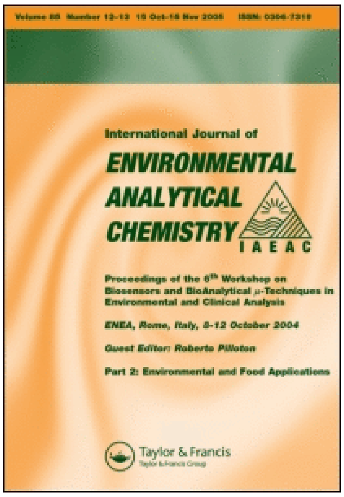

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1-Formyl-2,2-dimethylhydrazine as a new decomposition product of 1,1-dimethylhydrazine

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1-Formyl-2,2-dimethylhydrazine as a new decomposition product of 1,1-dimethylhydrazine

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A new decomposition product of 1,1-dimethylhydrazine (UDMH), 1-formyl-2,2-dimethylhydrazine (FDMH), was found in water and soil samples. The formation of FDMH was confirmed by LC-MS and NMR studies. The possibility of FDMH conversion to initial UDMH by alkaline hydrolysis was shown.

Keywords: Environmental pollution; 1,1-Dimethylhydrazine degradation; 1-Formyl-2, 2-dimethylhydrazine; LC-MS

1. Introduction

1,1-Dimethylhydrazine (UDMH) is widely used as a rocket fuel. UDMH enters the environment when the residues of fuel spill onto overland ecosystems during the landing of used rocket tanks. Therefore, attention has been focused on the evaluation of negative effects of UDMH to human health [1] and the development of techniques for UDMH determination [2–10]. However, the dangers of UDMH are its high reactivity and a huge list of possible decomposition products. Some of these, such as nitrosodimethylamine, are highly toxic and have carcinogenic and mutagenic properties. Moreover, it should be noted that UDMH is considered in the literature as an intermediate product of nitrosodimethylamine formation during chlorination for drinking-water disinfection [11].

The decomposition products of UDMH were identified by UV spectrometry [12], gas chromatography [12, 13], and GC-MS [14]. Nowadays, the identity of two UV spectra or a coincidence of retention times of test substances and standards on the one chromatographic column are not sufficient for confirmation of the compound structure. GC-MS is a powerful method providing two-scale information for the unequivocal identification of compounds, albeit with some limitations concerning polarity, volatility, and high-temperature stability of the test compound. Thus, some

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decomposition products of UDMH especially arising in aqueous phases can be lost. LC-MS does not have the above problems with compound properties and seems to be the most suitable method with which to study products of UDMH. The aim of this work was to study the decomposition products of UDMH using LC-MS.

2. Experimental

2.1 *Chemicals*

Merck 1,1-dimethylhydrazine (99+%) was used as a standard and the initial substance for FDMH synthesis [15] without further purification. All other reagents employed in this study were of reagent or analytical grade. Hydrochloric acid, acetic acid, sulfuric acid, sodium hydroxide, potassium chloride, potassium acetate, and ammonium acetate were from Aldrich Co. 1,1-Dimethylhydrazine and 1-formyl-2,2-dimethylhydrazine standard solutions ($1\,g\,L^{-1}$) were prepared in 1 M H_2SO_4 and deionized water, respectively, and stored in a dark place at 4°C. Working solutions were prepared daily in various concentrations by dissolving standard solutions with 10 mM H_2SO_4.

2.2 *Instrumentation and analytical methods*

A Shimadzu LCMS 2010A chromatographic system (Shimadzu, Japan) equipped with an LC-10 ADvp pump, DGU-14A degasser, Rheodyne 7725i injector with 0.02 mL sample loop, and quadrupole mass spectrometric detector was used. The MS-detection parameters are as follows: electrospray ionization (ESI); positive ion registration mode; a full scan, 40–150 m/z range; temperature source, 250°C; nitrogen flows for desolvatation and nebulizing gas, $10\,L\,min^{-1}$ and $1.5\,L\,min^{-1}$, respectively; and capillary voltage, 4 kV.

Another liquid chromatograph used was a modular system consisting of an LC-10ADvp pump (Shimadzu, Japan), a Rheodyne Model 7125 sample injector (Rheodyne, Cotati, CA) with a 0.25 mL sample loop, and a Tsvet-Yauza amperometric detector (Chimavtomatika, Russia) with a glassy-carbon working electrode; the applied potential was +1.3 V (DC mode).

