

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

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## Research Article

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# Abstract

Quantification of unsymmetrical dimethylhydrazine (UDMH) transformation products (TPs) in solid samples is an important stage in monitoring of environmental pollution caused by heavy rockets launches. The new method for simultaneous quantification of UDMH TPs in sand samples using vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) followed by gas chromatography-mass spectrometry (GC-MS) is proposed. Compared to regular HSSPME, Vac-HSSPME yielded 1.3–4.8 times higher responses for NDMA, MTA and PAI. Increasing air-evacuation time from 20 to 120 s at 23 °C resulted in decreased responses of analytes by 25–46%. Freezing of samples (-30 °C) had negligible effect on responses of analytes at air-evacuation time 20 s. The best combination of responses of analytes and their RSDs was achieved after air-evacuation of a sample ( $m = 1.00$  g) for 20 s at 23 °C, incubation for 30 min and 30-min extraction at 40°C by Car/PDMS fiber. Vac-HSSPME provided linear calibration plots in studied ranges of concentrations with coefficients of determination ranging from 0.9912 to 0.9938. The limits of detection for spiked sand samples varied from 0.035 to 3.6 ng g<sup>-1</sup>. Spike recoveries of target analytes from sand samples were 84–97% with RSDs 1–11%. The developed method was successfully tested in the experiment on studying losses of analytes from open vials with model sand spiked with UDMH TPs. The developed method can be recommended for analysis of trace concentrations of UDMH TPs when studying their transformation, migration and distribution in contaminated sand.

## Introduction

Unsymmetrical dimethylhydrazine (UDMH) is commonly used as a high-energy fuel of heavy-lift launch vehicles. In 2018, 47.4% of 114 orbital launchers used fuel containing UDMH (Gunter's Space Page 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 (U.S. EPA 1984; NIOSH 1997, 2018) posing a negative impact to the environment and human health (NIOSH 1997; 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. 2010b, 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. 2010b; 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. 2010a, 2011; Yegemova et al. 2015; Bakaikina et al. 2018; Orazbayeva et al. 2018b) 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 fall 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 internal standard (IS) calibrations methods (Llompart et al. 1999; Yegemova et al. 2015; Bakaikina et al. 2018), 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. (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. (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). The approach was successfully applied for the quantification of polycyclic aromatic hydrocarbons (PAHs) (Yiantzi et al. 2015; Beiranvand and Ghiasvand 2017) in soil samples, PAHs (Psillakis et al. 2012a, 2013), polychlorinated biphenyls (Yiantzi et al. 2016), chlorophenols (Psillakis et al. 2012b) and UDMH TPs (Orazbayeva et al. 2018a) in water samples.

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. (Orazbayeva et al. 2018b) 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 (RSDs < 5%,  $R^2 > 0.991$ , LODs 0.2-9 ng g<sup>-1</sup>, recoveries 90–103%), an additional sample preparation step of a preliminary extraction of analytes with water complicates the process. The analytes have high polarity and water solubility (Table 1) and could be easily extracted from soil. Nonetheless, Kenessov et al. (Kenessov et al. 2010b) showed that the addition of water to soil results in a decrease of the responses of analytes, which could

be caused by higher affinity of analytes to water than 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°C before air-evacuation overcame problems of volatiles (terpenes) losses due to aspiration. To exclude any discriminative losses from the headspace over time the authors also applied 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) and a dramatic increase of the later eluting analytes (being sampled at pre-equilibrium) with Vac- and regular HSSPME. To further decrease losses of analytes, a higher amount of sample was taken for extraction. This approach 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 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 (PAn), 1-methyl-1*H*pyrazole (MPA), *N*-nitrosodimethylamine (NDMA), 1-methyl-1*H*1,2,4-triazole (MTA) and 1*H*pyrazole (PAI). NDMA and MTA were chosen as the main UDMH TPs, for which maximum permissible concentrations in soil are established in Kazakhstan – 0.01 and 10 mg kg<sup>-1</sup> (Ministry 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).

## Experimental

### Reagents and materials

The list of UDMH TPs, their origin and physicochemical properties are provided in Table 1. SPME was conducted using 85-µm Carboxen/polydimethylsiloxane (Car/PDMS, Supelco, Bellefonte, PA, USA), which provides highest extraction effectiveness of UDMH TPs (Grebel et al. 2006; Kenessov et al. 2010b).

In-house modified crimp-top Mininert® valves (Thomas Scientific) 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.

### Model sand sample

Sand sample was air-dried and sieved through 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 (ISO 2009),

1.81 ± 0.09% of organic matter (ISO/CD), 34.0 ± 0.5 mg kg<sup>-1</sup> of nitrogen (ISO 1995), 61.0 ± 0.5 mg kg<sup>-1</sup> of phosphorus (ISO 1994b), 370 ± 6 mg kg<sup>-1</sup> of potassium (GOST 1996). pH of the sample was 8.40 ± 0.10 (ISO 1994a). 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<sup>-1</sup> (ISO 2018), respectively.

