ORIGINAL

GC–MS and GC–NPD Determination of Formaldehyde Dimethylhydrazone in Water Using SPME

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Abstract Formaldehyde dimethylhydrazone (FADMH) is one of the important transformation products of residual rocket fuel 1,1-dimethylhydrazine (1,1-DMH). Thus, recent studies show that FADMH toxicity is comparable to that of undecomposed 1,1-DMH. In this study, a new method for quantification of FADMH in water based on solid phase microextraction (SPME) in combination with gas chromatography (GC) with mass spectrometric (MS) and nitrogen-phosphorus detection (NPD) is presented. Effects of SPME fiber coating type, extraction and desorption temperatures, extraction time, and pH on analyte recovery were studied. The optimized method used 65 micron polydimethylsiloxane/divinylbenzene fiber coating for 1 min headspace extractions at 30 °C. Preferred pH and desorption temperature from the SPME fiber are >8.5 and 200 °C, respectively. Detection limits were estimated to be 1.5 and 0.5 $\mu g\ L^{-1}$ for MS and NPD, respectively. The method was applied to laboratory-scale experiments to quantify FADMH. Results indicate applicability for in situ sampling and analysis and possible first-time detection of free FADMH in water.

Introduction

Formaldehyde dimethylhydrazone (FADMH) is one of the most significant transformation products of residual rocket fuel 1,1-dimethylhydrazine (1,1-DMH) distributed in the environment following the drop of the burned-out first stage of "Proton" and "Dnepr" rockets [1, 2]. Many European, Russian, Indian, and Chinese heavy cargo rockets also use 1,1-DMH as fuel. Previous studies have suggested that FADMH toxicity can be compared to the undecomposed rocket fuel 1,1-DMH [3, 4] itself. On the basis of these findings it was proposed to include FADMH into the list of priority transformation products of 1,1-DMH in the environment. Although FADMH has not up to now been detected in on-site samples of soil, water or air from the rocket fall-out regions, laboratory experiments strongly suggest the important role of this compound in the eventual formation of the suite of transformation products previously studied [5].

One of the main reasons for not detecting FADMH in on-site samples is most likely its high volatility [4]. Another possible reason may be a high reactivity of FADMH causing degradation during transport of the on-site samples for the analysis in the laboratory. Finally, the conventional sampling preparation approaches for detecting 1,1-DMH transformation products and relatively high detection limits may have caused the apparent absence of FADMH in the samples. The research described in this paper addresses these limitations.

A new sensitive method for detection and quantification of FADMH in water has been developed using solid phase

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microextraction (SPME) coupled to GC–MS and GC-NPD. GC–MS was already proven to be a highly sensitive and efficient analytical method for detection [2] and quantitative determination [6] of volatile transformation products of 1,1-DMH. The use of nitrogen-phosphorus detection also provided highly sensitive gas chromatographic determination of hydrazines and *N*-nitrosodimethylamine in aqueous samples [7–9]. SPME technology combines sensitive sampling and sampling preparation. SPME has been used for quantification of an increasing number of complex environmental assessment applications such as indoor air [10, 11], biological processes [12], livestock waste characterization [13], and the desorption kinetics of PAHs from soils and sediments [14]. SPME in combination with GC–MS has already shown a high efficiency for screening of volatile transformation products in soils contaminated with 1,1-dimethylhydrazine [15]. The long term objective of this research program is to elucidate the possible environmental impact using an appropriate in situ sampling and analysis method for possible free FADMH as well as other important transformation products [3, 4]. These new and improved methods will enable researchers to conduct fundamental work on the chemistry and environmental fate of rocket fuel.

Experimental

Chemicals

Formaldehyde dimethylhydrazone (CAS 2035-89-4) was synthesized according to the method described in [16], which is based on interaction of 1,1-dimethylhydrazine with formaldehyde with subsequent purification of the product. The purity of synthesized compound was verified to 98% by GC–MS. Sodium chloride used was of 'chemically pure' quality.

