Quantification of trace transformation products of rocket fuel unsymmetrical dimethylhydrazine in sand using vacuum-assisted headspace solid-phase microextraction

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Abstract
Quantification of unsymmetrical dimethylhydrazine transformation products in solid samples is an important stage in monitoring of environmental pollution caused by heavy rockets launches. The new method for simultaneous quantification of unsymmetrical dimethylhydrazine transformation products in sand samples using vacuum-assisted headspace solid-phase microextraction without addition of water followed by gas chromatography-mass spectrometry is proposed. Decreasing air evacuation time from 120 to 20 s at 23 °C resulted in increased responses of analytes by 25–46% and allowed obtaining similar responses as after evacuation at −30 °C. The best combination of responses of analytes and their relative standard deviations (RSDs) was achieved after air evacuation of a sample (m = 1.00 g) for 20 s at 23 °C, incubation for 30 min at 40 °C, and 30-min extraction at 40 °C by Carboxen/polydimethylsiloxane (Car/PDMS) fiber. The method was validated in terms of linearity (R2 = 0.9912–0.9938), limits of detection (0.035 to 3.6 ng g−1), limits of quantification (0.12–12 ng g−1), recovery (84–97% with RSDs 1–11%), repeatability (RSDs 3–9%), and reproducibility (RSDs 7–11%). It has a number of major advantages over existing methods based on headspace solid-phase microextraction—lower detection limits, better accuracy and precision at similar or lower cost of sample preparation. The developed method was successfully applied for studying losses of analytes from open vials with model sand spiked with unsymmetrical dimethylhydrazine transformation products. It can be recommended for analysis of trace concentrations of unsymmetrical dimethylhydrazine transformation products when studying their transformation, migration and distribution in contaminated sand.

Keywords Vacuum-assisted headspace solid-phase microextraction · Gas chromatography-mass spectrometry · Soil analysis · Transformation products · Dimethylhydrazine · Rocket fuel

Introduction
Unsymmetrical dimethylhydrazine (UDMH) is commonly used as a high-energy fuel of heavy-lift launch vehicles. In 2018, 47.4% of 114 orbital launches used fuel containing UDMH (Krebs 2019). The total percentage of unsuccessful launches of Proton rocket launched from Baikonur Cosmodrome in Kazakhstan is about 10% (Kolesnikov 2014). Environmental pollution by highly toxic chemicals due to rocket launches is of a huge concern for every new launch. Once released in the environment, most UDMH is oxidized, e.g., by atmospheric oxygen, with a formation of many transformation products. UDMH is a toxic, carcinogenic, and mutagenic compound (US Environmental Protection Agency 1992; US Department of Health and Human Services 1993; The National Institute for Occupational Safety and Health (NIOSH) 2018) posing a negative impact to the...
environment and human health (US Department of Health and Human Services 1993; Carlsen et al. 2007, 2008, 2009). Trace amounts of UDMH transformation products (TPs) in soils can be detected several decades after the landing of rocket stage (Kenessov et al. 2010, 2012; Rodin et al. 2012; Kolesnikov 2014). Up until today, more than fifty UDMH TPs were identified (Rodin et al. 2008, 2012; Kenessov et al. 2012; Ul’yanovskii et al. 2017).

Common analytical methods used for the determination of UDMH TPs in soil are based on gas (Kenessov et al. 2010; Kosyakov et al. 2015; Ul’yanovskii et al. 2015; Bakaikina et al. 2018) and liquid (Kosyakov et al. 2014) chromatography coupled to various detectors. Conventional sample preparation methods for this type of determination are based on solvent extraction (Rodin et al. 2010; Kosyakov et al. 2014, 2015). Despite these methods provide high sensitivity and reliability, they are quite labor-intensive and costly.

Most prospective sample preparation methods for determination of UDMH TPs in soil samples (Kenessov et al. 2010, 2011; Yegemova et al. 2015; Bakaikina et al. 2018; Orazbayeva et al. 2018a) are based on headspace solid-phase microextraction (HSSPME). HSSPME is a simple, low cost, and environmentally friendly technique that is widely used in a variety of applications. The use of HSSPME allowed a low-cost collection of detailed information about distribution of transformation products in soil at the full places of burned-out parts of Proton rockets (Kenessov et al. 2012). Quantification of UDMH TPs in soil using HSSPME is limited by matrix effects, which are common for all semi-volatile organic compounds (SVOCs) (Llompart et al. 1999, 2019; Kenessov et al. 2016). Matrix effect can be controlled using standard addition (SA) and/or internal standard (IS) calibrations (Llompart et al. 1999; Yegemova et al. 2015; Bakaikina et al. 2018), multiple extraction (Hakkarainen 2007), and/or minimized using derivatization, solvent extraction, addition of excess water, increase of extraction temperature, and exhaustive extraction, e.g., by cold fiber (Kenessov et al. 2016). High reactivity of UDMH and some of its transformation products upon contact with air and water (Buryak et al. 2004; Rodin et al. 2008, 2012; Kenessov et al. 2012) is another problem resulting in a decreased accuracy of methods based on HSSPME, particularly at elevated temperatures (Zhubatov et al. 2016; Bakaikina et al. 2017, 2018).

Brunton et al. (2001) showed a positive effect of a decreased pressure during SPME on the extraction of volatile organic compounds (VOCs) from food samples. Psillakis et al. (2012a) investigated the pressure impact on extraction kinetics during non-equilibrium headspace SPME and established a dramatically increasing extraction rates and responses of analytes. The technique was called vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) and proved to be particularly beneficial for analytes with a low headspace-sample distribution constant (Psillakis 2017; Zhakupbekova et al. 2019). Faster extraction is achieved due to decreased diffusion coefficients of analytes in a headspace above a sample under a reduced pressure (Fig. 1). The approach was successfully applied for the quantification of polycyclic aromatic hydrocarbons (PAHs) (Yiantzi et al. 2015; Beiranvand and Ghiasvand 2017), BTEX (Beiranvand and Ghiasvand 2020a; Ghiasvand et al. 2020; Derikvand et al. 2021) in soil samples, PAHs (Beiranvand and Ghiasvand 2020b; Psillakis et al. 2012a, 2013; Beiranvand and Ghiasvand 2020b), polychlorinated biphenyls (Yiantzi et al. 2016), chlorophenols (Psillakis et al. 2012b), UDMH TPs (Orazbayeva et al. 2018b) in water samples, volatile compounds of extra virgin olive oil (Mascrez et al. 2020) and haloanisoles in wine (Vakinti et al. 2019), and volatile and semivolatile fractions of Boswellia spp. resins (Capetti et al. 2020).