## Vac-HSSPME procedure

Vac-HSSPME optimization procedure for analyzing UDMH TPs in sand samples included five consequent steps: 1) spiking a weighted sand sample, 2) storing a sample at -30 °C or frozen by LN2 (extra freezing step for investigation), 3) air-evacuation of the vial, 4) Vac-HSSPME of analytes; 5) desorption in the GC inlet (Fig. 1). For regular HSSPME, the air evacuation step was omitted. The laboratory was not equipped with a special tonometer to measure the pressure inside the vial through the Mininert valve and for air-evacuation, long air-evacuation time was chosen.

Prior to experiments, 20-mL crimp-top 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 ( $m = 1.00$  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<sup>-1</sup> 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 then located in a freezer ( $T = -30$  °C) or frozen by liquid nitrogen (LN2) till the evacuation.

The vials with sand samples were air-evacuated using a low-cost single-stage rotary vane pump (Russia). For HSSPME under atmospheric pressure, air-evacuation step was omitted. Incubation of the samples was held in the agitator of MPS2 autosampler (Gerstel, Germany), and manual extraction was performed at desired extraction temperature and time. After extraction, the SPME fiber was introduced into the GC inlet for desorption of analytes.

## GC-MS conditions

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 x 0.25 mm DB-WAXetr column (Agilent, USA) with a 0.5 µm film thickness at a constant flow of a carrier gas 1.0 mL min<sup>-1</sup> (> 99.995%, Orenburg-Techgas, Russia). The oven temperature was programmed from 80°C (held 5 min) to 240°C with a heating rate of 10°C min<sup>-1</sup> (held 2 min). Total GC run time was 23 minutes.

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 mode (SIM). The MS program used for the detection of the UDMH TPs in the SIM mode is provided in Table 2.

# Study of the effects of temperature during air-evacuation step and incubation time

HSSPME and Vac-HSSPME were compared at room temperature (23 °C). Three sample temperatures were tested during air-evacuation step for Vac-HSSPME: 23 °C, -30 °C and frozen by LN<sub>2</sub>. Vac-HSSPME of spiked samples was conducted as described in Sect. 2.2 after air-evacuation for 120 s. The samples were incubated for 30 min in the agitator of the autosampler at 40 °C followed by 30-min manual extraction at the same temperature. After extraction, the SPME fiber was introduced into the GC inlet for desorption of analytes. Three pre-incubation times (30, 60 and 120 min) were tested with extraction time and temperature for Vac-HSSPME set at 15 min and 40 °C, respectively.

## Study of the effects of extraction temperature and time

The effect of extraction temperature was tested at 30, 40, 50 and 60 °C. In this set of experiments, spiked sand samples were stored at freezing temperature (-30 °C) before air-evacuation for 120 s. The incubation and extraction times were set at 30 min.

Extraction profiles for each target analyte were obtained at 40 °C using extraction times 5, 15-, 30-, 60- and 120-min. Air-evacuation was conducted for 20 s at 23 °C, pre-incubation lasted for 30 min at 40 °C.

## Study of the effects of air-evacuation time and temperature

Four air-evacuation times (20, 45, 60, 120 s) and two air-evacuation temperatures (23 °C and -30 °C) were studied. After incubation for 30 min, extraction for 30 min at 40 °C was conducted.

## Analytical performance of the developed method

Vac-HSSPME of sand samples was conducted for 30 min at 40 °C, evacuation time was 20 s at 23 °C, pre-incubation lasted for 30 min at 40 °C. For calibration, five standard samples were prepared by spiking 1.00 g of sand with 10.0 µL of standard solutions of target 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<sup>-1</sup> for Pan, MPA, NDMA, MTA and Pal, respectively. 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<sup>-1</sup> for PAN, 25.5 ng g<sup>-1</sup> for MPA, 69.8 ng g<sup>-1</sup> for NDMA, 131 ng g<sup>-1</sup> for MTA, 77.6 ng g<sup>-1</sup> for PAL.

## Application of the developed method

The developed method was applied for studying 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<sup>-1</sup> for Pan, MPA, NDMA, MTA and Pal, respectively (Table S1). Then, samples in open vials were kept at room

temperature (23 °C) in the hood for 3 d and then located in the freezer (-18 °C) for 5 d before analyzing using the developed method at optimized parameters.

## Results And Discussion

### *Effect of temperature during air-evacuation step*

Responses of MTA and PAI obtained by Vac-HSSPME at 23 °C were 2.1-2.3 times higher than those obtained by HSSPME while responses of Pan, MPA, and NDMA were lower by 32-76% (Fig. 2). Lower responses of Pan, MPA and NDMA after Vac-HSSPME could be caused by the losses of analytes during the air-evacuation step. Molecules of analytes are present in the headspace and can be removed from a vial together with air. To avoid such losses, freezing a sample before air-evacuation step was used as proposed by (Capetti et al. 2020).

Freezing samples before air-evacuation yielded 1.3-3.4 times higher responses of analytes (Fig. 2). These results prove that the decrease of temperature during air-evacuation allows decreasing losses of analytes. Vac-HSSPME after air-evacuation at -30 °C provided 1.3-4.8-fold higher responses of NDMA, MTA and PAI compared to HSSPME. The effect of low pressure on Pan and MPA was negligible, probably, because of their higher headspace-soil distribution constants and solid-phase resistance (Psillakis et al. 2012a).