The separation was carried out using a 2 × 150 mm stainless steel column packed by Nucleosil 10 SA (5 μm). The flow rate was $0.2\,mL\,min^{-1}$. Ammonium acetate buffer solution (100 mM, pH 5.4) was used as a mobile phase.

Column eluates were collected by a Shimadzu FRC-10A fraction collector for subsequent examination. NMR spectra (^1H and ^{13}C) were recorded in CD_3OD using a Varian Inova 400 NMR spectrometer at 400 MHz.

2.3 *Oxidation of UDMH in solution*

The $500\,mg\,L^{-1}$ solution of UDMH was prepared by dissolution of a 0.5 g weighed portion of this compound in deionized water in a 1 L volumetric flask. Half of the solution was removed, and the flask was stoppered and stored for 6 months at room temperature in a place with no direct sunlight, so as to allow slow oxidation of UDMH in aqueous solution by air oxygen.

2.4 *Oxidation of UDMH in soil suspension*

A weighed soil sample (5 g) was placed in a 100 mL beaker and mixed with a 50 mL volume of UDMH solution (500 mg L^{-1}). After 24 h of oxidation, an appropriate amount of the reagent (listed in table 1) was added to the suspension to obtain a 1 M reagent solution in the aqueous phase. Next, the suspension was shaken for 1 h and the soil removed by filtration. The extract was analysed directly and after a distillation procedure. When NaOH was used, the extract was acidified before the injection.

2.5 *Distillation procedure*

An aliquot of the extract (50 mL) was placed in a round-bottom 250 mL flask. A 10 mL volume of 40% NaOH solution containing sodium sulfide (200 g L^{-1}) was added to the flask. A 10 mL aliquot of 10 mM sulfuric acid was placed into the receiver. The distillation took place in a nitrogen atmosphere to avoid oxidation. The flask was heated to provide a moderate distillation speed, and the procedure was finished after the complete removal of liquid from the flask. Next, the contents of the receiver were poured into a 100 mL volumetric flask and filled with deionized water.

2.6 *NMR sample preparation*

Column eluates in chromatographic vials were evaporated to dryness at 25°C in an inert atmosphere under low pressure (0.3 bar). The solid residue was extracted with CD_3OD.

3. Results and discussion

The estimation of soil mobility of UDMH using various extractants showed significant differences in UDMH concentrations between a direct injection of an extract and an extract subjected to distillation (table 1). We supposed that this phenomenon could be explained, provided the product of decomposition of UDMH was formed and was

Table 1. Effect of distillation on UDMH content in an aqueous phase of soil–water suspension (extractant: 1 M reagent solution).

	UDMH concentration in extract (μg mL^{-1})	
Reagent	Direct injection	After distillation[a]
HCl	1.0	3.7
NaOH	0.5	4.3
KCl	0.15	3.1
CH_3COOK	0.07	3.3

[a]The values were calculated to the initial volume of extract.