Fig. 1 Comparison of Vac-HSSPME and HSSPME. Notes: $D$, diffusion coefficient; $C_S$, equilibrium concentration of an analyte in a sample; $C_h$, equilibrium concentration of an analyte in a headspace; $C_f$, equilibrium concentration of an analyte in a fiber; $K_{hp}$, analyte distribution constant between fiber and headspace; $K_{hs}$, analyte distribution constant between headspace and sample.
Preparing evacuated extraction vessels with solid samples is much more difficult compared to liquid samples. A liquid sample can be introduced into an evacuated vessel with a septum using a syringe (Yiantzi et al. 2016; Trujillo-Rodríguez et al. 2017). For soil, such technique cannot be used, and air evacuation is carried out in the presence of the sample (Yiantzi et al. 2015) or in specially designed extraction vessels (Beiranvand and Ghiasvand 2017; Ghiasvand et al. 2018a, b). The first approach can result in losses of analytes (Yiantzi et al. 2015; Capetti et al. 2020), while the second one requires non-standard equipment and does not allow an automation. Orazbayeva et al. (2018a) developed the method for quantification of UDMH TPs in aqueous extracts from soil samples based on Vac-HSSPME. Despite the method provides good analytical parameters (relative standard deviations (RSDs) <5%, $R^2 >0.991$, limits of detection (LODs) 0.2–9 ng g$^{-1}$, recoveries 90–103%), an additional sample preparation step of a preliminary extraction of analytes with water complicates the process. The analytes have a high polarity and a water solubility (Table S1 in SM) and could be easily extracted from soil. Nonetheless, Kenessov et al. (2010) showed that the addition of water to soil results in a decrease of the responses of analytes, which could be caused by the higher affinity of analytes to water than to soil. When analyzing water-containing samples by Vac-HSSPME, total pressure in the vial and extraction rates will be limited by the vapor pressure of water, particularly at higher extraction temperatures (Psillakis et al. 2013).

Recently, Capetti et al. (2020) reported that storing the frankincense samples for 1 h at $-18^\circ$C before air evacuation overcame problems of volatiles (terpenes) losses due to aspiration. Authors tested air evacuation times of 45 and 120 s to the frozen samples and reported perfectly overlapping patterns for the most volatile compounds (being sampled at equilibrium). To further decrease losses of analytes, a higher amount of sample was taken for extraction. The approach of Capetti et al. (2020) is advantageous because it uses standard vials and does not require any complex procedures during sample preparation.

The objective of this study was to develop the new method for accurate quantification of UDMH TPs in sand samples based on Vac-HSSPME from 20-mL vials without addition of water. During the optimization step, effects of temperature and time during air evacuation, incubation and extraction time, extraction temperature on the intensity, and precision of analytes’ responses were evaluated. The target UDMH TPs were pyrazine (PA), 1-methyl-$^1H$-pyrazole (MPA), N-nitrosodimethylamine (NDMA), 1-methyl-$^1H$-1,2,4-triazole (MTA), and $^1H$-pyrazole (PA). NDMA and MTA were chosen as the main UDMH TPs, for which maximum permissible concentrations in soil are established in Kazakhstan $\sim 0.01$ and $10$ mg kg$^{-1}$ (Minister of National Economy of the Republic of Kazakhstan 2015), respectively. Other analytes represent most stable TPs, which can be used as markers of soil contamination with UDMH (Kenessov et al. 2012). Because this study is the first attempt to quantify UDMH TPs in solid samples using Vac-HSSPME without a preliminary extraction with water, it was decided to focus only on sand representing the simplest matrix (with the lowest matrix effect).

## Materials and methods

### Materials

The list of UDMH TPs, their origin, and physiochemical properties are provided in Table S1 in SM. SPME was conducted using 85-µm Carboxen/polydimethylsiloxane (Car/ PDMS, Supelco, Bellefonte, PA, USA), which provides the highest extraction effectiveness of UDMH TPs (Grebel et al. 2006; Kenessov et al. 2010).

In-house modified crimp-top Mininert® valves (Thomas Scientific) for 20-mL vials were built as described in (Trujillo-Rodríguez et al. 2017). A cylindrical Thermogreen®LB-1 septum with half-hole (6 mm diameter × 9 mm length, Supelco, USA) was placed into a 5-mm i.d. hole drilled in Mininert® valve to ensure leak-tight sealing of the valve. The optimized valve position in commercially available headspace vials was achieved by fitting O-rings having thickness 1–2 mm. In-house modified crimp-top Mininert® valves with cylindrical Thermogreen®LB-1 septa were chosen for Vac-HSSPME because they are compatible with standard 20-mL vials and can hold the reduced pressure for up to 24 h without a significant loss in precision and accuracy (Orazbayeva et al. 2018b).

### Model sand sample

Sand sample was air-dried and sieved though a 6-mm mesh before analysis. The air-dried sample contained 86.8±0.9% of sand, 8.6±0.1% of dust, 4.6±0.1% of silt, 0.36±0.02% of water (GOST 1993), 1.81±0.09% of organic matter (ISO/ CD), 34.0±0.5 mg kg$^{-1}$ of nitrogen (ISO 1995), 61.0±0.5 mg kg$^{-1}$ of phosphorus (ISO 1994a), and 370±6 mg kg$^{-1}$ of potassium (GOST 1996). pH of the sample was 8.40±0.10 (ISO 1994b). Concentrations of exchangeable Ca, Mg, Na, and K were 5.3±0.2, 2.93±0.15, 0.041±0.004, and 0.190±0.010 cmol kg$^{-1}$ (ISO 2018), respectively.

