations in the inlet. It was shown that water addition to soil leads to a significant decrease of response of almost all the main transformation products of UDMH.

The use of headspace SPME-GC-MS resulted in high efficiency of collection, detection and identification of UDMH transformation products in soil samples contaminated with hydrazine-based rocket fuel providing high sensitivity, speed, small labor consumption due to an automation and simplicity of use. Comparing to the previously used methods of sample preparation, SPME was more effective tool for detection of UDMH transformation products in soil samples allowing detection of the broader range of analytes from volatile to semivolatile compounds. The total of 55 new compounds were identified effectively increasing the number of confirmed and known transformation products by 80% (from 15 to 27). The SPME-based sampling and sample preparation can be recommended for environmental assessment of areas affected by rocket launch activities.

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References

[1] V.V. Adushkin, C.I. Kozlov, A.V. Petrov, Ecological Problems and Risks of Rocket-Space Techniques Impacts on Environment, Ankil, Moscow, 2000. (In Russian)

[2] N.S. Kassimov, V.B. Grebenyuk, T.V. Koroleva, Yu.V. Proskuryakov, Pochvovedeniye 9 (1994) 110-120. (In Russian)

[3] Toxicological Profile for Hydrazines, US Department of Health and Human Services, Public Health Service, ATSDR, 1997.

[4] L. Carlsen, B.N. Kenessov, S.Ye. Batyrbekova, Environ. Toxicol. Pharmacol. 27 (2009) 415-423.

[5] L. Carlsen, B.N. Kenessov, S.Ye. Batyrbekova, Environmental Health Insights 1 (2008) 11-20.

[6] A.K. Buryak, O.G. Tataurova, A.V. Ulyanov, Russ. J. Mass Spectrom. 1-2 (2004) 147-152. (In Russian)

[7] A.D. Smolenkov, I.A. Rodin, A.V. Shpak, O.A. Shpigun, Int. J. Environ. Anal. Chem. 87 (2007) 351-359.

[8] I.A. Rodin, D.N. Moskvin, A.D. Smolenkov, O.A. Shpigun, Russ. J. Phys. Chem. A 82 (2008) 911-915.

[9] B.N. Kenessov, Bull. Nat. Acad. Sci. Rep. Kazakhstan, Chem. Series 5 (2008) 48-53. (In Russian)

[10] L. Carlsen, O.A. Kenesova, S.E. Batyrbekova, Chemosphere 67 (2007) 1108-1116.

[11] Development of Nexus in Kazakhstan, UNDP, LEM Printhouse, Almaty, 2004.

[12] S.Ye. Batyrbekova, System Analysis of Environmental Objects Affected by Rocket Space Activity of Baikonur Cosmodrome, Author's Abstract of Dissertation for the Degree of Doctor of Chemical Sciences, Almaty, 2008. (In Russian)

[13] D.P. Samsonov, G.V. Bornovalova, R.I. Pervunina, N.P. Zhiryukhina, J. Anal. Chem. 53 (1998) 191-194. (In Russian)

[14] S.A. Savchuk, Ye.S. Brodskiy, A.A. Formanovskiy, B.A. Rudenko, J. Anal. Chem. 53 (1998) 759-763. (In Russian)

[15] M.I. Yevgenyev, I.I. Yevgenyeva, S.M. Goryunova, S.Yu. Garmonov, L.Sh. Gazizulina, J. Anal. Chem. 53 (1998) 650-654. (In Russian)

[16] Ye.Ye. Yergozhin, V.A. Solomin, V.V. Lyapunov, A Method for Determination of 1,1-Dimethylhydrazine, Prelim. Patent of the Republic of Kazakhstan No. 10232, Nat. Patent. Agency of Kazakhstan, Almaty, 2000. (In Russian)

[17] A.A. Denisov, A.D. Smolenkov, O.A. Shpigun, J. Anal. Chem. 59 (2004) 452-456.