Instrumentation

Analyses by GC–MS and GC–NPD were carried out using an Agilent 6890/5973 N (Agilent, Santa Clara, USA) system equipped with NPD (G1575A, Agilent) and a CTC Combi-PAL autosampler (CTC Analytics AG, Switzerland). The autosampler was equipped with a 32-position 10/20 mL tray, 10/20 mL agitator, SPME fiber holder and a conditioning station. The GC was equipped with split/splitless inlet working in splitless mode to a 30 m × 0.25 mm HP-Innowax column with a 0.25 μm film thickness (Agilent). Helium (99.995%, Orenburg, Russia) was used as carrier with a constant flow rate of 1 mL min^{-1}. Air was supplied to NPD using Parker Balston (Denmark)

Zero Air Generator model 75-83-220 and Jun-Air (Denmark) OF302-25B compressor. Hydrogen was supplied to NPD using Parker Balston (Denmark) H2-90 Hydrogen Generator. Oven temperature was programmed from 40 °C (5 min) to 110 °C using a 5 °C min^{-1} ramp followed by a 10 °C min^{-1} ramp to 240 °C. Total run time was 32 min.

The mass spectrometric detection (MSD) was carried out in electron impact ionization mode (70 eV). The temperatures of source and quadrupole were set to 230 and 150 °C, respectively and the temperature of the MS interface being 240 °C. Detection was performed in selected ion monitoring (SIM) mode selecting molecular ion having $m/z = 72$ (dwell time = 100 ms) as the target for FADMH. ChemStation (ver. E.01.01.335) software was used to control the instrumentation including autosampler and data treatment. Wiley 7th edition and NIST'05 MS libraries were used for mass spectral searches.

Nitrogen-phosphorus (NP) detection was carried out under the following parameters: temperature = 250 °C, hydrogen flow = 3 mL min^{-1}, air flow = 60 mL min^{-1}, makeup flow (He) = 20 mL min^{-1}, and current offset = 30 pA. Before the first run, the detector was running in "adjust offset" mode as recommended by the manual.

SPME

Ten milliliter headspace screw top vials (Agilent P/N 5188-2753) with ultra clean 18 mm PTFE/silicone septa screw caps were used for all experiments. Prior to use, vials and caps were washed with double-distilled water followed by conditioning for 3 h at 180 °C. Three different fiber coatings were tested for selectivity to FADMH: 65 μm divinylbenzene/polydimethylsiloxane (DVB/PDMS), 50/30 μm DVB/Carboxen/PDMS and 85 μm Carboxen/PDMS (CAR/PDMS) using sampling time 10 min, sampling temperature 30 °C and desorption temperature 200 °C. All fibers were obtained from Supelco, Bellefonte, PA, USA. Headspace sampling and sample preparation with SPME was carried out using the CTC Combi-PAL autosampler. Prior to the first use, fibers were conditioned in the injector port at their respective recommended conditioning temperatures. Water sample volume in all experiments was chosen to be 2 mL. Sodium chloride (0.7 g) was added to the vials prior to sampling to increase the FADMH volatilization. Subsequently, SPME was carried out in headspace mode without stirring. Optimal sampling and desorption temperatures and time as well as appropriate sample pH were determined experimentally (vide infra). All the experiments on optimization of SPME parameters were carried out using MS detection.

Calibration Curves

A calibration curve for GC–MS was obtained on the basis of the analyses of eight FADMH standard solutions of 5.0, 10.0, 30, 50, 100, 200, 500 and 1,000 $\mu g\ L^{-1}$, respectively, using the below determined and optimized sampling and sample preparation parameters.

A calibration curve for GC–NPD was obtained on the basis of the analyses of seven FADMH standard solutions of 1.0, 3.0, 10.0; 30; 50; 100 and 200 $\mu g\ L^{-1}$, respectively, using the below determined and optimized sampling and sample preparation parameters.