### Vac-HSSPME procedure

Prior to experiments, 20-mL crimp vials (HTA, Brescia, Italy) were washed with distilled water and pre-conditioned at 150 °C for 2 h to remove possible interferences and contaminants. The air-dried and sieved sand sample ($m = 1.00$ kg)
g) was introduced into 20-mL vial and spiked with 10 µL of UDMH TPs standard aqueous solution of pre-determined concentrations 0.67, 1.74, 2.45, 5.80, and 3.45 ng µL\(^{-1}\) for Pan, MPA, NDMA, MTA, and Pal, respectively. Then, vials were crimped with aluminum caps and polytetrafluoroethylene (PTFE)/silicone septa (Zhejiang Aijiren Technology Co, China), kept for 12 h at room temperature (23 °C) for equilibration and located in a freezer (−30 °C) until the evacuation (step 2). Freezing was used to minimize losses of analytes during long-term storage of samples and further air evacuation of the vials (Capetti et al. 2020).

The vials with sand samples were air evacuated using a low-cost single-stage rotary vane pump (Russia). Evacuated vials were then incubated in the agitator of MPS2 autosampler (Gerstel, Germany) and extracted manually. After extraction, the SPME fiber was introduced into the GC inlet for desorption of analytes.

**GC-MS conditions**

The GC-MS conditions were based on previous studies (Orazbayeva et al. 2018a, b). All analyses were conducted on a 7890A/5975C GC-MS (Agilent, USA) equipped with split/splitless and PTV (CIS4, Gerstel, Germany) inlets and MPS2 (Gerstel, Germany) autosampler. UDMH TPs were desorbed from the Car/PDMS SPME fiber in a GC inlet in a splitless mode at 240 °C using 0.75-mm i.d. liner (Supelco, USA). Separation of analytes was conducted using a polar 60 m × 0.25 mm DB-WAXetr column (Agilent, USA) with a 0.5 µm film thickness at a constant flow of helium (>99.995%, Orenburg-Techgas, Russia) 1.0 mL min\(^{-1}\). The oven temperature was programmed from 80 (held 5 min) to 240 °C with a heating rate of 10 °C min\(^{-1}\) (held 2 min). Total GC run time was 23 min. Temperatures of the MS interface, ion source and quadrupole were 240, 230, and 150 °C, respectively. MS detection was performed using the electron impact ionization at 70 eV in the selection ion monitoring (SIM) mode. The MS program used for the detection of the UDMH TPs in the SIM mode is provided in Table S2 in SM.

**Study of the effects of pre-incubation time**

Air evacuation of nine vials with spiked samples was conducted immediately after removing each sample from the freezer. At such low temperature, concentrations of analytes in the headspace are very low, which should result in their minimal losses. Air evacuation was conducted for 120 s as proposed by Capetti et al. (2020). Evacuated vials were pre-incubated at 40 °C for 30, 60, and 120 min and extracted for 15 min at 40 °C. Extraction parameters were selected based on previous studies (Kenessov et al. 2010; Yegemova 2015; Bakaikina et al. 2018; Orazbayeva et al. 2018a). In previous studies, pre-incubation of unfrozen solid samples was conducted for 5 min (Bakaikina et al. 2017) and 10 min (Yegemova et al. 2015; Orazbayeva et al. 2018b). For this experiment, higher pre-incubation times were tested because equilibration of frozen samples also includes their melting.

**Study of the effects of extraction temperature**

Twelve spiked sand samples were evacuated for 120 s immediately after removing each sample from the freezer (highest value used by Capetti et al. 2020), incubated at the chosen extraction temperature for 30 min, and extracted at 30, 40, 50, and 60 °C for 30 min. The range of extraction temperatures was limited to 60 °C because its further increase could decrease the benefits of Vac-HSSPME due to a substantial decrease in fiber-air distribution constants and increase in the pressure (Psillakis 2017; Zhakupbekova et al. 2019).

**Study of the effects of air evacuation time and temperature**

Spiked sand samples were air evacuated for 20, 45, 60, and 120 s immediately after removing from freezer (at −30 °C) or at least 30 min after removing from the freezer when temperature of a sample reached room temperature (23 °C). Evacuated samples were incubated at 40 °C for 30 min and extracted at 40 °C for 30 min. The experiment was conducted three times. Studied air evacuation time was limited to 120 s because it was the highest optimal value reported in the literature: 45 and 120 s (Capetti et al. 2020), 60 s (Beiranvand and Ghiasvand 2017), 90 s (Trujillo-Rodríguez et al. 2017), and 120 s (Orazbayeva et al. 2018a, b).

**Study of the effects of extraction time**

Spiked sand samples were air evacuated for 20 s at 23 °C, pre-incubated for 30 min at 40 °C, and extracted at 40 °C for 5, 15, 30, 60, and 120 min. This is a typical range of extraction times for optimization of methods based on HSSPME (Pawliszyn 2012).

**Analytical performance of the developed method**

Five calibration standards were prepared by spiking 1.00 g of sand with 10.0 µL of standard solutions of analytes in water with concentrations 0.15–2.4, 0.26–4.1, 0.70–11.2, 1.31–20.9, and 0.78–12.4 ng µL\(^{-1}\) for Pan, MPA, NDMA, MTA, and Pal, respectively. Ranges of concentrations were chosen based on previous studies (Orazbayeva et al. 2018a, b). Then, samples were stored for 12 h at 23 °C for equilibration and located in the freezer (−30 °C) until the analysis using the optimized method (evacuation for 20 s at 23 °C, pre-incubation for 30 min at 40 °C, and extraction for 30 min at 40 °C). Calibration slopes and their
standard deviations were determined using the method of least squares and LINEST function of MS Excel. Spike recoveries of UDMH TPs were determined by analyzing sand sample spiked (10.0 µL) at the following concentrations of analytes: 15.1 ng g⁻¹ for PAN, 25.5 ng g⁻¹ for MPA, 69.8 ng g⁻¹ for NDMA, 131 ng g⁻¹ for MTA, and 77.6 ng g⁻¹ for PAL.

Repeatability and reproducibility were evaluated using sand samples spiked (10.0 µL) at the following concentrations of analytes: 25.5 ng g⁻¹ for PAN, 29.5 ng g⁻¹ for MPA, 84.5 ng g⁻¹ for NDMA, 162 ng g⁻¹ for MTA, and 110 ng g⁻¹ for PAL. Concentrations for spiking were chosen from mid-points of calibration plots. Intra-day repeatability was estimated by analyzing five replicate spiked sand samples during one day, while inter-day reproducibility was estimated by analyzing five replicate spiked sand samples per day on 3 consecutive days (15 samples in total).

