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Determination of 2,4,6-Trinitrotoluene in Wastes and Sewage Water from Mining Industry by Chromato-Mass Spectrometry

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Abstract

A method for determination of 2,4,6-trinitrotoluene in geoenvironmental subjects by gas chromatography with mass-spectrometric detection was proposed. The distribution of 2,4,6-trinitrotoluene in wastes and sewage water samples from mining plants was studied. The presence of this compound in surface water was established. Other nitrogen-containing compounds, in particular, 2-amino-4,6-dinitrotoluene and 2,4,-dinitrotoluene, were also identified in the studied samples.

The 2,4,6-trinitrotoluene (TNT) is the most important shattering explosive used for blasting out. This compound is highly toxic and stable to biodegradation. The TNT belongs to the second hazard class (highly hazardous); its maximum permissible concentration (MPC) in drinking water sources was strongly restricted, from 0.5 to 0.01 mg/L.

A method for determination of 2,4,6-trinitrotoluene in surface water, sewage water and wastes by gas chromatography with mass-spectrometric detection has been developed. The TNT calibration curve was shown to be linear over the concentration range of 1.6-160 μg/mL, and the correlation factor of the line was equal to 0.997.

The distribution of 2,4,6-trinitrotoluene in sewage water and wastes from mining plants has been studied. Mine water in the case of underground mining has high TNT concentrations, which cannot be decreased by the existing traditional methods of sewage water treatment. TNT is detected also in surface water after mine water disposal. Note that the TNT concentrations can exceed many times the maximum permissible concentrations prescribed for water works system.

2-amino-4,6-dinitrotoluene and 2,4,-dinitrotoluene, which can be considered as products of TNT metabolism, were also identified in the studied samples.

The developed method and results of the present study make it possible to introduce the quantitative determination of TNT and its metabolites into the programs for monitoring of surface water, sewage water and wastes in the mining plant sites in different countries as well in Russia, namely in Kuzbass.

Introduction

The destruction of rocks by explosion energy is a universal and virtually sole highly efficient method that is used to prepare hard rocks for processing. Heavy charges of explosives are finding increasing use to solve routine problems of mining industry, charges up to 1000 tons being exploded at open-cast mining, and up to 100 tons at underground mining [1]. Thus, mining industry is among the main sources of contamination of the environment by nitrocompounds.

The 2,4,6-trinitrotoluene (TNT) is the most important shattering explosive used for blasting out. This compound is highly toxic and stable to biodegradation [2]. The disturbance of total environmental situation caused by this xenobiotic shows up, in particular, as changes in the biological activity of soil [3, 4]. The 2,4,6-trinitrotoluene belongs to the second hazard class (highly hazardous); its maximum permissible concentration (MPC) in drinking water sources was strongly restricted, from 0.5 to 0.01 mg/L [5].

The present work was aimed to develop a method for determination of 2,4,6-trinitrotoluene in wastes and sewage water from mining industry by gas chromatography with mass-spectrometric detection (GC/MS) and to study subjects at geoenvironmental sites in the Kemerovo region for the content of TNT and associated compounds.

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Experimental

Since sewage water and wastes from mining plants are complex multicomponent subjects, qualitative and quantitative assessment of their composition is a topical task of analytical chemistry in the context of environmental problems. Among modern instrumental methods of analysis, gas chromatography with mass-spectrometric detection (GC/MS) is widely used for identification of organic pollutants [6]. The identification is based on two criteria: retention time on the column and patterns of mass fragmentation against reference substances.

Such advantages of mass spectrometry as high sensitivity and selectivity as well as the possibility to analyze samples in different aggregative states and perform rapid analysis and structural identification make it the key tool for analyzing the environmental subjects at different stages of investigation: structural determination of unknown compounds, qualitative and quantitative analysis of mixtures, monitoring and screening [7].

In this work, the following equipment was used for identification and qualitative determination of organic substances: a SATURN 2000 chromato-mass spectrometer (Varian, USA) comprising a STAR 3400 high-resolution chromatograph and a SATURN 2000 mass-spectrometer, and a DB-5 ms capillary quartz column (J&W Scientific, USA) with the length of 30 m, diameter 0.25 mm, layer thickness 0.25 μm, and 5% diphenyl - 95% dimethylpolysiloxane phase.

The electron impact mass spectra of organic compounds were obtained at the ionizing electron energy of 70 eV and ionization chamber temperature of 160 ºC. Individual compounds were identified by searching over the NIST92 mass spectrometry library and estimating the retention time of reference substances. The TNT mass spectrum is displayed in Fig. 1. The main chromatographic and mass-spectrometric characteristics of TNT are listed in Table 1.