Further decrease in air-evacuation temperature by applying LN2 did not result in a substantial increase in responses of analytes (Fig. S1 in SM). Therefore, freezing of samples at -30°C was selected as optimal for the air-evacuation step and used in the following experiments.

### *Effect of pre-incubation time*

Pre-incubation of a sample at extraction temperature is required prior to extraction for its equilibration with headspace and ensuring a reproducibility (Risticvic et al. 2010). A proper pre-incubation of a frozen sample is particularly important due to longer time of water melting and sample heating to the extraction temperature. For all UDMH TPs, responses dramatically decreased when increasing the pre-incubation time up to 30 min (Fig. S2 in SM). The highest responses of all analytes were observed at pre-incubation time 30 min. At shorter pre-incubation times, remarkably high RSDs were observed reaching 30% after 10-min pre-incubation, which can be caused by a very slow melting of frozen samples. 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*

Responses of all analytes increased by 27-80% when extraction temperature increased from 30 to 40 °C (Fig. 3). Further heating of sand samples to 50 °C led to decreased extraction effectiveness of PAn, MPA and NDMA by 26-36%, whereas responses of MTA and PAI increased by 43-60% and reached their maxima. Heating samples from 50 °C to 60 °C yielded a decrease in responses of all analytes by 10-28%.

RSDs at all studied extraction temperatures varied from 2.0 to 22%. The local maxima of extraction temperature profiles can be due to the reduction of the fiber-headspace distribution constant due to the increase of extraction temperature (Schulten and Schnitzer 1997; Kenessov et al. 2010b). An extraction temperature of 40 °C was chosen as optimal, for which RSDs were below 22%.

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

Evacuating samples for 120 s at room temperature resulted in substantial losses of analytes. It was therefore decided to investigate the effect of air-evacuation time on analyte losses as a function of sample temperature i.e. at room temperature and -30°C. Four air-evacuation times, ranging from 20 to 120 s were tested for each temperature (Fig. 4). At room temperature, reducing the evacuation time from 120 to 20 s resulted in a 25-46 % increase in responses. At the same time, decreasing the air-evacuation time of frozen samples yielded similar responses considering the variability range (RSDs) 1.0-15% (Fig. 4, b). Paired sample *t*-test confirmed that there was no significant difference between analytes' responses obtained by Vac-HSSPME at air-evacuation times of 20 and 120 s at -30°C ( $P > 0.05$  for four analytes). Moreover, the results for 20 s of evacuation were the same for the two sample temperatures tested (Fig. 5).

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, 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. Based on the above results and discussion, it was decided to air-evacuate the samples at room temperature for 20 s.

### ***Effect of extraction time***

For all studied UDMH TPs, responses increased when increasing the extraction time from 5 to 30 min (Figure 6). A plateau of PAn, MPA and NDMA responses was reached at extraction time 30 min. 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.

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 as it apparently provides best combination of precision and sensitivity for determination of UDMH TPs in sand samples using Vac-HSSPME. Longer extraction time may cause an increase in errors due to the saturation of SPME fiber coating and enhanced competition with matrix compounds (Risticvic 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 3). 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<sup>-1</sup>.

Spike recoveries of target analytes from sand samples were 84-97% with RSDs 1.0-11% (Table 4), 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 d of storage in open vials showed substantial losses varying from 41 to 94% (Table 5). 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, highest relative losses (%) were observed at highest initial concentrations. For Pal, there was no trend. Among analytes, highest losses (90.2-94.3%) were observed for Pan. Lowest losses (41-42%) were for MPA at initial concentrations 20 and 30 ng g<sup>-1</sup>, while initial concentration of MPA 39 ng g<sup>-1</sup> yielded a 69±4% reduction. Initial concentrations of NDMA 60 and 89 ng g<sup>-1</sup> resulted in 76±4 and 73.3±1.7% decrease, respectively, whereas the concentration 119 ng g<sup>-1</sup> showed an 85.4±1.8% reduction.

### *Comparison of the developed method to other methods based on HSSPME*

Compared to existing methods based on HSSPME, the developed method provides lower detection limits (Table 6), 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.

## **Conclusion**

Thus, the new method has been developed for simultaneous quantification of major transformation products of toxic rocket fuel unsymmetrical dimethylhydrazine in sand using vacuum-assisted headspace solid-phase microextraction. Extraction under vacuum at 30°C allowed achieving 1.3-4.8-fold higher responses of NDMA, MTA and PAI compared to regular HSSPME. Air-evacuating the sample for 120 s at room temperature resulted in major losses of analytes. Decreasing the air-evacuation time from 120 to 20 s at room temperature allowed 25–46% fold 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 room temperature, 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 varied from 0.035 to 3.6 ng g<sup>-1</sup>.

It has been proven 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 confirmed 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 developed method has several important advantages over existing methods including lower detection limits, better accuracy and precision. Its major advantage over other existing methods based on HSSPME is the extraction at the 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 soil contaminated with rocket fuel. It could be used for research experiments on transformation and evaporation of UDMH transformation products where their concentrations can reach 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.

## Declarations

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Availability of data and materials** All data generated or analysed 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.