Application of the developed method

The developed method was applied for studying the evaporation and transformation of UDMH TPs in model sand samples. Three model sand samples (m = 1.00 g) were prepared in three replicates in nine 20-mL vials by spiking with 10.0 (sample S1), 15.0 (sample S2), and 20.0 (sample S3) µL of the standard solution of target analytes in water with concentrations 1.81, 1.97, 5.96, 11.1, and 6.59 ng µL⁻¹ for PAN, MPA, NDMA, MTA, and PAL, respectively. Then, samples in open vials were kept at room temperature (23 °C) in the fume hood for 3 days and then located in the freezer (−18 °C) for 5 days before analyzing using the developed method at optimized parameters.

Cost assessment of the methods based on HSSPME

The cost assessment of analytical methods is based upon the expenses of used standards for calibration, materials, labor, instrument, and facilities time (GC-MS) and the number of samples to be analyzed. Since all methods are based on GC-MS, capital costs were omitted from the cost assessment. Cost of the used standards for calibration was not considered, too, because pure substances are purchased only once and can be used even for 1 M analyses (Yegemova et al. 2015).

Results and discussion

Effect of pre-incubation time

Pre-incubation of a sample vial at extraction temperature is required prior to extraction for its uniform heating to the target temperature, equilibration of the sample with the headspace, and ensuring a reproducibility (Risticevic et al. 2010). A proper pre-incubation of a frozen sample is particularly important because ice present in a sample should be melted. Preliminarily conducted experiments showed that shorter pre-incubation time (10 min) yielded remarkably high RSDs (up to 30%).

The highest responses of all analytes were observed at pre-incubation time 30 min (Fig. S1 in SM). The best combination of responses of analytes and their RSDs (≤7%) was achieved at pre-incubation time 30 min, which was chosen as optimal for further experiments.

Effect of extraction temperature on analytes response

In HSSPME, increasing extraction temperature results in the increase of the headspace-sample distribution constant (Khs) and in the decrease of the fiber-headspace distribution constant (Kfh) (Pawliszyn 2012). Increase in the responses of analytes can be achieved only if the product of these two constants (Khs ∙ Kfh) increases—when Khs increases faster than Kfh decreases. In addition, higher extraction temperature can decrease responses of analytes due to their transformation (Kenessov et al. 2010), enhanced competition and displacement on SPME fiber (Jia et al. 2000).

Responses of all analytes increased by 27–80% when extraction temperature increased from 30 to 40 °C (Fig. 2). Further heating of sand samples to 50 °C led to decreased responses of PAN, MPA, and NDMA by 26–36%, whereas responses of MTA and PAL increased by 43–60% and reached their maxima. Heating samples from 50 to 60 °C yielded a decrease in responses of all analytes by 10–28%. The obtained plots are typical for HSSPME: at some point, a decrease in Kfh values becomes so strong that responses of analytes start decreasing (Pawliszyn 2012). RSDs at all
studied extraction temperatures varied from 2.0 to 22%. The extraction temperature 40 °C was chosen as optimal because it provided the best combination of responses of analytes.

**Effect of the duration of the air evacuation step at different sample temperatures**

Air evacuation of vials with solid samples without freezing can result in substantial losses of analytes (Capetti et al. 2020). The hypothesis of this experiment was that using a lower evacuation time at room temperature (23 °C) will provide the same responses of analytes as after evacuation at −30 °C for 120 s. At 23 °C, reducing the evacuation time from 120 to 20 s resulted in a 25–46 % increase in responses (Fig. S2 in SM). At the same time, decreasing the air evacuation time of frozen samples yielded similar responses considering the variability range (RSDs 1.0–15% (Fig. S2, b in SM). Paired sample t-test confirmed that there was no significant difference between most analytes’ responses obtained by Vac-HSSPME at air evacuation times of 20 and 120 s at −30°C (P > 0.05 for NDMA MTA and PAI, 0.036 for Pan and 0.008 for MPA). The difference between the results obtained after evacuation at 20 s at 23 °C and after 120 s of evacuation at −30 °C for all analytes except MPA was in the range of a standard deviation (Fig. 3), which proved the hypothesis.

Freezing the samples is an effective approach to minimize losses of analytes during air evacuation in the presence of the sample. The results presented here confirmed that air evacuation time must always be kept minimum as depending on the sample type, which can eliminate the extra step of freezing samples. In any case, when removing the air in the presence of the sample, the effects of air evacuation time and the sample temperature must be studied and optimized. Based on the above results and discussion, it was decided to air evacuate the samples at room temperature for 20 s because it allows greater flexibility when analyzing batches of samples.

**Effect of extraction time**

A reduced pressure allows increasing extraction rates and decreasing equilibration times (Brunton et al. 2001; Darrouzès et al. 2005; Psillakis et al. 2012b, 2013; Yiantzi et al. 2016; Psillakis 2017; Trujillo-Rodríguez et al. 2017; Capetti et al. 2020). However, too long extraction times can increase competition between analytes and matrix components, which can lead to a decrease in responses of analytes with lower affinities to the fiber coating. Thus, a study and optimization of the extraction time is very important for achieving the best combination of responses of analytes and their precision.

For all studied UDMH TPs, responses increased when increasing the extraction time from 5 to 30 min (Fig. 4). A plateau of PAN, MPA, and NDMA responses was reached at extraction time 30 min, which is typical for HSSPME (Pawliszyn 2012). Further increase in extraction time (>30 min) resulted in a minor increase in responses of PAN, MPA, and NDMA (by 6–10%). Responses of MTA and PAI continued increasing even after 120 min of extraction, which can be caused by higher $K_{fh}$ and/or lower $K_{hs}$ values for these analytes.

RSDs of UDMH TPs responses for all studied extraction times varied from 1.0 to 21%. Maximum value of RSDs (21%) was obtained at extraction time 5 min. Lowest RSDs (≤14%) were observed after 30 and 120 min of extraction.