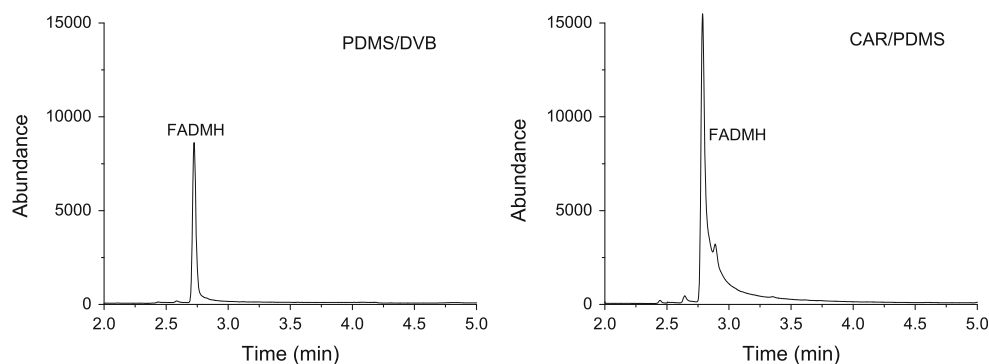All solutions were prepared in 0.005 M solution of KOH and analyzed in triplicate.

Calculation of Method Detection Limits

Method detection limit was calculated using EPA 40CFR136 protocol, where seven standard solutions of FADMH with concentrations equal to 10 $\mu g\ L^{-1}$ were analyzed using the developed method. Then the calculated value of standard deviation was multiplied by Student's t number for 99% confidence (2.896).
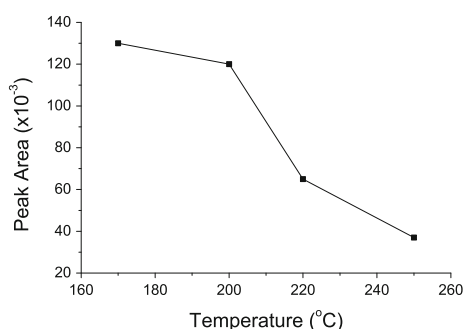
Fig. 1 The effect of GC injection-thermal desorption temperature on FADMH recovery

Results and Discussion

Selection of the optimal thermal desorption parameters

It is known that FADMH has a high reactivity and becomes quite unstable at elevated temperatures [2]. The possible effect of GC inlet temperatures equal to 170, 200, 220 and 250 °C on the FADMH recovery was studied using 85 μm CAR/PDMS fiber (Fig. 1). The data summarized in Fig. 1 unambiguously disclosed that with an increase of temperature, significant decrease of the FADMH recovery occurred when the GC inlet temperature was increased to above 200 °C, which was selected as optimal GC inlet temperature.

Selection of the Optimal SPME Fiber and Optimization of GC Injection: Thermal Desorption Parameters

Selection of the fiber coating was based on FADMH recovery and peak shape both of which significant affect efficiency of separation and sensitivity of detection.

In spite of the fact that the 85 μm CAR/PDMS fiber coating provided the highest recovery of FADMH, it was observed that its very strong affinity to the analyte lead to the much slower desorption of FADMH from the fiber in GC inlet port resulting in a highly unsymmetrical tailing peak of FADMH and poor resolution making chromatographic separation impossible for real field samples contaminated with 1,1-DMH.

Comparison of the chromatograms obtained using different fibers showed that the best peak shape was observed when using 65 μm PDMS/DVB fiber (Fig. 2) which was chosen as optimal SPME coating for the method.

Determination of the Optimal Extraction Temperature

To determine the optimal extraction temperature, solutions of FADMH having concentration 50 $\mu g\ L^{-1}$ were analyzed using extraction temperatures 30 °C (lowest possible

Fig. 2 SIM (*m/z* 72) chromatograms of FADMH solution (100 $\mu g\ L^{-1}$) obtained using PDMS/DVB and CAR/PDMS fibers
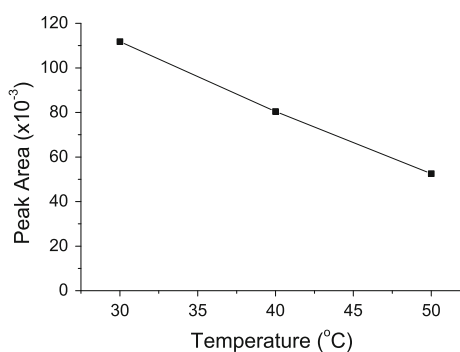
Fig. 3 Effect of extraction temperature on FADMH response ($C_{\text{FADMH}} = 50 \, \mu g \, L^{-1}$)

temperature for agitator of CTC Combi-PAL autosampler), 40 and 50 °C (Fig. 3).