**Competing interests** The authors declare that they have no competing interests.

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## Authors' contributions

**Aray Zhakupbekova:** Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – Review & Editing, Visualization. **Nassiba Baimatova:** Conceptualization, Methodology, Writing – original draft, Writing – Review & Editing, Project administration. **Elefteria Psillakis:** Conceptualization, Writing – Review & Editing. **Bulat Kenessov:** Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition.

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## Tables

**Table 1**

Physicochemical properties of analytes.

Analytes		Molecular weight (Da)	$K_H$ (atm m <sup>3</sup> mole <sup>-1</sup> )	log $K_{ow}$	Boiling point (°C)
PAn (≥99.0%)	Meryer, China	80.1	$2.92 \cdot 10^{-6}$	-0.26	115
MPA (≥98.0%)		82.1	$7.88 \cdot 10^{-5}$	0.23	127
MTA (≥98.0%)		83.1	$3.26 \cdot 10^{-5}$	-0.21	187
Pal (≥99.0%)		68.1	$3.69 \cdot 10^{-6}$	0.26	187
NDMA (≥99.5%)	Supelco, USA	74.1	$1.82 \cdot 10^{-6}$	-0.57	154

**Table 2**

MS detection program for UDMH TPs in SIM mode.

Analyte	Retention time (min)	CAS Number	Quantification ions ( $m/z$ , (dwell))	Confirmation ion ( $m/z$ )	Group start time (min)
PAn	10.9	290-37-9	80 (100)	53	10.0
MPA	11.5	930-36-9	82 (100)	81	
NDMA	12.8	62-75-9	74 (100)	42	13.0
MTA	16.9	6086-21-1	83 (100)	56	16.0
PAI	19.5	288-13-1	68 (100)	41	18.6

**Table 3**

Analytical performance of the developed method.

Compound	Concentration range (ng g <sup>-1</sup> )	R <sup>2</sup>	RSDs of slope (%)	LOD (ng g <sup>-1</sup> )	LOQ (ng g <sup>-1</sup> )
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

**Table 4**

Recoveries of target analytes from spiked sand samples obtained using the developed method based on Vac-HSSPME.

Analytes	Spiked (ng g <sup>-1</sup> )	Determined (ng g <sup>-1</sup> )	Recovery (%)
PAn	15.1	12.7±0.5	84±4
MPA	25.5	23±2	89±11
NDMA	69.8	63±4	91±7
MTA	131	122.5±1.3	93.7±1.0
PAI	77.6	75±8	97±10

**Table 5**

Concentrations of analytes in model sand samples after keeping them in open 20-mL vials for 3 d determined using the developed method.

Compound	Spiked concentration (ng g <sup>-1</sup> )			Measured concentration (ng g <sup>-1</sup> )			Losses (%)		
	S1	S2	S3	S1	S2	S3	S1	S2	S3
PAn	18	27	36	1.70±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	17.0±2.2	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

**Table 6**

Methods for determination of UDMH TPs in soil samples based on HSSPME.

Analytes	Sample amount (g)	Volume of extraction solvent (mL)	Sample preparation	Optimized parameters	Quantification approach	Detection limit (ng g <sup>-1</sup> )	Analytical parameters		Ref
							R <sup>2</sup>	RSD (%)	
21 UDMH TPs	1	5	HSSPME from aqueous extracts	85- $\mu$ m Car/PDMS at 40 °C for 60 min, 1.5 g NaCl	Screening	-	-	-	(Kenessov et al. 2010b)
MTA	1	-	HSSPME	85- $\mu$ m Car/PDMS at 80 °C for 1 min	Isotopic dilution	1000	n/p	<17	(Yegemova et al. 2015)
19 UDMH TPs	1	-	HSSPME	Pre-incubation for 5 min, 85- $\mu$ m Car/PDMS at 40 °C for 60 min	Standard addition + internal standard	1.0-14	0.9352-0.9921	<22	(Bakaikina et al. 2018)
Pan MPA NDMA MTA MIA PAI	2	7	Vac-HSSPME from aqueous extracts	Incubation for 10 min, evacuation for 120 s, 85- $\mu$ m Car/PDMS at 50 °C and 1500 rpm for 30 min, 35% NaCl	Standard addition	0.2-9	0.991-0.998	0.9-7.7	(Orazbayeva et al. 2018b)
Pan MPA NDMA MTA PAI	1	-	Vac-HSSPME	Pre-incubation for 30 min, evacuation for 20 s, 85- $\mu$ m Car/PDMS at 40 °C for 30 min	-	0.04-4	0.9912-0.9938	<4.7	This study