Based on the obtained results, extraction time 30 min was chosen as optimal because it apparently provides best combination of precision and sensitivity for determination of UDMH TPs in sand samples using Vac-HSSPME. Longer
extraction time can cause an increase in errors due to the saturation of SPME fiber coating and enhanced competition with matrix compounds (Risticivc et al. 2010).

**Analytical performance of the developed method**

Calibration plots with determination coefficients ($R^2$) in the range from 0.9912 to 0.9938 in studied concentration ranges were obtained (Table 1). RSDs of the slopes of obtained calibration plots were 3.9–4.7% for all studied analytes. The developed method provided low detection limits (LODs) ranging from 0.035 to 3.6 ng g⁻¹; limits of quantification (LOQs) varied from 0.12 to 12 ng g⁻¹. RSDs indicating intra-day repeatability and inter-day reproducibility were 3–9% and 7–11%, respectively, providing a satisfactory precision of the method (Table 2). Spike recoveries of target analytes from sand samples were 84–97% with RSDs 1.0–11% (Table 3), which proves the accuracy of the developed method.

### Application of the developed method

The developed method was applied for studying evaporation and transformation of UDMH TPs in model sand samples. Determined concentrations of analytes in sand samples after 3 days of storage in open vials showed substantial losses varying from 41 to 94% (Table 4). As most of these compounds show good chemical stability, the losses were mostly caused by their evaporation. Such a quick evaporation can be caused by the low moisture content and surface area of sand and its low affinity to analytes. RSDs of three replicates of the samples did not exceed 14%. For Pan, MPA, NDMA, and MTA, the highest relative losses (%) were observed at highest initial concentrations. For Pal, there was no trend. Among analytes, the highest losses (90.2–94.3%) were

| Compound | Concentration range (ng g⁻¹) | $R^2$ | RSDs of slope (%) | LOD (ng g⁻¹) | LOQ (ng g⁻¹) |
|----------|-----------------------------|------|-------------------|-------------|-----------|
| PAn      | 1.5–24                      | 0.9919 | 4.5               | 0.035       | 0.12      |
| MPA      | 2.6–41                      | 0.9912 | 4.7               | 0.17        | 0.56      |
| NDMA     | 7.0–112                     | 0.9913 | 4.7               | 0.22        | 0.73      |
| MTA      | 13–209                      | 0.9938 | 3.9               | 3.6         | 12        |
| PAI      | 7.8–124                     | 0.9930 | 4.2               | 0.35        | 1.2       |

Note: The LODs and LOQs were calculated as 3:1 and 10:1 signal-to-noise (S/N) ratios, respectively. S/N ratios were calculated from chromatograms of sand samples with lowest concentration of each analyte.

| Analytes | Spiked (ng g⁻¹) | Intra-day repeatability | Inter-day reproducibility | Mean spike recovery (%) |
|----------|-----------------|-------------------------|---------------------------|-------------------------|
|          | Determined (ng g⁻¹) | RSD | Determined (ng g⁻¹) | RSD |
| PAn      | 25.5            | 28.0±1.0 | 3.6          | 29±2      | 7.4       | 112±8     |
| MPA      | 29.5            | 33±2      | 5.2          | 35±3      | 8.2       | 119±10    |
| NDMA     | 84.5            | 97±3      | 2.7          | 96±9      | 9.5       | 114±11    |
| MTA      | 162             | 158±9     | 5.8          | 166±19    | 11.5      | 103±12    |
| PAI      | 110             | 116±10    | 8.8          | 117±10    | 8.5       | 107±9     |

| Compound | Spiked concentration (ng g⁻¹) | Measured concentration (ng g⁻¹) | Losses (%) |
|----------|-------------------------------|---------------------------------|-------------|
|          | S1   | S2   | S3   | S1   | S2   | S3   | S1   | S2   | S3   | S1   | S2   | S3   |
| PAn      | 18   | 27   | 36   | 1.7±0.15 | 2.65±0.13 | 2.1±0.2 | 90.6±0.8 | 90.2±0.5 | 94.3±0.6 |
| MPA      | 20   | 30   | 39   | 11.3±1.2 | 17.6±1.6 | 12.1±1.5 | 42±6   | 41±5   | 69±4  |
| NDMA     | 60   | 89   | 119  | 15±2   | 23.8±1.5 | 17±2   | 76±3   | 73.3±1.7 | 85.4±1.8 |
| MTA      | 111  | 167  | 222  | 21±2   | 33.0±0.6 | 28.2±1.9 | 81±2   | 80.2±0.4 | 87.3±0.8 |
| PAI      | 66   | 99   | 132  | 12.28±0.07 | 23.6±0.5 | 26±3   | 81.36±0.10 | 76.1±0.5 | 81±2  |
observed for Pan. Lowest losses (41–42%) were for MPA at initial concentrations 20 and 30 ng g\(^{-1}\), while initial concentration of MPA 39 ng g\(^{-1}\) yielded a 69±4% reduction. Initial concentrations of NDMA 60 and 89 ng g\(^{-1}\) resulted in 76±4 and 73.3±1.7% decrease, respectively, whereas the concentration 119 ng g\(^{-1}\) showed an 85.4±1.8% reduction.

**Comparison of the developed method to other methods**

Compared to the methods based on gas chromatography and solvent extraction (Table S3 in SM), the developed method (Fig. 5) provided 1.4–8 times lower LODs for MTA and NDMA. These methods are not considered green because they require substantial volumes of toxic organic solvents—acetone, methanol, acetonitrile, or dichloromethane (Kenessov et al. 2008; Bednar et al. 2009; Smirnov et al. 2010).

Compared to existing methods based on HSSPME, the developed method provides lower detection limits (Table 4) and better precision and accuracy due to the absence of oxygen during extraction. Its main advantage over the only existing method based on Vac-HSSPME is a simpler sample preparation because a preliminary extraction by water is not required. In addition, it results in a better precision and accuracy at 2.5–8 times lower LODs. These methods provide the same cost of analysis per sample (Table S4 in SM). Compared to the method of Yegemova et al. (2015), the cost of analysis using the developed method based on Vac-HSSPME is ~10% higher. However, the main advantage of the developed method is a possibility to simultaneously quantify five analytes. The method of Bakaikina et al. (2018) was most expensive.
because it uses quantification based on standard addition calibration and requires six extractions per one sample.

