

DETERMINATION OF TRANSFORMATION PRODUCTS OF UNSYMMETRICAL DIMETHYLHYDRAZINE IN SOIL BY NUCLEAR MAGNETIC RESONANCE METHOD

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Abstract: Experimental works are organized on determination nitrosodimethylamine, tetramethyltetrazene and 1-methyl-1,2,4-[1H]-triazole in ground by nuclear magnetic resonance spectroscopes and gas chromatography with mass-selective detection methods.

Keywords: unsymmetrical dimethylhydrazine, nitrosodimethylamine, tetramethyltetrazene, 1-methyl-1,2,4-[1H]-triazole, nuclear magnetic resonance method, soil

1. Introduction

The most important task of scientific and technological progress at the beginning of the third millennium - is the engaging of all types of natural organic materials in the processing using new technologies that meet the complex and often hard conflicting requirements such as environmental safety, low energy consumption and waste-free.

Progress is impossible without expanding the base of accurate methods for the quantitative analysis that adequately describe not only the elemental composition, but molecular structure of organic material, intermediates and final products. These characteristics allow reliably assess the situation.

When developing new techniques for analysis of nitrous compounds features of their characteristics such as multi-component, structural and phase inhomogeneity, polydispersity, etc. cannot be ignored.

These features is caused not only variation of properties in a wide range, depending on the environment, but also significantly limit the applicability of (and in general - sufficiency) standard chemical and physic-chemical methods of analysis, in particular, the most common in practice, atomic spectral, spectrophotometric, chromatographic and electrochemical methods.

At present time certified techniques developed by Russian scientists [1-5] are used for determination of 1,1-dimethylhydrazine (UDMH) and its transformation products, in particular nitrosodimethylamine (NDMA), tetramethyltetrazene (TMT) in the soil.

Characteristics of UDMH and its derivatives are described above, and methods of their determination are presented in Table 1.

Table 1. Comparative evaluation of methods for determining the content of UDMH and its transformation products in soil samples

Methods of measurement, number of procedures	Measurement range	Relative error at P = 0.95
Photocolorimetric (UDMH) MUK 4.1.018 -06 [1]	0.02-10 mg/kg	±50% - for a measuring range of 0.02-0.2 mg/kg; ±44% - over 0.2-1.0 mg/kg; ±40% - over 1.0-10.0 mg/kg.
Ion chromatography with amperometric detection (UDMH), MVI no. 41-01 ^b [2]	0.05-10.0 mg/kg	Not more than ±53%.
Reversed-phase chromatography with spectrophotometric detection (NDMA), MVI no. 103-08 [3]	0.05-2.5 mg/kg, Mass concentration in the soil extract 0.02 - 1.00 mg/dm ³ , respectively	Not more than ±28%.
Photocolorimetric (NDMA) MUK 4.1.019-06 [4]	0.1-50.0 mg/kg dry-air sample	±55% - at concentrations of 0.1-1.0 mg/kg; ±40% - over 1.0-5.0 mg/kg; ±30% - over 5.0-50.0 mg/kg.
Ion chromatography with amperometric detection (TMT), MVI no. 85-09 [5]	0,05-5,00 mg/dm ³	Not more than ±45%.

UDMH. $(\text{CH}_3)_2\text{N}_2\text{H}_2$ is colorless or slightly yellowish transparent liquid with pungent odor, typical for amines. The boiling point is + 63 °C, the crystallization temperature is - 57 °C, and density is 790 kg /m³. It mixes well with water, ethanol, petroleum products and many organic solvents. It is hygroscopic, absorbing moisture from the air. Flooding leads to a decrease in specific impulse of 100 N·s/kg for every 0.5 % of water [6].

NDMA. $\text{ONN}(\text{CH}_3)_2$ as the other N-nitroso compounds, is relatively easily formed in weakly acidic medium from secondary amines and nitrosating substances, such as sodium nitrite or nitrogen oxides. Nitrite does not react with itself, but nitrous acid freed from it. It is possible that under the influence of hydrogen ions nitrogen trioxide is previously formed, which then gives nitrosamines. NDMA is a yellowish liquid with specific smell of amines. The molecular weight of NDMA is 74.064 the boiling point is 151.5-152.5 °C. Specific gravity is 1.015. UV absorption spectrum of NDMA in solution of ethanol is 346 nm and 231 nm [7].