Note: n/p - not provided

## Figures

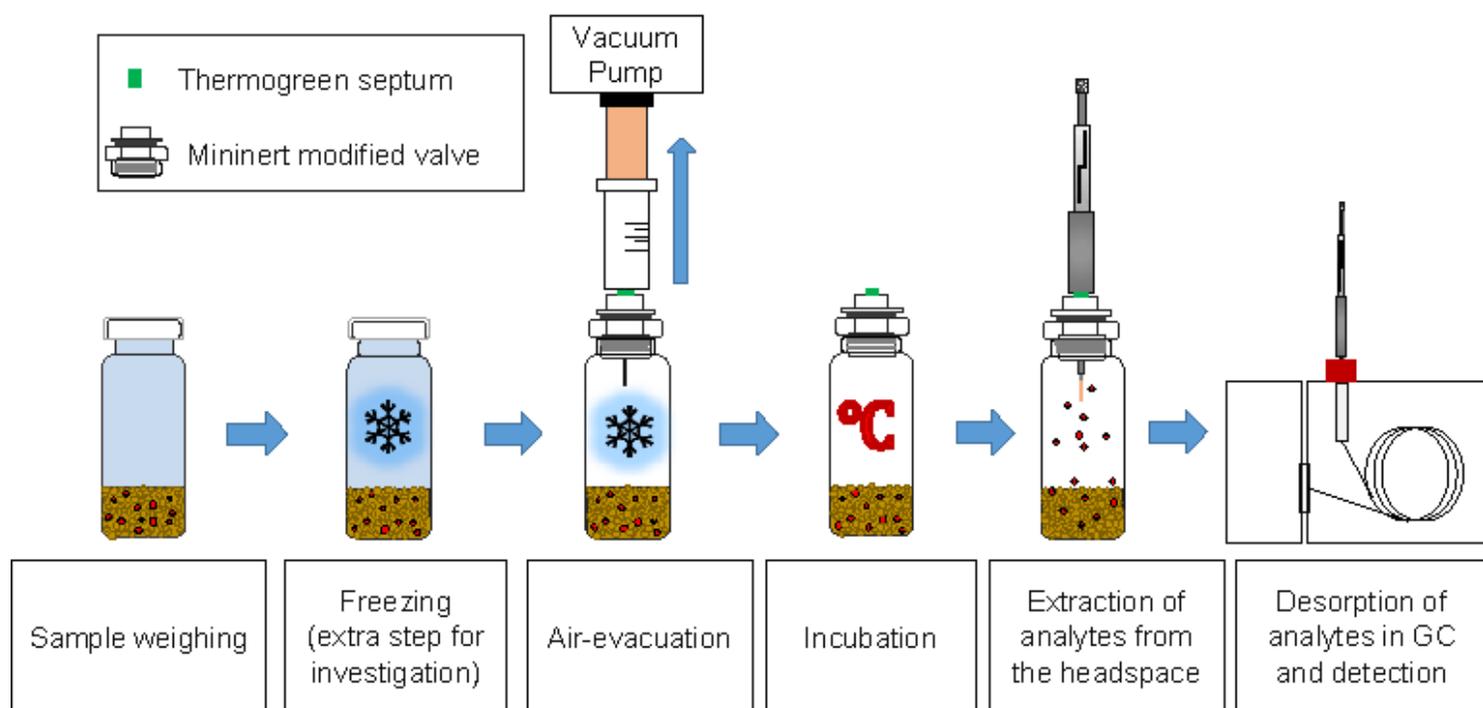


Figure 1

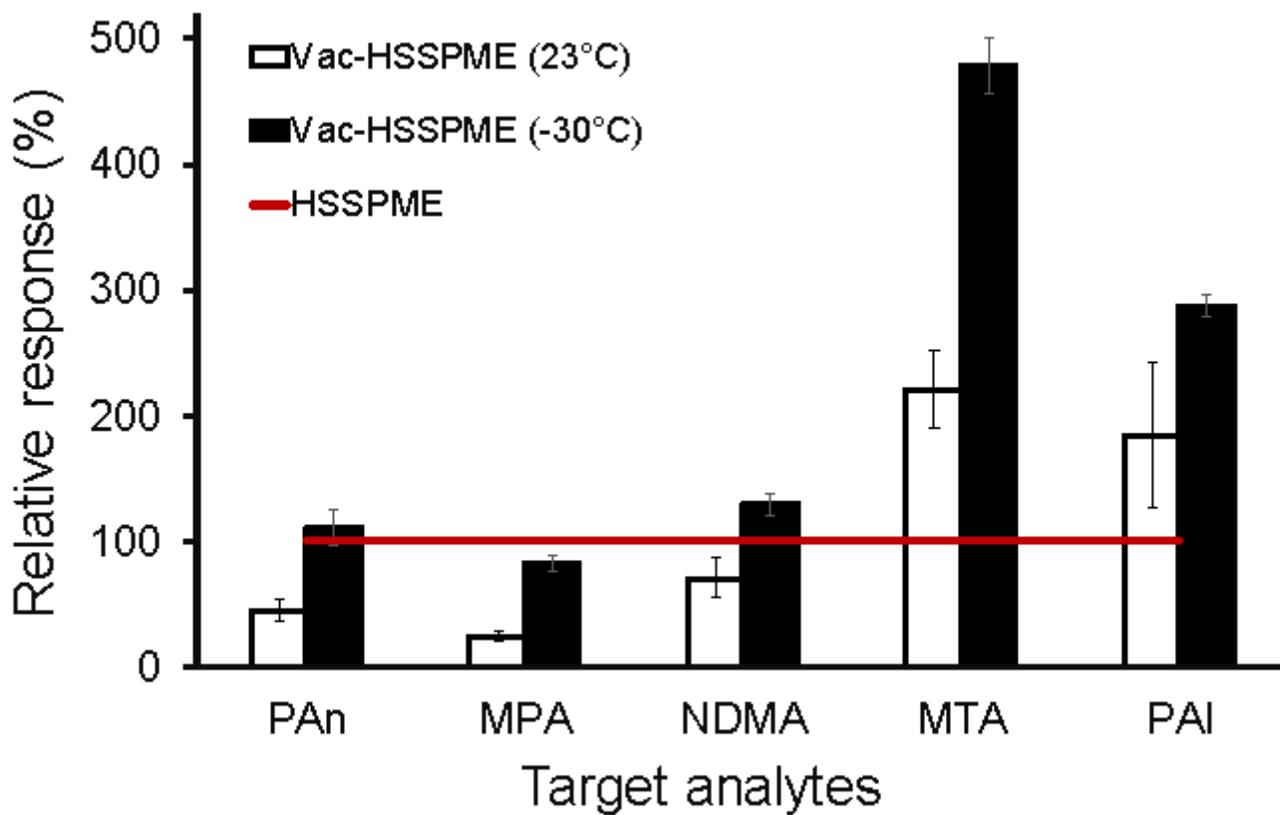


Figure 2

Effect of air-evacuation temperature on UDMH TPs responses by Vac-HSSPME in comparison with HSSPME. Evacuation time 120 s, incubation