**Conclusion**

Thus, the new method has been developed for simultaneous quantification of major transformation products of toxic rocket fuel unsymmetrical dimethyldihydrazine in sand using vacuum-assisted headspace solid-phase microextraction. Decreasing the air evacuation time from 120 to 20 s at room temperature (23 °C) allowed a 25–46% increase in responses of analytes obtained by Vac-HSSPME. At −30 °C, no significant change in responses of analytes was observed at varying air evacuation times. The best combination of responses and their RSDs was achieved after air evacuation of a sample (m = 1.0 g) for 20 s at 23 °C, incubation for 30 min, and extraction for 30 min at 40°C. The developed method provided linear calibration plots with coefficients of determination ranging from 0.9912 to 0.9938 in studied ranges of concentrations. LODs and LOQs varied from 0.035 to 3.6 ng g⁻¹ and 0.12–12 ng g⁻¹, respectively.

It has been confirmed that freezing the samples is an effective approach to minimize analyte losses during air evacuation in the presence of the solid sample. The results presented here indicated that air evacuation time must always be kept to a minimum as depending on the sample type this may eliminate the extra step of freezing samples. In any case, when removing the air in the presence of the sample, the effects of air evacuation time and the sample temperature must be evaluated and optimized.

The method showed its several advantages over other methods based on HSSPME such as lower detection limits, simplicity, rapidity, lower or similar cost, and better accuracy and precision. Its major advantage over other existing methods based on HSSPME is the extraction at a substantially decreased concentration of oxygen, which should minimize oxidation processes and changes in concentrations of analytes. It can be further expanded to a greater number of analytes and soil types.

The method can be recommended for application in environmental analytical laboratories dealing with analysis of sand contaminated with rocket fuel. It could be used for research experiments on transformation and evaporation of UDMH TPs where their concentrations can reach part-per-billion (ppb) levels. The method can also be useful for studying the horizontal and vertical migration of UDMH TPs in sand and a more accurate mapping of the contamination of fall places of carrier rockets and their burned-out stages.

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**Data availability** All data generated or analyzed during this study are included in this published article (and its supplementary information files). Besides, the datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.
Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Bakaikina NV, Kenesson B, Ul’yanovskii NV et al (2017) Quantification of transformation products of unsymmetrical dimethylhydrazine in water using SPME and GC-MS. Chromatographia 80:931–940. https://doi.org/10.1007/s10337-017-3286-2

Bakaikina NV, Kenesson B, Ul’yanovskii NV, Kosyakov DS, (2018) Quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in soils using SPME and GC-MS. Talanta 184:332–337. https://doi.org/10.1016/j.talanta.2018.02.047

Bednar AJ, Karn RA, Mao C-R (2009) Determination of low level NDMA in soils. US Army Corps Eng Desember:1–24

Beiranvand M, Ghiasvand A (2017) Simple, low-cost and reliable device for vacuum-assisted headspace solid-phase microextraction of volatile and semivolatile compounds from complex solid samples. Chromatographia 80:1771–1780. https://doi.org/10.1007/s10337-017-3422-z

Beiranvand M, Ghiasvand A (2020a) An ultrasound-assisted pressure-regulated solid-phase microextraction setup for fast and sensitive analysis of volatile pollutants in contaminated soil. Environ Sci Pollut Res 27:36306–36315. https://doi.org/10.1007/j. ejpba.2020.02.007

Beiranvand M, Ghiasvand A (2020b) Design and optimization of the VA-TV-SPME method for ultrasensitive determination of the PAHs in polluted water. Talanta 212:120809. https://doi.org/10.1016/j. talanta.2020.120809

Brunton NP, Cronin DA, Monahan FJ (2001) The effects of temperature and pressure on the performance of Carboxen/PDMS fibres during solid phase microextraction (SPME) of headspace volatiles from cooked and raw turkey breast. Flav Frag J 16:294–302. https://doi.org/10.1021/fj0001000

Buryak AK, Tataruova O, Ulyanov A (2004) Study of transformation products of unsymmetrical dimethylhydrazine on model sorbents by the method of gas chromatography/mass spectrometry. Mass Spectrom 1:147

Capetti F, Rubiolo P, Bicchi C et al (2020) Exploiting the versatility of vacuum-assisted headspace solid-phase microextraction in combination with the selectivity of ionic liquid-based GC stationary phases to discriminate Boswellia spp. resins through their volatile and semivolatile fractions. J Sep Sci 43:1–11. https://doi.org/10.1002/jssc.202000084

Carlsen L, Kenesova OA, Batyrbekova SE (2007) A preliminary assessment of the potential environmental and human health impact of unsymmetrical dimethylhydrazine as a result of space activities. Chemosphere 67:1108–1116. https://doi.org/10.1016/j. chemosphere.2006.11.046

Carlsen L, Kenesson BN, Batyrbekova SY (2008) A Qsar/Qsrt study on the environmental health impact by the rocket fuel 1,1-dimethyl hydrazine and its transformation products. Environ Health Insights 1:11–20. https://doi.org/10.1016/j.ehpt.2009.01.005

Carlsen L, Kenesson BN, Batyrbekova SY et al (2009) Assessment of the mutagenic effect of 1,1-dimethyl hydrazine. Environ Toxicol Pharmacol 28:448–452. https://doi.org/10.1016/j.etap.2009.08.004

Darrouzès J, Bueno M, Pécheyran C et al (2005) New approach of solid-phase microextraction improving the extraction yield of butyl and phenyltin compounds by combining the effects of pressure and type of agitation. J Chromatogr A 1072:19–27. https://doi.org/10.1016/j.chroma.2005.02.026

Derikvand A, Ghiasvand A, Dalvand K, Haddad PR (2021) Fabrication and evaluation of a portable low-pressure headspace solid-phase microextraction device for on-site analysis. Microchem J 168:106362. https://doi.org/10.1016/j.microc.2021.106362

Ghiasvand A, Koonani S, Yazdankhah F, Farhadi S (2018a) A comparison study on a sulfonated graphene-polyaniline nanocomposite coated fiber for analysis of nicotine in solid samples through the traditional and vacuum-assisted HS-SPME. J Pharm Biomed Anal 149:271–277. https://doi.org/10.1016/j. jpba.2017.11.020