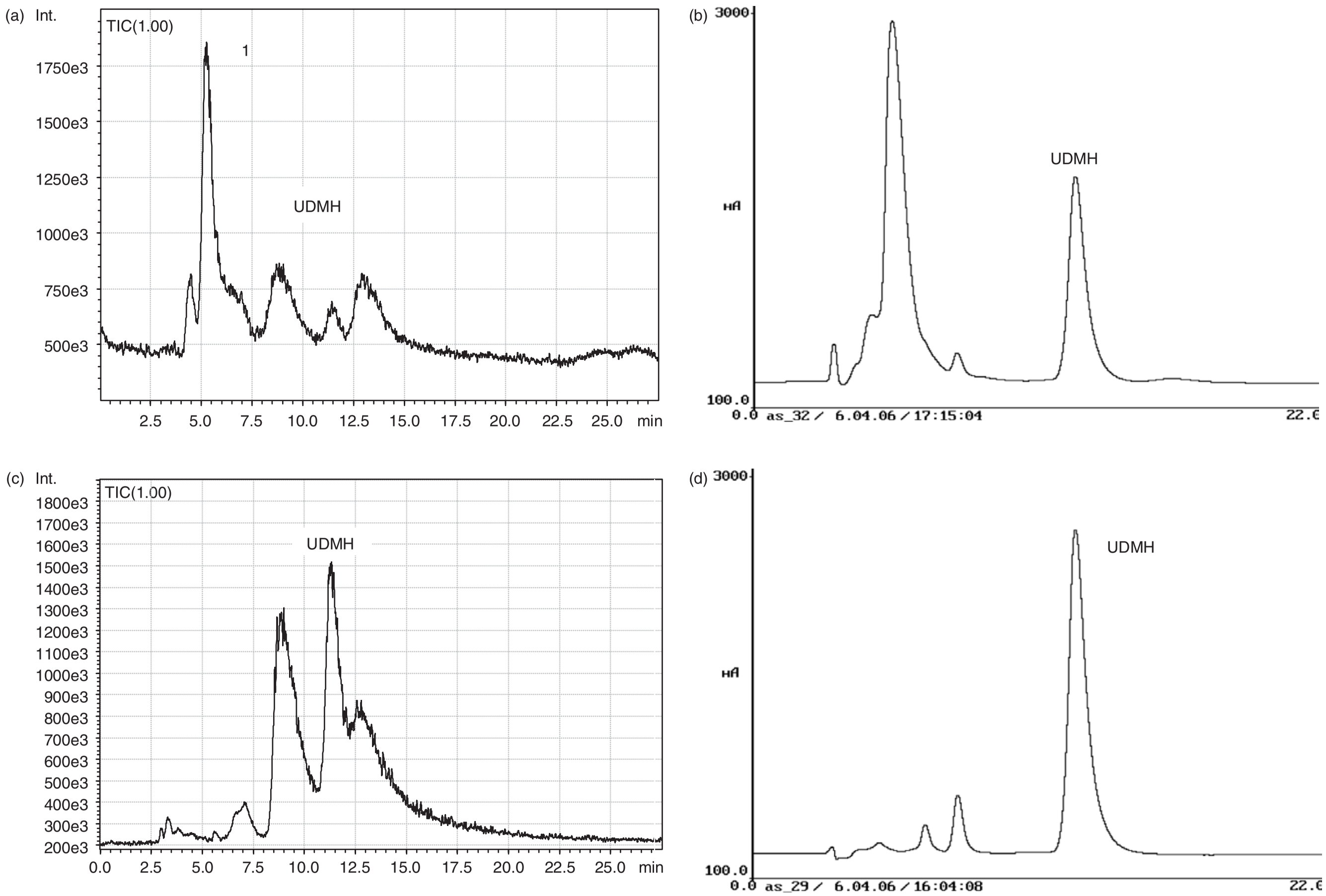


Figure 1. Chromatograms of a UDMH solution prior to (a: MS detector; b: amperometric detector) and after distillation (c: MS detector; d: amperometric detector). The MS detector was operated in a total ion chromatogram mode. 1: peak of the investigated decomposition product.

capable of being transformed to the original UDMH under strong alkaline solutions during distillation. therefore, it may result in the appearance of UDMH in the environment; and both its toxicity and other negative effects to the environment and humans should be investigated after the identification of its structure. A simpler object of research such as aqueous solutions has been chosen for the identification of the unknown product of UDMH.

Figure 1 illustrates typical chromatograms of a UDMH solution subjected to slow oxidation by air oxygen before and after distillation for MS and amperometric detectors. The results of both detectors show that the UDMH concentration increases 3.6 times after the distillation, and the peak labelled '1' disappears after distillation.

Considering the chromatographic conditions it is possible to assume that the unknown compound is a weak base since it is retained on the cation-exchanger column. Another structural feature of the decomposition product is the presence of an N–N bond in its molecule which can be readily oxidized at a potential of +1.3 V.

The ESI mass spectrum of the chromatographic peak of the decomposition product showed a major protonated molecular ion of *m*/*z* 89 (figure 2a) and an ion at *m*/*z* 44 formed in mass spectra of compounds including $(CH_3)_2N^+$ moiety, for example UDMH (figure 2b). Considering the molecular weight of the decomposition product, the ratio of intensities of isotope peaks, and the nitrogen rule, we presumed that this unknown compound was 1-formyl-2,2-dimethylhydrazine or, in other words, formic acid dimethylhydrazide (table 2). As well as the dimethylhydrazide of succinic acid, this compound can decompose to UDMH [16].

The correctness of the assumption on the structure of the decomposition product was confirmed by the coincidence of retention times of synthesized standard and decomposition product, their MS spectra for LC-MS separation and NMR spectra of FDMH, and the eluate corresponding to the chromatographic peak of the decomposition product (table 3).