time 30 min, extraction time 30 min, Car/PDMS fiber

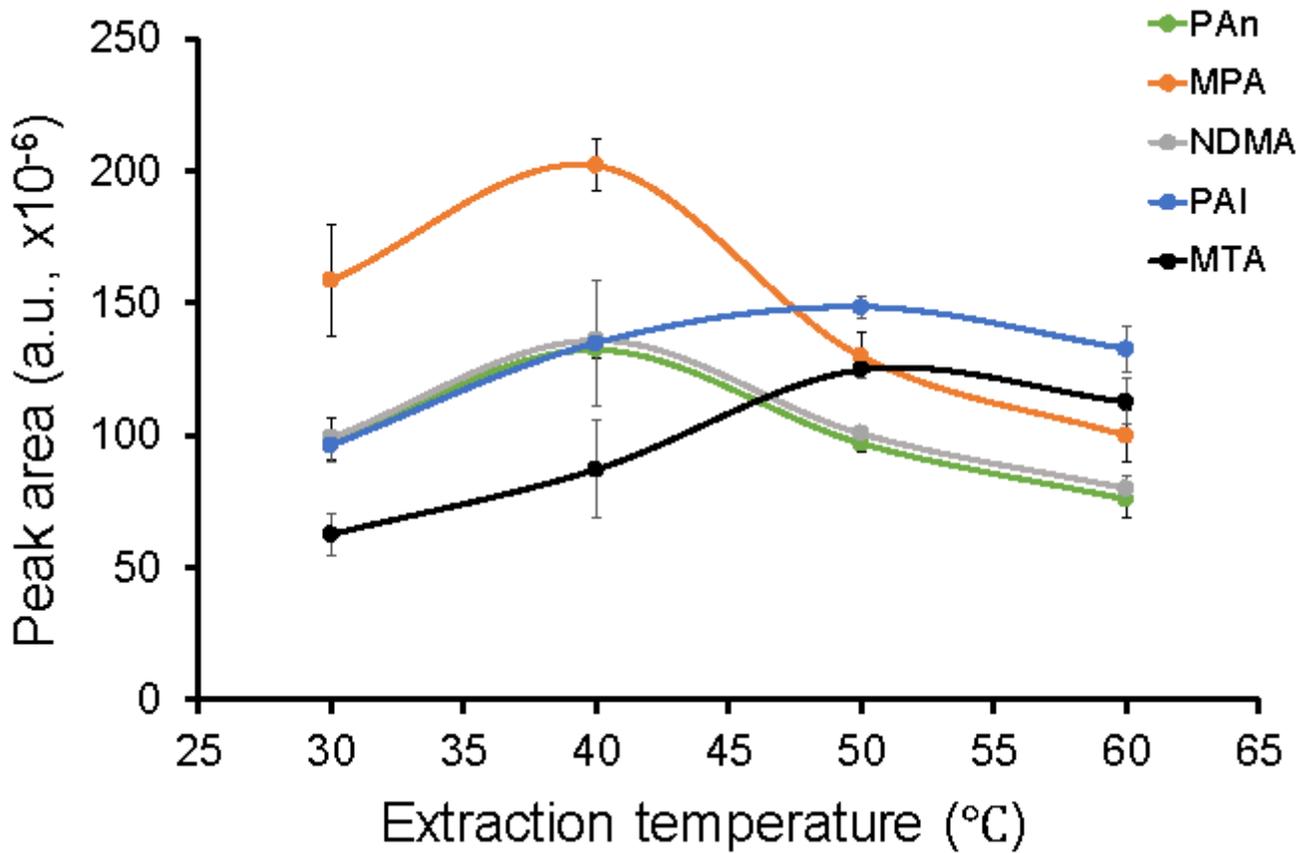


Figure 3

Effects of extraction temperatures on UDMH TPs responses by 30-min Vac-HSSPME of sand samples (air-evacuated at -30°C for 120 s, incubated for 30 min, Car/PDMS fiber)