TMT. $\text{C}_4\text{N}_{12}\text{N}_4$, physic-chemical properties: aggregate state (20 °C, 760 mm Hg) is liquid, the boiling point (at 97 mm Hg) is 70 °C, and density is 0.91 g /cm³, oily, colorless liquid with a

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yellowish tinge and a sharp aromatic odor. Soluble in water and fats. Partially soluble in water (10 g/L), readily soluble in organic solvents and acids. Depending on the pH of the medium may be in solution in various forms, in an alkaline medium - in a molecular form, in acidic - in the form of radicals. It shows the basic properties. When heated in the weakly acidic environment its quantitative decomposition occurs with the formation of di- and monomethylamine, formaldehyde and nitrogen [8].

Determination of UDMH and its derivatives in soil by ion chromatography is carried out by extracting its mobile forms by hydrochloric acid, steam distillation of the substance being determined in the acid solution and subsequent analysis by ion chromatography, distillation at liquid ion chromatograph with an appropriate detector. Thus relative error at $P = 0.95$ is in the range of 28 to 53%.

2. Materials and methods

Widespread use of gas chromatography in various fields of science, technology and industry, is due to its advantages over other methods of analysis. These are high separation ability, versatility of the method, a low detection limit, high sensitivity, rapidity, etc. despite the high advantages of gas chromatography, this method has its drawbacks. In gas chromatography, measurements are relative, because concentrations measured at the output are very different from the initial concentration in the sample. When entering into a stream of carrier gas it is diluted, and then when moving through the layer of sorbent in the column it is even further diluted by diffusion and kinetic factors. Therefore, calibration is needed, i.e. dependence between the concentrations in the sample and the signal obtained at the outlet of the column. When changing any condition of the separation a new calibration is required [9].

Sufficient flexibility among the widespread non-destructive methods of analysis of natural organic materials is owned only by the methods of spectroscopy - optical, Nuclear magnetic resonance (NMR).

Today NMR spectroscopy has the richest and the most successful experience in establishing the chemical structure of individual organic compounds of natural and synthetic origin and details of their electronic and spatial structure.

We have carried out studies on determination of NDMA, TMT, 1-methyl-1,2,4-[1H]-triazole (MT).

Spectra were recorded on Bruker Avance 500 Spectrometer operating at 500 MHz (for proton).

3. Results and discussion

According to the literature, in the ^1H NMR spectrum of UDMH there is a single signal at 3.035 ppm as a singlet attributable to the protons of two methyl groups [10].

Fig.1 (a) shows the ^1H NMR spectrum of NDMA in deuteromethanol. In the spectrum at 2.9-5.0 ppm there are four intense signals, a multiplet at 3.20 ppm is a methyl group of deuteromethanol and its multiplicity is due to spin-spin interactions of protons with two atoms of deuterium. A singlet signal at 4.70 ppm refers to water molecules and OH groups of methanol. Only two singlet signals at 2.99 and 3.69 ppm refer

to the N-methyl's of NDMA molecule, separate appearance of signals of two methyl groups is explained by the lack of symmetry axis of N-N bound due to the asymmetric arrangement of oxygen atom of the nitroso group.

Fig.1 (b) shows ^1H NMR spectrum of MT in deuteromethanol. In the spectrum, a multiplet at 3.20 ppm and the singlet signal at 4.70 ppm refer to the molecules of water and methanol. The singlet signal at 3.87 ppm refer to the N-methyl molecules of 1-methyl-1-2-4-[1H]-triazole, and two singlet's in the range of aromatic protons at 7.84 and 8.29 belong to the protons of the triazole ring.