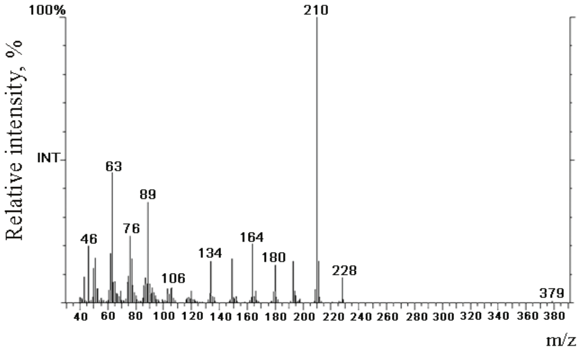

Fig. 1. Mass spectrum of 2,4,6-trinitrotoluene.

Table 1

Chromatographic and mass-spectrometric characteristics of TNT (obtained on a DB-5 chromatographic column)

Substance	Retention time, min	Mass numbers of ions, amu	
		Main ion	Confirmatory ions
2,4,6-trinitrotoluene	18.16	210	63,89

To make a calibration plot, we used 5 sets of TNT calibration solutions, one of them having a concentration close to the lower limit of detection. The calibration curve was shown to be linear over the concentration range of 1.6-160 μg/mL, and the correlation factor of the line was equal to 0.997.

The degree of TNT recovery and its extraction factor were found from the calibration solutions of the substance in water. The calibration solutions were subjected to extraction and analysis with subsequent calculation of the content of substance recovered from water. The degree of TNT recovery was 65.8%.

Analytical Procedure

1 dm^3 of water was supplemented with a 50% solution of sulfuric acid in order to bring pH to 2. A water sample was extracted with dichloromethane by shaking a separating funnel for 2 min. After fractionation into organic and aqueous phases, an extract was separated from water and transferred to a 100 cm^3 round-bottom flask. The water sample was sequentially extracted two more times by the indicated procedure using 20 cm^3 portions of dichloromethane. The combined extracts (60 cm^3) were dried by passing through the column with a 10 g layer of anhydrous sodium sulfate. The extract was evaporated in flowing nitrogen to the volume of 1 cm^3; the resulting solution was analyzed chromato-mass-spectrometrically.

The content of water-soluble part of TNT in the wastes was determined using aqueous extracts of the samples (50 g of the wastes was held for 24 h in 500 mL of distilled water).

Nomenclature of the Tested Samples

The study was performed with 7 samples of sewage water, 3 samples of wastes from mining plants where iron ore and coal were produced by open-cast and underground mining, and 4 samples of surface water collected in 2005-2010 in the south of Kuzbass.

Results and Discussion

A typical chromatogram of the surface water sample polluted with TNT is displayed in Fig. 2. Along with TNT, some other nitrogen-containing organic compounds were also identified in the tested samples: 2- amino-4,6-dinitrotoluene (2ADNT) and 2,4-dinitrotoluene (DNT). Mass spectra of the indicated compounds are depicted in Figs. 3 and 4. Quantitative assessment of their content in the studied subjects was not completed. However, one can see from Fig. 2 that the content of these compounds is low as compared to TNT.

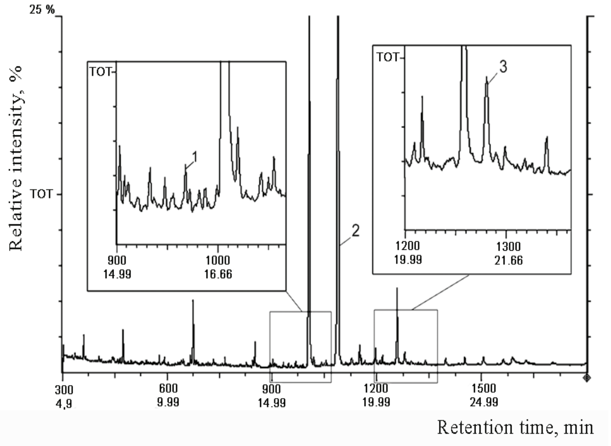

Fig. 2. A typical total ion current chromatogram of the surface water sample polluted with 2,4,6- trinitrotoluene. Chromatographic peaks: 1 – 2,4-dinitrotoluene (retention time 16.13 min, 16x magnification of the fragment), 2 – 2,4,6-trinitrotoluene (retention time 18.16 min), 3 – 2-amino-4,6-dinitrotoluene (retention time 21.35 min, 8x magnification of the fragment).

Some assumptions concerning the origin of the indicated compounds in the studied subjects can be made. It is known that these substances can be employed as taggants [8]. In the legal industrial production of explosives, their composition is often deliberately supplemented with more volatile components that have a similar structure but a higher vapor pressure. The presence of such substances, the so-called taggants or markers, strongly facilitates the detection of explosives and often makes it possible to reveal their production source. It was show that the main way for biotransformation of this xenobiotic is its reductive conversion by a wide scope of microorganisms to produce amino-dinitrotoluenes, hydroxylamino-dinitrotoluenes, dinitrotoluenes, and other derivatives [9-15]. According to the study of TNT biotransformation in soils [16], 2-aminodinitrotoluene and 4-aminodinitrotoluene are the main products of its metabolism, the amount of TNT extracted with acetonitrile decreasing from 30-40% to 0-6% within a month, which is caused by TNT sorption and partial microbial transformation. In [17], TNT conversion by Bacillus sp. 1 and Bacillus sp. 2 bacteria was shown to produce 2-amino-4,6-dinitrotoluene as the main TNT metabolite in soil. Thus, for characterization of all contaminants of mining industry we have to study the distribution of not only TNT itself but also its possible metabolites in environmental subjects.