It was observed that 30 °C was the optimal extraction temperature and the increase of temperature lead to a decrease of FADMH response, which could be caused by the decrease of distribution constant of FADMH between fiber and headspace.

Determination of the Optimal Sampling Time

Increase of SPME sampling time usually results in an increase in analyte recovery [12] and therefore improved detection limits. However, it should be taken into account that an increase in sampling time may also lead to a proportional increase in error of the quantitative method due to the limited sorption capacity of porous SPME fiber coatings [17–19]. To determine the optimal sampling time for the quantitative method, aqueous solutions of FADMH with a concentration of 50 $\mu g \, L^{-1}$ were analyzed using extraction times of 0.17, 0.33, 0.5, 1, 2, 5 and 10 min.

It is noted that the obtained plot is virtually linear in the range of 0–1 min followed by a gradual levelling off, eventually reaching a plateau. It can further be noted that the increase of sampling time to higher than 1 min only leads to minor increase in the eventual recovery. Thus, taking all practical factors into account, a 1 min sampling time has been chosen as optimal as it apparently provides a satisfactory high sensitivity, whereas additional increase of a sampling time may cause an increase of errors due to the limited sorption capacity of SPME fiber coating [18, 19].

Effect of pH on FADMH Recovery

FADMH is a weak base with the pK_a value of the corresponding acid being estimated to be 5 ± 1.9 [20] that is rapidly hydrolyzed in acidic medium [21]. We studied the FADMH sample recovery as a function of pH in order to select the optimal pH for the analyses to avoid hydrolysis (and to maximize sample recovery) during the analyses.
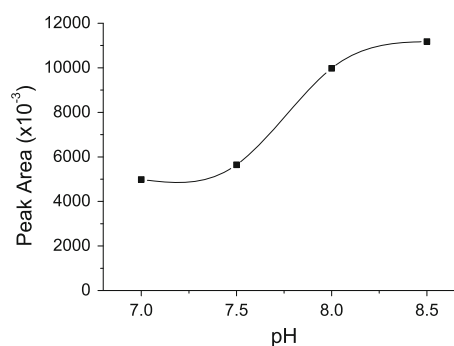
Fig. 4 Effect of pH on FADMH response using SPME–GC–MS

Thus, FADMH solutions of 10 mg L^{-1} in buffer solutions of pH 7.0, 7.5, 8.0, and 8.5, respectively, were analyzed using SPME (10 min headspace extractions at 30 °C) followed by analyses on GC–MS (Fig. 4).

The shape of the curve is in agreement with the calculated pK_a value. It is obvious (Fig. 4) that an increase in pH results in a significant increase in FADMH recovery due to the increased stability of FADMH the basic medium. Thus, it was concluded that all analyses of FADMH samples should then be carried out only following adjustment of the sample pH to values above 8.5, by adding an appropriate amounts of a KOH solution.

Calibration Curves

The calibration curve when using MS and NP detection is linear in the concentrations interval of 5–500 $\mu g \, L^{-1}$ and 1–100 $\mu g \, L^{-1}$, respectively, and can be described by the following equations:

$$S = 2.3135 \times C_{\text{FADMH}} + 8.14 \, (\text{for MS}, R^2 = 0.9998)$$

$$S = 123.6 \times C_{\text{FADMH}} + 222 \, (\text{for NP}, R^2 = 0.9997)$$

where S–FADMH peak area, $\times 10^{-3}$ and C_{FADMH} the FADMH concentration, $\mu g \, L^{-1}$.

Detection limit calculated using standard deviation method was found equal to 1.5 $\mu g \, L^{-1}$ for MS and 0.5 $\mu g \, L^{-1}$ for NP detection. The relative standard deviations were in all cases found to be less than 10%.

Evaluation of the Method Precision

Evaluation of precision (repeatability and reproducibility), accuracy and uncertainty of determination of FADMH in water for the whole range of concentrations being determined was made according to the State Standard of Kazakhstan [22].