It should be noted that peaks on chromatograms (figure 1) except UDMH and FDMH belong to other decomposition products, the structures of which are still under discussion and confirmation.

The formation of FDMH as a decomposition product of UDMH in environment was demonstrated by the analysis of a water extract from sod-podzolic loamy soil (10 : 1 m/m) polluted with UDMH (figure 3). In a day after the UDMH spill at the soil surface, the estimated concentration of FDMH in the extract was about $30\,mg\,kg^{-1}$.

4. Conclusion

This work has demonstrated the successful application of LC-MS for discovering a new product of UDMH decomposition, which was not described previously in the literature. Future work can expand the list of decomposition products even further. It has been shown that 1-formyl-2,2-dimethylhydrazine is formed in significant quantities during UDMH oxidation in model experiments and in the environment.

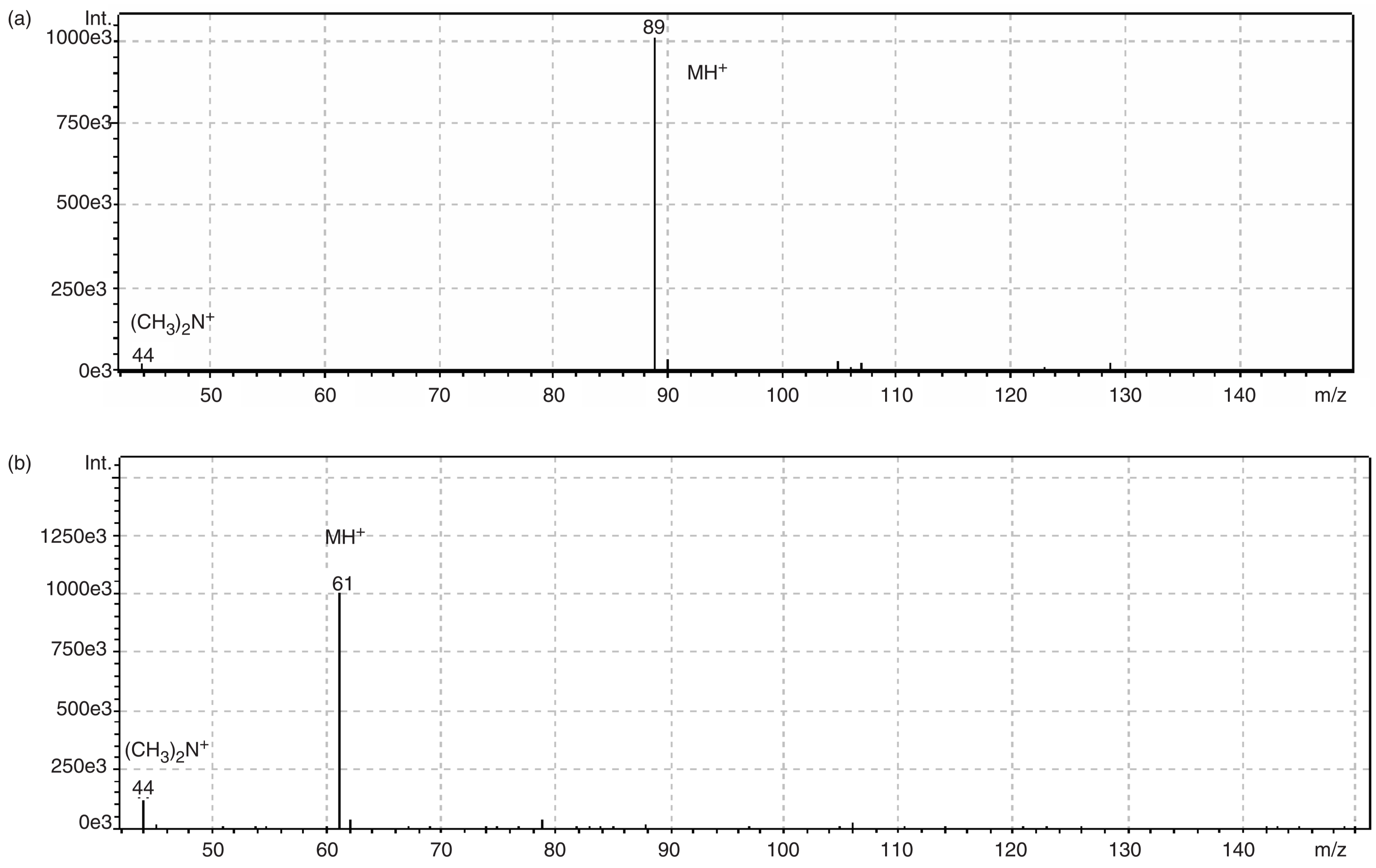


Figure 2. ESI (+) mass spectra of (a) the decomposition product and (b) UDMH.