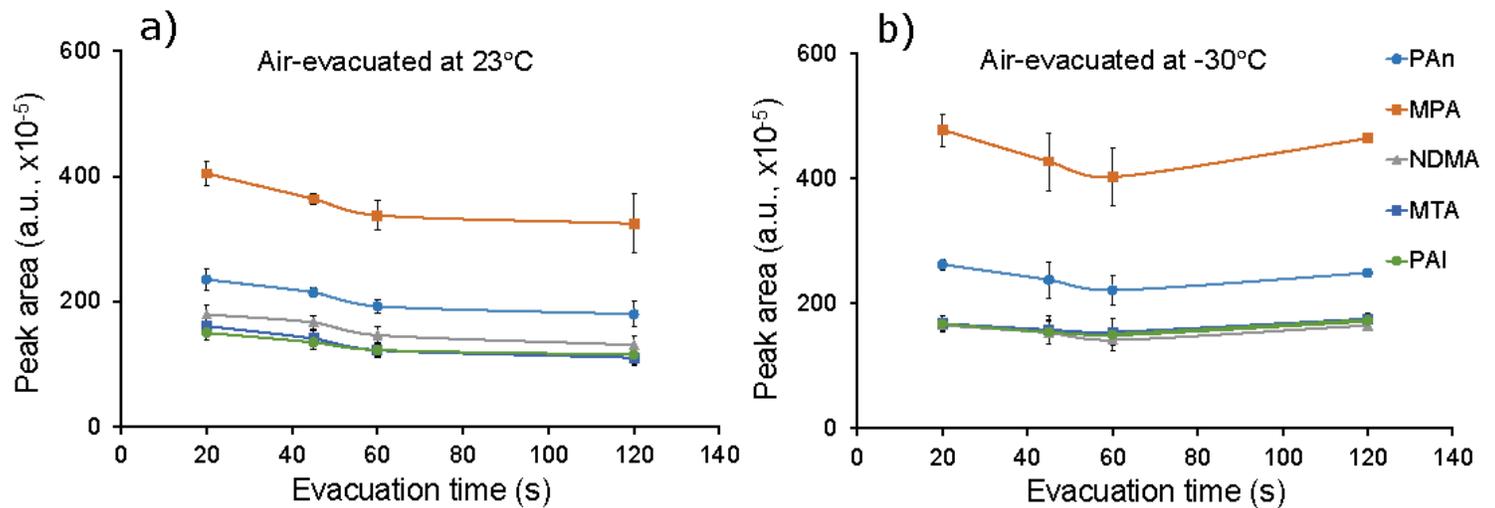
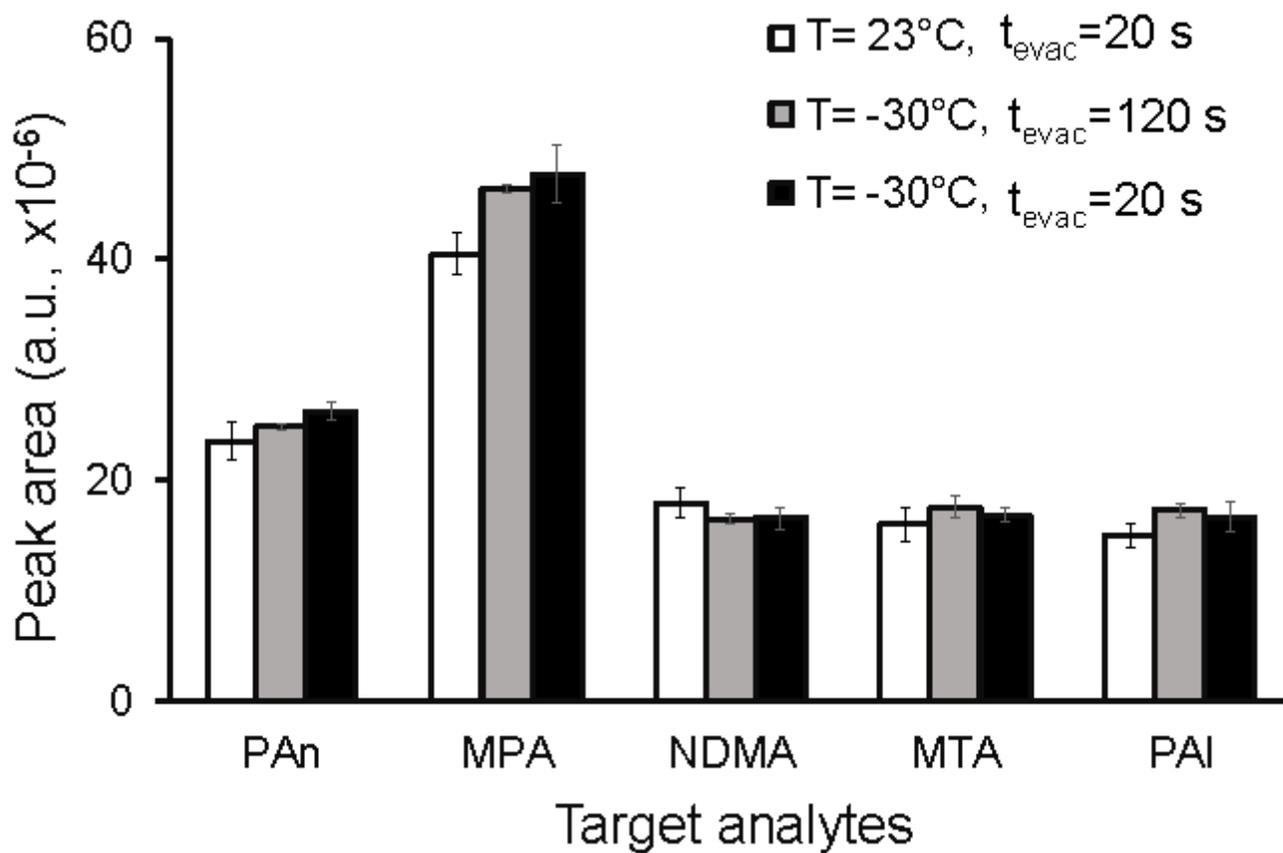


