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## Determination of transformation products of unsymmetrical dimethylhydrazine in water using vacuum-assisted headspace solid-phase microextraction<sup>☆</sup>

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### ABSTRACT

A new, sensitive and simple method based on vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) followed by gas chromatography-mass-spectrometry (GC-MS), is proposed for the quantification of rocket fuel unsymmetrical dimethylhydrazine (UDMH) transformation products in water samples. The target transformation products were: pyrazine, 1-methyl-1*H*-pyrazole, *N*-nitrosodimethylamine, *N,N*-dimethylformamide, 1-methyl-1*H*-1,2,4-triazole, 1-methyl-imidazole and 1*H*-pyrazole. For these analytes and within shorter sampling times, Vac-HSSPME yielded detection limits (0.5–100 ng L<sup>-1</sup>) 3–10 times lower than those reported for regular HSSPME. Vac-HSSPME sampling for 30 min at 50 °C yielded the best combination of analyte responses and their standard deviations (<15%). 1-Formyl-2,2-dimethylhydrazine and formamide were discarded because of the poor precision and accuracy when using Vac-HSSPME. The recoveries for the rest of the analytes ranged between 80 and 119%. The modified Mininert valve and Thermogreen septum could be used for automated extraction as it ensured stable analyte signals even after long waiting times (>24 h). Finally, multiple Vac-HSSPME proved to be an efficient tool for controlling the matrix effect and quantifying UDMH transformation products.

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### 1. Introduction

The use of toxic unsymmetrical dimethylhydrazine (UDMH) in heavy rockets launched from Kazakhstan, Russia, India, and China causes contamination of the environment at adjacent territories with toxic fuel residuals [1,2]. After release into the aerobic environment, UDMH undergoes oxidative decomposition with formation of numerous classes of compounds including triazoles, nitrosoamines, pyrazoles, imidazoles and pyrazines [2–4]. The major health risks associated with UDMH and its transformation products are caused by their hepatotoxic, carcinogenic, mutagenic, teratogenic and embryotoxic properties [1,5–7]. Severe liver damages including internal bleeding and cancer, as well

as lung cancer and fetal death are linked to exposure to *N*-nitrosodimethylamine [8,9] and *N,N*-dimethylformamide [10–12]. The most stable transformation product of UDMH, 1-methyl-1*H*-1,2,4-triazole, was reported to cause adverse effects on cell membranes, blood system and hemodynamics [6].

Gas (GC) [3,13] and liquid chromatography (LC) [14] coupled to various detectors are typically used for the analysis of UDMH transformation products with GC offering greater selectivity and cost-efficiency for the more volatile UDMH transformation products. At the same time, headspace solid-phase microextraction (HSSPME) proved to be advantageous for the extraction of UDMH transformation products offering low detection limits and simplicity [13,15]. However, HSSPME extraction times as long as 60 min are needed to extract the trace amounts of these polar analytes with low Henry's law constants ( $K_H$ ) from aqueous samples [15].

Vacuum-assisted HSSPME (Vac-HSSPME) was previously reported to accelerate extraction rates of low  $K_H$  analytes [16–18]. For these analytes, lowering the total pressure was found to reduce gas-phase resistance and, as such, enhance mass transfer of analytes from the aqueous or solid sample to the gas phase

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and then to the SPME coating [18,19]. The theory behind HSSPME sampling under low-pressure conditions has been discussed in the past [18–20], and different gas-tight devices have been proposed [19,21,22]. For aqueous samples, the most simple and effective form of Vac-HSSPME consists of introducing the liquid sample into a pre-evacuated vial sealed with a modified Mininert® valve, equilibrating the sample with the gas phase, and headspace extraction with an SPME fiber [22].

In general, the accuracy of quantification for HSSPME can be affected by the matrix effects originating from the different extraction efficiencies of analytes from different samples. Among all approaches for matrix effect control [23], multiple HSSPME (MHSSPME) has the greatest potential for the simultaneous quantification of many analytes because it allows quick determination of their total masses in each sample without using complicated calibration approaches [24,25]. MHSSPME is based on consecutive extractions from the same sample vial and obtaining the dependence of responses of an analyte after each extraction on the extraction number [25]. Based on this dependence, extraction effectiveness and total mass of an analyte in the sample can be calculated. Compared to the standard addition approach, MHSSPME does not require spiking the sample with a standard of an analyte before extraction, which is particularly important for unstable analytes. The selection of internal standard(s) suitable for the quantification of UDMH transformation products [26] and other analytes [27,28] in environmental samples when using HSSPME can be complicated.