[18] E.E. Sotnikov, A.S. Moskovkin, J. Anal. Chem. 61 (2006) 129-132.

[19] M.I. Yevgenyev, I.I. Yevgenyeva, S.Yu. Garmonov, R.N. Ismailova, D.G. Pobedimskiy, Factorial Laboratory, Testing of Materials 7 (2006) 14-16. (In Russian)

[20] US EPA Method 521 (1.0), Cincinnati, Ohio, 2004.

[21] J.E. Grebel, C.C. Young, I.H. Suffet, J. Chromatogr. A 1117 (2006) 11-18.

[22] A Standard Method for Determination of Tetramethyltetrazene in Samples of Natural Water Using Ion Chromatography with Amperometric Detection (MVI 4-02), Moscow State University, Moscow, 2002. (In Russian)

[23] A Standard Method for Determination of Tetramethyltetrazene in Samples of Soil Using Ion Chromatography with Amperometric Detection (MVI 2-02), Moscow State University, Moscow, 2002. (In Russian)

[24] A Standard Method for Determination of Nitrosodimethylamine in Samples of Natural Water Using Reversed Phase Chromatography with Spectrophotometric Detection (MVI 3-02), Moscow State University, Moscow, 2002. (In Russian)

[25] A Standard Method for Determination of Nitrosodimethylamine in Samples of Soil Using Reversed Phase Chromatography with Spectrophotometric Detection (MVI 1-02), Moscow State University, Moscow, 2002. (In Russian)

[26] Ye.Ye. Yergozhin, V.A. Solomin, V.V. Lyapunov, V.G. Tsukerman, A Method for Determination of 1,1-Dimethylhydrazine and Nitrosodimethylamine, Prelim. Patent of the Republic of Kazakhstan No. 8455, Nat. Patent. Agency of Kazakhstan, Almaty, 2000. (In Russian)

[27] S.A. Ponomarenko, Simultaneous Determination of Several Hydrazines and Nitrosodimethylamine Using Ion Pair Chromatography, Author's Abstract of Dissertation for the Degree of Candidate of Chemical Sciences, Moscow, 2009 (In Russian)

[28] B. Kenessov, S. Batyrbekova, M. Nauryzbayev, T. Bekbassov, M. Alimzhanova, L.

508 Carlsen, Chromatographia 67 (2008) 421-424.

509 [29] B.N. Kenessov, Ye. Sailaukhanuly, B.A. Musrepov, A.K. Kaldarov, Kazakh Nat. Univ.
510 Chem. Bull. 1 (2008) 184-190. (In Russian)

511 [30] M.B. Alimzhanova, B.N. Kenessov, S.Ye. Batyrbekova, L. Carlsen, M.K. Nauryzbayev,
512 Bull. Nat. Acad. Sci. Rep. Kazakhstan, Chem. Series 1 (2009) 87-92. (In Russian)

513 [31] B.N. Kenessov, Development of Methods for Determination of 1,1-Dimethylhydrazine and
514 1-Methyl-*1H*-1,2,4-triazole, Author's Abstract of Dissertation for the Degree of Candidate of
515 Chemical Sciences, Almaty, 2007. (In Russian)

516 [32] J. Pawliszyn (editor), Handbook of Solid Phase Microextraction. Chemical Industry Press
517 of China, Beijing, , 2009.

518 [33] Y.C. Lo, J.A. Koziel, L. Cai, S.J. Hoff, W.S. Jenks, H. Xin, J. Environ. Qual. 37 (2008)
519 521-534.

520 [34] L. Cai, J.A. Koziel, M.E. O'Neal, J. Chromatogr. A 1147 (2007) 66-78.

521 [35] L. Cai, J.A. Koziel, J. Davis, Y.C. Lo, H. Xin, Anal. Bioanal. Chem. 386 (2006) 1791-1802.

522 [36] L. Cai, J.A. Koziel. Y.C. Lo, S.J. Hoff, J. Chromatogr. A 1102 (2006) 60-72.