Ghiasvand A, Zarghami F, Beiranvand M (2018b) Ultrasensitive direct determination of BTEX in polluted soils using a simple and novel pressure-controlled solid-phase microextraction setup. J Iran Chem Soc 15:1051–1059. https://doi.org/10.1007/s13738-018-1302-6

Ghiasvand A, Yazdankhah F, Paul B (2020) Heating-, cooling- and vacuum-assisted solid-phase microextraction (HCV-SPME) for efficient sampling of environmental pollutants in complex matrices. Chromatographia (83):531–540. https://doi.org/10.1007/s13737-020-3869-0

GOST (1996) GOST 26205-91. Soils. Determination of mobile compounds of phosphorus and potassium by Machigina method modified by CINAO

Grebel JE, Young CC, Suffet IH, Mel (2006) Solid-phase microextraction of N-nitrosamines. J Chromatogr A 1117:11–18. https://doi.org/10.1016/j.chroma.2006.03.044

Hakkarainen M (2007) Developments in multiple headspace extraction. J Biochem Biophys Methods 70:229–233. https://doi.org/10.1016/j. jbbm.2006.08.012

ISO (1994a) ISO 11263:1994. Soil quality. Determination of phosphorus. Spectrometric determination of phosphorus soluble in sodium hydrogen carbonate solution

ISO (1994b) ISO 10390:1994. Soil quality. Determination of pH

ISO (1995) ISO 11261:1995. Soil quality. Determination of total nitrogen. Modified Kjeldahl method

ISO (2009) ISO 11277:2009. Soil quality. Determination of particle size distribution in mineral soil material. Method by sieving and sedimentation

ISO (2018) ISO 23470:2018. Soil quality. Determination of effective cation exchange capacity (CEC) and exchangeable cations using a hexamminecobalt (III) chloride solution

GOST (1993) GOST 26212-91. Soils. Methods for determination of organic matter

Jia M, Koziel JA, Pawliszyn J (2000) Fast field sampling/sample preparation and quantification of volatile organic compounds in indoor air by solid-phase microextraction and portable gas chromatography. F Anal Chem Technol 4:73–84

Kenesson B, Batyrbekova S, Nauryzbayev M et al (2008) GC-MS Determination of 1-methyl-1H-1,2,4-triazole in soils affected by rocket fuel spills in Central Kazakhstan. Chromatographia 67:421–424. https://doi.org/10.1085/s10337-008-0535-4

Kenesson BN, Koziel JA, Grotenhuis T, Carlsen L (2010) Screening of transformation products in soils contaminated with unsymmetrical dimethylhydrazine using headspace SPME and GC-MS. Anal Chim Acta 674:32–39. https://doi.org/10.1016/j.aca.2010.05.040

Kenesson B, Sailaukhanuly Y, Koziel JA, et al (2011) GC-MS and GC-NPD determination of formaldehyde dimethylhydrazine in water using SPME. Chromatographia 73:123–128. https://doi.org/10.1007/s10337-010-1820-6

Kenesson B, Alimzhana M, Sailaukhanuly Y et al (2012) Transformation products of 1,1-dimethylhydrazine and their distribution

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in soils of fall places of rocket carriers in Central Kazakhstan. Sci Total Environ 427–428:78–85. https://doi.org/10.1016/j.scitotenv.2012.04.017

Kenessov B, Koziel JA, Bakaikina NV, Orazbayeva D (2016) Perspectives and challenges of on-site quantification of organic pollutants in soils using solid-phase microextraction. TrAC - Trends Anal Chem 85:111–122. https://doi.org/10.1016/j.trac.2016.04.007

Kolesnikov S (2014) Oxidation of unsymmetrical dimethylhydrazine (heptyl) and identification of its transformation products during spills. SibAK, Novosibirsk

Kosyakov DS, Ul’yanovskii NV, Bogolitsyn KG, Shigpun OA (2014) Simultaneous determination of 1,1-dimethylhydrazine and products of its oxidative transformations by liquid chromatography–tandem mass spectrometry. Int J Environ Anal Chem 94:1254–1263. https://doi.org/10.1080/03067319.2014.940342

Kosyakov DS, Ul’yanovskii NV, Pokryshkin SA et al (2015) Rapid determination of 1,1-dimethylhydrazine transformation products in soil by accelerated solvent extraction coupled with gas chromatography–tandem mass spectrometry. Int J Environ Anal Chem 95:1321–1337. https://doi.org/10.1080/03067319.2015.1090569

Krebs G (2019) Orbital Launches of 2018. In: Gunter’s Sp. Page. https://space.skyrocket.de/doc_chr/lau2018.htm

Llopí Mart, Li b K, Fingas M B (1999) Headspace solid phase micro-extraction (HSSPME) for the determination of volatile and semi-volatile pollutants in soils. Talanta 48:451–459. https://doi.org/10.1016/S0039-9140(98)00263-X

Llopí Mart, Celeró M, García-Jares C, Dagnac T (2019) Environmental applications of solid-phase microextraction. Trends Anal Chem. 112:1–12. https://doi.org/10.1016/j.trendscan.2018.12.020

Maszer S, Psillakis E, Purcaro G (2020) A multifaceted investigation on the effect of vacuum on the headspace solid-phase microextraction of extra-virgin olive oil. Anal Chim Acta 1103:106–114. https://doi.org/10.1016/j.feca.2019.12.053

Merck (2018) SPME for GC analysis. Getting Started with Solid Phase Microextraction. http://www.supelco.com/tc/C-01-SPME-Fiber.pdf

Minister of National Economy of the Republic of Kazakhstan (2015) “On the approval of hygienic standards for atmospheric air in urban and rural settlements” from 28.02.2015, Annex 3 to the order No. 168 of the Ministry of National Economy of the Republic of Kazakhstan, Astana, Kazakhstan. (In Russian)

Orazbayeva D, Kenessov B, Psillakis E et al (2018a) Determination of transformation products of unsymmetrical dimethylhydrazine in water using vacuum-assisted headspace solid-phase microextraction. J Chromatogr A 1555:30–36. https://doi.org/10.1016/j.chroma.2018.04.048

Orazbayeva D, Kenessov B, Zhakupbekova A (2018b) Quantification of transformation products of unsymmetrical dimethylhydrazine in aqueous extracts from soil based on vacuum-assisted headspace solid-phase microextraction. Chem Bull Kazakh Nat Univ 2:4–11. https://doi.org/10.15328/cb1014

Pawliszyn J (2012) Handbook of Solid Phase Microextraction. Elsevier Inc.