Fig.1 (c) shows ^1H NMR spectrum of TMT in deuteromethanol. In the spectrum, an intense signal from all four methyl groups of TMT is observed at 2.73 ppm, as well as signals of water and methanol as multiplet at 3.20 ppm and the singlet signal at 4.70 ppm. Figure 4 shows the spectrum of the soil extract sample after the catalytic processing.

The most interesting is ^1H NMR spectrum after processing showed in **Fig.1 (d)**. The signals from methyltriazole and dimethyltriazole occur in the aromatic part. Signals of N-methyl of heptyle and its decay products appear in the region of 2.0-4.0 ppm. Chemical shifts of the methyl groups allow concluding that the spectrum clearly revealed the signals from heptyle, dimethylformamide, NDMA, MT, TMT and dimethyltriazole. There are slightly signals from the other decay products of UDMH, which is difficult to attribute to specific substances.

Similar studies were carried out by GC-MS method using Agilent 6890N/5975C MSD. In **Fig. 2** shows the mass spectra of NDMA, TMT, MT.

The standard mass-spectrometric conditions: interface temperature is 250 °C, the energy of ionizing electrons is 70 eV, and accelerating voltage is 2 kV, the range of mass numbers from 35 to 350 m/z.

Identification was carried out using a library search in NIST existing base of mass-spectral data and comparison with the mass spectra of standard compounds (NDMA, MT, TMT).

Obtained chromatograms are presented not only by the total ion current chromatogram (TIC), but also in the form of mass chromatograms for selected ions, characteristic for studied molecules. The internal standard - o-picoline – was used for quantitative analysis.

To eliminate the possible influence of the content of the various substances present in the soil sample on the results of analyzes analysis of acetone extracts of soil were carried out. Two types of soil (medium loamy and brown, heavy saline soil) collected in area of impact 15, 25 region of fall of separating parts of launch vehicle "Proton-M" in Ulytau area of Karaganda region were used in the experiments.

Analysis showed the absence of interfering in soil. Chromatogram of soil extract (brown saline, medium loamy) from area of impact 15, 25 region of fall is shown in **Fig.2 (d)**.