The repeatability and reproducibility were evaluated by statistical processing of the results of analysis of water samples having concentrations of FADMH. For each

**Table 1** Determined values of the method precision

No	Detection	Average concentration of FADMH, µg L^{-1}	Index of repeatability, µg L^{-1} (%)	Index of reproducibility, µg L^{-1} (%)
1	MS	26.7	2.2 (8.2)	2.6 (9.7)
2		67.7	5.1 (7.5)	6.3 (9.3)
3		217.2	18.3 (8.4)	16.5 (7.6)
1	NP	2.6	0.22 (8.5)	0.25 (9.6)
2		17.0	1.4 (8.2)	1.5 (8.8)
3		75.2	5.3 (7.0)	6.0 (8.0)

method, linear concentration interval was divided into a three sub-ranges. For each sample, 10 experiments were made in duplicates according to the developed method.

The determined values are represented in Table 1.

Application of the Method for Analysis of Real Samples

Analyses of six real water samples taken from rivers located in the heavy rocket-carries fall-out zones in Central Kazakhstan 6 months before analysis did not allow to detect FADMH as well as other transformation products of 1,1-DMH transformation. An experimental data on FADMH fate in the environment required for organization of a detailed sampling in fall-out zones is absent. The developed method will be further used for investigation of FADMH formation and transport in the environment.
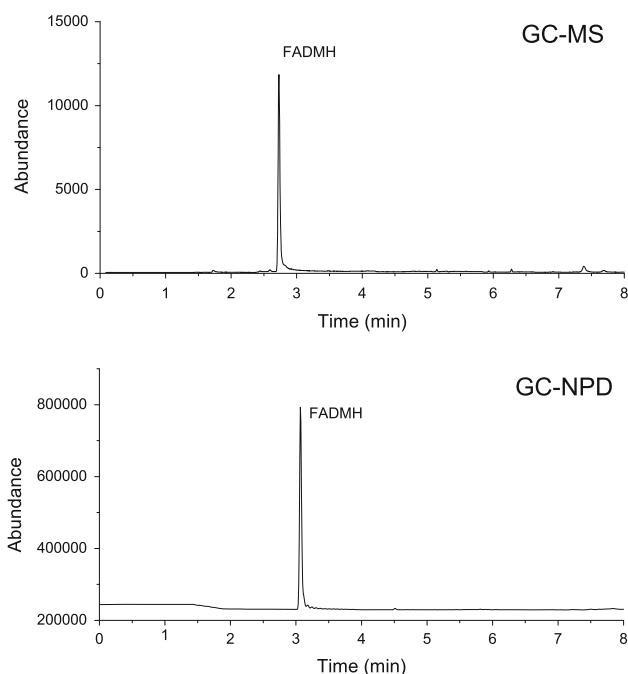
The developed method was successfully applied to a series of samples originating from laboratory-scale experiments on the transformations of spiked 1,1-DMH in water and aqueous extracts from native Kazakh soils taken from the fall out regions of burned-out rockets in Central Kazakhstan. An illustrative example of the resulting chromatogram of generated FADMH is presented in Fig. 5. The measured concentration of FADMH in the studied sample was 102 µg L^{-1} (MSD) and 100 µg L^{-1} (NPD). The use of the developed method allowed about two orders of magnitude decrease of FADMH detection limit compared to the HPLC–DAD method used in similar experiments described in the paper [5].

Conclusions

The present paper described a highly sensitive analytical method for determining formaldehyde dimethylhydrazone in aqueous solutions. The analytical method is based on solid phase microextraction in combination with gas chromatography with mass spectrometric and nitrogen phosphorus detection. Optimal parameters for the developed analytical procedure are presented. These involve 1 min headspace extractions with 65 micron PDMS/DVB fiber coating at 30 °C. Preferred pH and desorption temperature from the SPME fiber are >8.5 and 200 °C, respectively. The detection limit was estimated to be 1.5 and 0.5 µg L^{-1} for GC–MS and GC–NPD methods, respectively. The method was applied to laboratory-scale experiments to quantify FADMH. Results indicate applicability for in situ sampling and analysis and possible first-time detection of free FADMH in water.

Fig. 5 Chromatogram of a water sample polluted with FADMH obtained using GC–MS and GC–NPD. Conditions: 65 µm PDMS/DVB fiber, sampling 30 °C (1 min), desorption 200 °C (2 min)

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