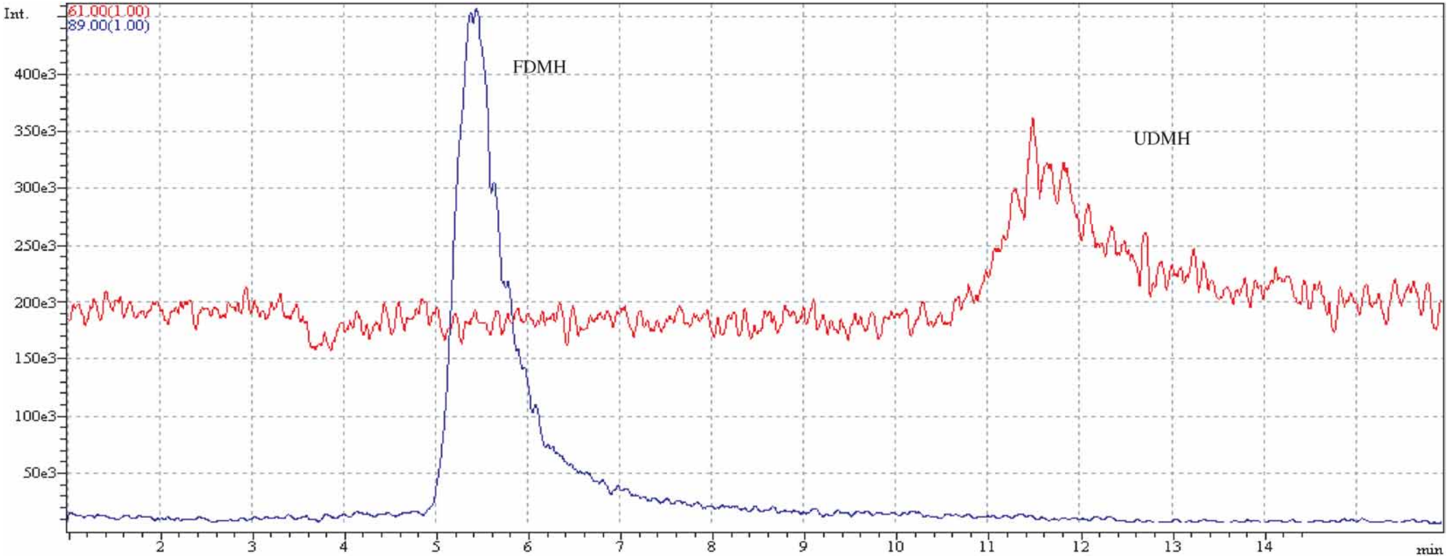


Figure 3. Chromatogram of a soil extract polluted with UDMH; MS detection. Extracted ion chromatogram of m/z 89 (FMDH) and 61 (UDMH).

Table 2. Mass spectral data for the investigated decomposition product of UDMH.

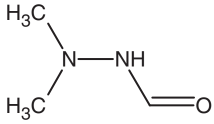
Mass spectrum ion, *m*/*z*	Isotopic ratio M/M + 1 (%)	Molecular formula	Structure
89 (MH^+)	4.2	$C_3H_8N_2O$	
44 ($(CH_3)_2N^+$)	–		

Table 3. Comparison of parameters for FDMH from the standard and oxidized UDMH in an aqueous solution.

Evaluated criterion	Synthetic FDMH standard	FDMH from water solution
Retention time (min)	5.37	5.39
Mass spectrum	89 (100%)	89 (100%)
	90 (4.2%)	90 (4.1%)
	44 (3.2%)	44 (3.4%)
NMR ^{1}H	2545 ppm (CH_3), s	2545 ppm (CH_3), s
	2572 ppm (CH_3), s	2573 ppm (CH_3), s
	7787 ppm (NH), s	7785 ppm (NH), s
	8224 ppm (COH), s	8220 ppm (COH), s
NMR ^{13}C	47,345 ppm (CH_3)	47,345 ppm (CH_3)
	48,876 ppm (CH_3)	48,883 ppm(CH_3)
	167,230 ppm (COH)	167,306 ppm (COH)

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