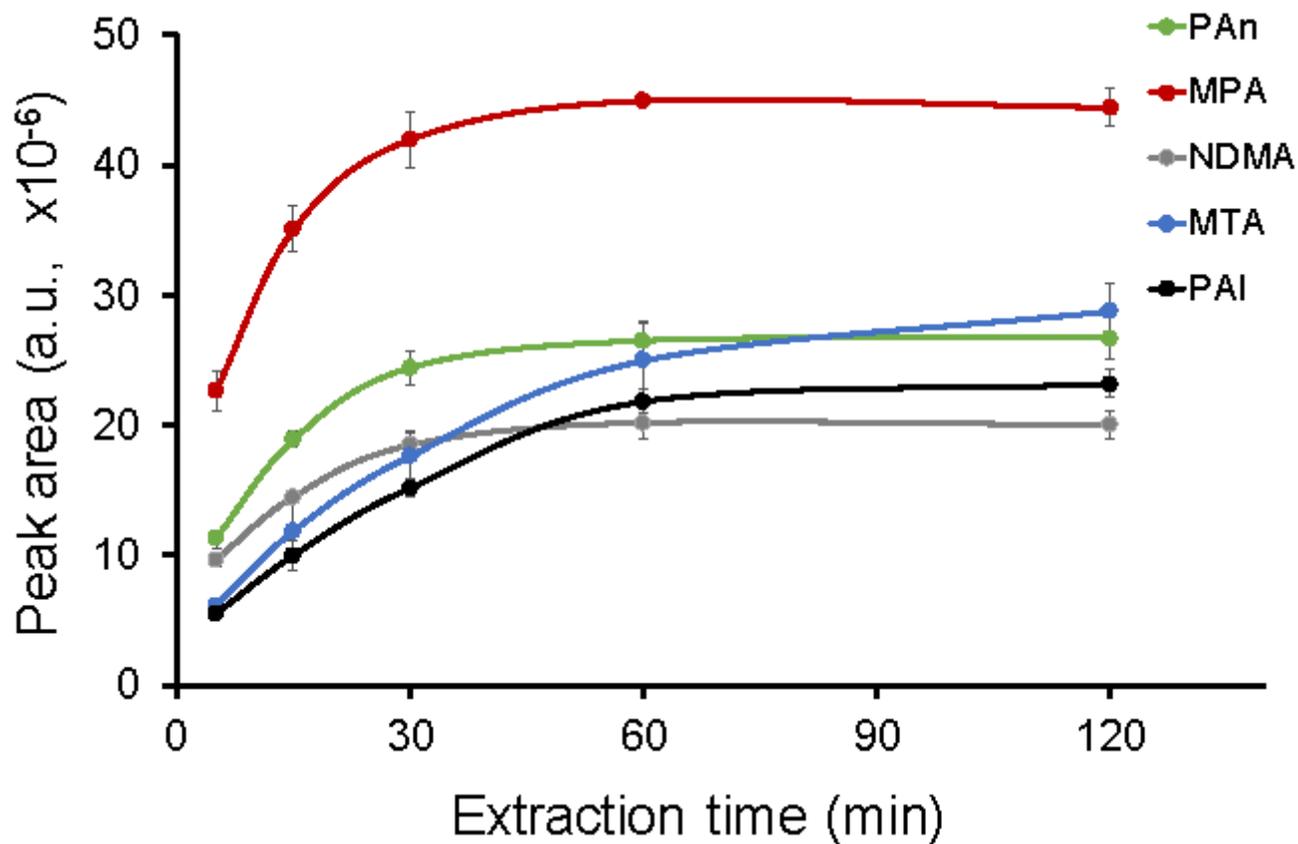
Figure 4

Effect of evacuation time at sample temperatures 23 °C (a) and -30 °C (b) on UDMH TPs responses after Vac-HSSPME at 40°C for 30 min using Car/PDMS fiber



**Figure 5**

Effects of air-evacuation time and temperature on response of analytes (extraction temperature  $40^{\circ}\text{C}$ , incubation time 30 min, extraction time 30 min, Car/PDMS fiber)



**Figure 6**

Effects of extraction time on UDMH TPs responses. Tevac=23°C, tevac=20 s, T = 40°C, tinc=30 min, Car/PDMS fiber

## Supplementary Files

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