In this work, a new method based on Vac-HSSPME was optimized and used for the quantification of UDMH transformation products in water samples. The target transformation products were pyrazine (PAn), 1-methyl-1H-pyrazole (MPA), N-nitrosodimethylamine (NDMA), N,N-dimethylformamide (DMF), 1-methyl-1H-1,2,4-triazole (MTA), 1-formyl-2,2-dimethylhydrazine (FDMH), 1-methyl-imidazole (MIA), formamide (FA) and 1H-pyrazole (PAI). During the optimization step, the effects of extraction temperature and time on the intensity and precision of analytes' responses were evaluated. The proposed Vac-HSSPME method was applied to the quantification of UDMH transformation products in water samples collected at the sites of heavy rocket operation. The ability of the modified Mininert® valves to maintain stable analyte signals for extended waiting times was evaluated, and the potential for automation was discussed. The possibility of using multiple Vac-HSSPME (MVac-HSSPME) for a matrix effect control and quantifying the transformation products of UDMH has been demonstrated.

## 2. Experimental

### 2.1. Reagents, materials and samples

The list of reagents (transformation products of UDMH) and their properties are given in Table A.1 (in Supplementary material). SPME was conducted using a 85- $\mu\text{m}$  Carboxen/polydimethylsiloxane (Car/PDMS, Supelco, USA) fiber.

In-house modified Mininert® valves (Restek, USA) were prepared as described in the past [22]. A cylindrical Thermogreen® LB-1 septum with half-hole (6 mm diameter  $\times$  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.

Real water sample (melted snow with a pH 6.6) collected in Almaty, Kazakhstan, and distilled water (pH 6.4) were used for the preparation of the spiked samples and standard solutions. The effect of pH on Vac-HSSPME was not studied in this work because

any change of pH can result in a degradation of UDMH and some of its transformation products [29,30] with the loss of accuracy and precision of the method. In any case, the effect of varying pH was previously found to be non-significant for the HSSPME sampling of nitrosamines [31].

### 2.2. Parameters of gas chromatography-mass spectrometry (GC-MS) analysis

All GC-MS analyses were performed on 6890N/5973N and 7890A/5975C systems (Agilent, USA) equipped with split/splitless and PTV (CIS 4, Gerstel, Germany) inlets, Combi-PAL (CTC Analytics, Switzerland) and MPS2 (Gerstel, Germany) autosamplers, respectively. Analytes were desorbed from the SPME fibers at 240 °C in a GC inlet working in a splitless mode. Separation was conducted using a polar 60 m  $\times$  0.25 mm DB-WAXetr (Agilent, USA) column with a 0.50  $\mu\text{m}$  film thickness at the constant helium (>99.995%, Orenburg-Tehgas, Russia) flow 1.0 mL min<sup>-1</sup>. The oven temperature was programmed from 40 °C (held for 10 min) to 240 °C (held for 0 min), with the heating rate 5 °C min<sup>-1</sup>. The temperatures of the MS ion source, quadrupole and interface were 230, 150 and 240 °C, respectively. Detection was conducted using the electron impact ionization at 70 eV in the selected ion monitoring (SIM) mode. The MS program used for the detection of the UDMH transformation products in the SIM mode is provided in Table A.2 (in Supplementary material).

### 2.3. Vac-HSSPME procedure

20-mL crimp-top headspace vials containing 1.75 g of NaCl and a magnetic stir bar coated with polytetrafluoroethylene (PTFE) (10  $\times$  6 mm) were sealed with modified Mininert® valves and air-evacuated for 120 s using a low-cost single-stage rotary vane pump (Russia). A 5-mL sample was introduced into a 20-mL crimp-top headspace vial using a 5-mL gas-tight syringe (Bioject, China). Then the sample vial was placed on the top of the magnetic stirrer PE-6100 (Ecros, Russia) connected to the in-house made thermostated heating device with the temperature controller REX-C100 (Japan) and type K thermocouple 5TC-GG-K-20-36 (Omega, USA) (Fig. A.1. in Supplementary material). The samples were then incubated for 10 min at a preset temperature and a maximum (1500 rpm according to the specifications of the magnetic stirrer) stirring speed. Upon equilibration, the SPME fiber was exposed to the headspace of the sample, and manual HSSPME extraction was performed for a preset time. After extraction, the SPME fiber was transferred to the GC inlet for desorption of analytes.

### 2.4. Comparing the efficiencies of Vac-HSSPME and regular HSSPME

This set of experiments was conducted using aqueous samples spiked with PAn and MPA at 100  $\mu\text{g L}^{-1}$ , NDMA and DMF at 200  $\mu\text{g L}^{-1}$ , and MTA, FDMH, MIA, FA, PAI at 600  $\mu\text{g L}^{-1}$ . For HSSPME [15], 5.00 mL of the spiked sample were introduced into a 20-mL crimp-top headspace vial, which was then sealed with PTFE/silicone septum and aluminum caps (Zhejiang Aijiren Technology Co., China). The sample was incubated for 10 min in the agitator of the autosampler at 50 °C and 250 rpm followed by a 30-min extraction at the same temperature and agitation speed. Vac-HSSPME of the spiked sample was conducted as described in the Section 2.3 with the extraction temperature and time set at 50 °C and 30 min, respectively.

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