Psilakis E, Mousouraki A, Yiantzi E, Kalogerakis N (2012a) Effect of Henry’s law constant and operating parameters on vacuum-assisted headspace solid phase microextraction. J Chromatogr A 1244:55–60. https://doi.org/10.1016/j.chroma.2012.05.006

Psilakis E, Yiantzi E, Sanchez-Prado L, Kalogerakis N (2012b) Vacuum-assisted headspace solid phase microextraction: Improved extraction of semivolatiles by non-equilibrium headspace sampling under reduced pressure conditions. Anal Chim Acta 742:30–36. https://doi.org/10.1016/j.aca.2012.01.019

Psilakis E, Yiantzi E, Kalogerakis N (2013) Downsizing vacuum-assisted headspace solid phase microextraction. J Chromatogr A 1300:119–126. https://doi.org/10.1016/j.chroma.2013.02.009

Psilakis E (2017) Vacuum-assisted headspace solid-phase microextraction: A tutorial review. Anal Chim Acta 986:12–24. https://doi.org/10.1016/j.aca.2017.06.033

Ristichev N, Lord H, Górecki T et al (2010) Protocol for solid-phase microextraction method development. Nat Protoc 5:122–139. https://doi.org/10.1038/nprot.2009.179

Rodin I, Moskvin DN, Smolencov AD, Shigpun OA (2008) Transformations of asymmetric dimethylhydrazine in soils. Russ J Phys Chem A 82:911–915. https://doi.org/10.1134/S003602400806006X

Rodin I, Aanæ eva IA, Smolencov AD, Shigpun OA, (2010) Determination of the products of the oxidative transformation of unsymmetrical dimethylhydrazine in soils by liquid chromatography/mass spectrometry. J Anal Chem 65:1405–1410. https://doi.org/10.1134/S1061934810130150

Rodin I, Smirnov RS, Smolencov AD et al (2012) Transformation of unsymmetrical dimethylhydrazine in soils. Eurasian Soil Sci 45:386–391. https://doi.org/10.1134/S1064229312040096

Smirnov RS, Rodin IA, Smolencov AD, Shigpun OA (2010) Determination of the products of the oxidative transformation of unsymmetrical dimethylhydrazine in soils by liquid chromatography/mass spectrometry. J Anal Chem 65:1405–1410. https://doi.org/10.1134/S1061934810130150

The National Institute for Occupational Safety and Health (NIOSH) (2018) The NIOSH pocket guide to chemical hazards is intended as a source of general industrial hygiene information on several hundred chemicals/classes for workers, employers, and occupational health professionals. https://www.cdc.gov/niosh/rtecs/ MV256250.html

Trujillo-Rodriguez MJ, Pino V, Psilakis E et al (2017) Vacuum-assisted headspace-solid phase microextraction for determining volatile free fatty acids and phenols. Investigations on the effect of pressure on competitive adsorption phenomena in a multi-component system. Anal Chim Acta 962:41–51. https://doi.org/10.1016/j.aca.2017.01.056

U.S. Department of Health and Human Services (1993) Registry of toxic effects of chemical substances (RTECS, online database)

U.S. Environmental Protection Agency (1992) Health and environmental effects profile for 1,1-dimethylhydrazine

Ul’yanovskii NV, Kosyakov DS, Pokryshkin SA, Bogolitsyn KG (2015) Determination of transformation products of 1,1-dimethylhydrazine by gas chromatography–tandem mass spectrometry. J Anal Chem 70:1553–1560. https://doi.org/10.1134/S1061934810130080

Ul’yanovskii NV, Kosyakov DS, Pikovskoi II, Khabarov YG, (2017) Characterisation of oxidation products of 1,1-dimethylhydrazine by high-resolution orbitrap mass spectrometry. Chemosphere 174:66–75. https://doi.org/10.1016/j.chemosphere.2017.01.118

Vakinti M, Mela SM, Fernández E, Psilakis E (2019) Room temperature and sensitive determination of haloanisoles in wine using vacuum-assisted headspace solid-phase microextraction. J Chromatogr A 1602:142–149. https://doi.org/10.1016/j.chroma.2019.03.047

Yegemova S, Bakaikina NV, Kenessov B et al (2015) Determination of 1-methyl-1H-1,2,4-triazole in soils contaminated by rocket fuel using solid-phase microextraction, isotope dilution and gas chromatography–mass spectrometry. Talanta 143:226–233. https://doi.org/10.1016/j.talanta.2015.05.045

Yiantzi E, Kalogerakis N, Psilakis E (2015) Vacuum-assisted headspace solid phase microextraction of polycyclic aromatic hydrocarbons in solid samples. Anal Chim Acta 890:108–116. https://doi.org/10.1016/j.aca.2015.05.047

Yiantzi E, Kalogerakis N, Psilakis E (2016) Design and testing of a new sampler for simplified vacuum-assisted headspace solid-phase microextraction. Anal Chim Acta 927:46–54. https://doi.org/10.1016/j.aca.2016.05.001
Yoneyama T (1981) Detection of N-nitrosodimethylamine in soils amended with sludges. Soil Sci Plant Nutr 27:249–253. https://doi.org/10.1080/00380768.1981.10431276
Zhakupbekova A, Baimatova N, Kenessov B (2019) A critical review of vacuum-assisted headspace solid-phase microextraction for environmental analysis. Trends Environ Anal Chem 22:65. https://doi.org/10.1016/j.teac.2019.e00065
Zhubatov ZK, Kenessov B, Bakaikina NV et al (2016) Fast determination of 1-methyl-1H-1,2,4-triazole in soils contaminated by rocket fuel using solvent extraction, isotope dilution and GC–MS. Chromatographia 79:491–499. https://doi.org/10.1007/s10337-016-3054-8

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