523 [37] J.A. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, Anal. Chim. Acta 400 (1999) 153-
524 162.

525 [38] N. Akdeniz, J.A. Koziel, H.K Ahn, T. Glanville, B. Crawford, R.D. Raman, J. Agric. Food
526 Chem. 57 (2009) 5658-5664.

527 [39] Z. Zhang, M.J. Jang, J. Pawliszyn, Anal. Chem. 66 (1994) 844A-853A.

528 [40] M. Llompart, K. Li, M. Fingas, Talanta 48 (1999) 451-459.

529 [41] S. Brown, M. Rickrode, T. Caldwell, Fuel 87 (2008) 2334-2338.

530 [42] J.L. Campbell, J.W. Fisher, Inhalation Toxicol. 19 (2007) 265-273.

[43] C.M.B. Jaraula, F. Kenig, P.T. Doran, J.C. Priscu, K.A. Welch, Sci. Total Environ. 407 (2008) 250-262.

[44] M. Jia, J.A. Koziel, J. Pawliszyn, Field Anal. Chem. Technol. 4 (2000) 73-84.

[45] J.A. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178-5186.

[46] M.F. Faskutdinov, I.P. Tuchyk, K.M. Beketov, Chem. J. Kazakhstan 3 (2007) 262-267. (In Russian)

Figure captions

Fig. 1. MS detector response to headspace sample collected with four different SPME fibers over soil contaminated with UDMH and 1 min (a) and 1 hr (b) sampling.

Note: m/z of the used for integration ion for each compound is given in brackets; soil incubation temperature 20 ºC. Soil sample was prepared by spiking ~0.67 µL UDMH into 1 g blank soil collected from Fall Region #25,15 in October, 2008 (samples were 6 months old when analyzed).

Fig. 2. MS detector response to UDMH transformation products at different sampling times used for soil headspace sampling with 85 µm CAR/PDMS SPME at room temperature (20 ºC). Soil sample was collected in fallout zone in Kazakhstan and spiked with ~0.67 µL of UDMH.

Fig. 3. Effects of water addition on MS responses to UDMH transformation products obtained by HS SPME of 1g soil samples spiked with ~0.67 µL of UDMH using a 85 µm CAR/PDMS fiber and 1 hr sampling time.

Fig. 4. Effect of temperature and addition of salt on MS responses to UDMH transformation products obtained by HS SPME of 1 g soil samples spiked with ~0.67 µL of UDMH using a 85 µm CAR/PDMS fiber with 5 mL of water (and salt) added.

Fig. 5. Effect of temperature on MS responses to UDMH transformation products obtained by 1 hr headspace SPME sampling of 1g blank soil sample spiked with ~0.67 µL of UDMH using a 85 µm CAR/PDMS SPME fiber, and 1 hr sampling time.

Fig. 6. Effect of temperature on MS detector responses of UDMH transformation products obtained by 18 hr headspace SPME sampling of 1 g blank soil sample spiked with ~0.67 µL of UDMH using a 85 µm CAR/PDMS SPME fiber.

Fig. 7. Comparisons of chromatograms of 1 g soil sample spiked with ~0.67 µL of UDMH obtained by headspace SPME with 85µm CAR/PDMS fiber using different GC inlet temperature programs: (a) 170 ºC hold for 0.1 min, than 1 ºC/sec ramp to 250 ºC, hold for 40 min; (b) constant temperature of 250 ºC. Sampling conditions: time = 15 sec, room temperature (20 ºC), and soil sample weight of 1 g.

Note: Peaks: 1 - dimethylamine; 2 - methanediamine, N,N,N',N'-tetramethyl-; 3 – tetramethylhydrazine; 4 – formaldehyde dimethylhydrazone (coeluting with UDMH); 5 – acetaldehyde dimethylhydrazone; 6 – tetramethyltetrazene; 7 – N1,N1-dimethyl-N2-(dimethylamino)formamidine.