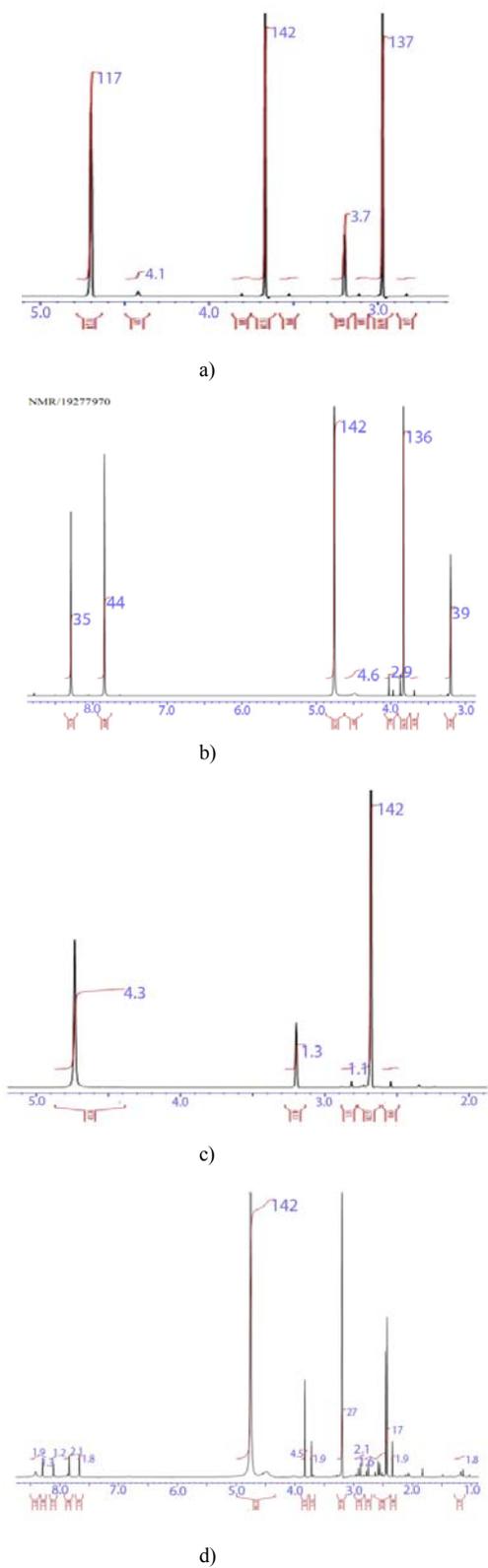


Figure 1. ¹H NMR spectra in deuterio-methanol (CD₃OD):
 A) - NDMA, B) – MT, C) - TMT, D) - after treatment.
 (vertically)

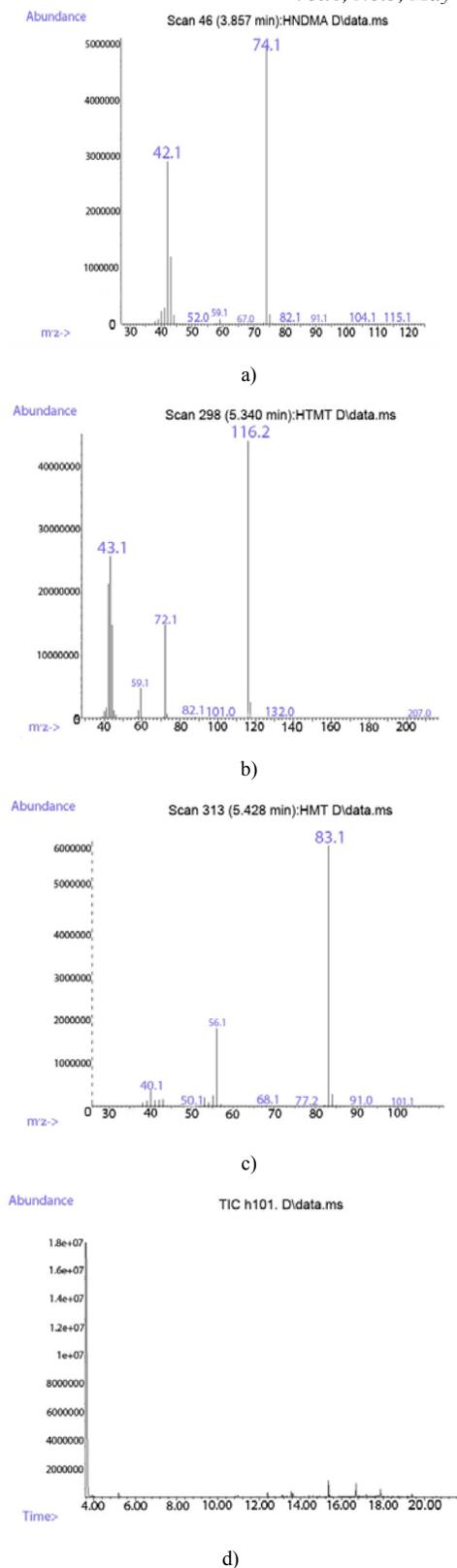


Figure 2. Mass spectra: a) – NDMA, b) – MT,
 c) – TMT, d) – soil
 (vertically)

4. Conclusions

Analysis of obtained spectra shows that NMR spectroscopy can be used for qualitative and quantitative analyzes of real soil samples. Unlike other methods of analysis, NMR spectroscopy does not require standards for calibration. The integrated area of signal is proportional to the molar concentration of the substance.

Work on assessing the sensitivity of NMR spectroscopy for N-methyl containing substances is needed to be carried out, which would make the conclusion about the possibility of establishing methods of quantitative analysis.

Depending on the operating frequency of the device, which determines the sensitivity of the spectrometer, it is possible to create a technique superior by its metrological characteristics among the existing analogues based on gas and liquid chromatography. NMR spectroscopy can provide the error in quantitative analysis of less than 5 %, and the existing chromatographic techniques allow for 25-53 % accuracy.

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