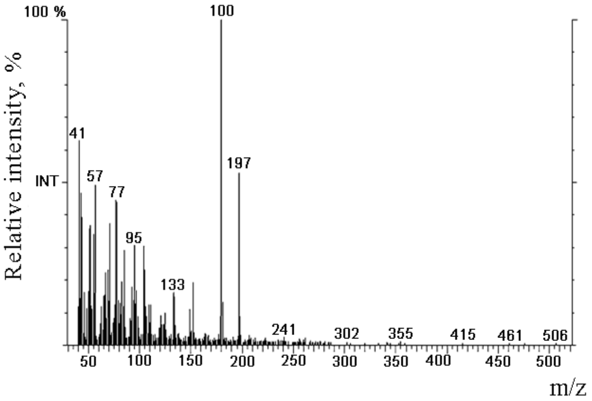

Fig. 3. Mass spectrum of 2-amino-4,6-dinitrotoluene.

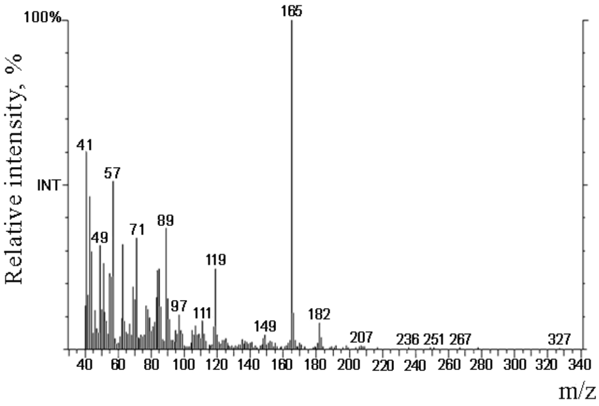

Fig. 4. Mass spectrum of 2,4-dinitrotoluene.

The distribution of TNT in sewage water from mining plants and in surface water is presented in Table 2. As follows from the data obtained, mine water in the case of underground mining has high TNT concentrations, which cannot be decreased by the existing traditional methods of sewage water treatment. TNT is detected also in surface water after mine water disposal. Note that the TNT concentrations can exceed many times the maximum permissible concentrations prescribed for water works system.

Table 2
Distribution of TNT in sewage water from mining plants and surface water

Mining method	Subject of inquiry	TNT content, mg/L	MPC_w [4], mg/L	Identified nitrocompounds
Underground mining of iron ore.	Mine water before treatment	0.200		2ADNT, DNT
	Mine water after treatment	0.198		2ADNT, DNT
	Mine drainage (background)	0.051		2ADNT
	River water before mine water disposal	< 0.0016	0.01	–
	River water after mine water disposal	0.0223	0.01	2ADNT
Underground mining of iron ore.	River water downstream of sewage disposal	1.130	0.01	2ADNT, DNT
Open-cast coal mining.	Strip mine water before filter medium (section 1)	0.0091		–
	Strip mine water after filter medium (section 1)	0.0124		–
	Strip mine water before filter medium (section 2)	0.0690		2ADNT, DNT
	Strip mine water after filter medium (section 2)	< 0.0016		–

In the case of open-cast mining, samples of strip mine water also contain TNT, however, in a much lower concentration. This pollutant is detected also in the mining plant wastes (Table 3).

Table 3
Distribution of TNT in mining plant wastes

Mining method	Subject of inquiry	TNT content, mg/kg	Identified nitrocompounds
Open-cast mining of iron ore	Overburden rock	0.0015	–
	Sludge maps of waste disposal plants at strip mine drainage	0.0624	2ADNT, DNT
	Slurry deposit	2.882	2ADNT, DNT

Thus, the possibility to study the distribution of TNT and its metabolites in sewage water and wastes of mining industry has been demonstrated. The acquired data can be used to assess the anthropogenic load on the environment and to search for pollution sources at mining sites in different countries, as well in Russia (Kuzbass) with an aim to include determination of TNT and its metabolites in to the programs for analysis of wastes, surface water and sewage water at these sites.

Conclusions

1. A method for determination of 2,4,6-trinitrotoluene in surface water, sewage water and wastes by gas chromatography with mass-spectrometric detection has been developed.
2. The distribution of 2,4,6-trinitrotoluene in sewage water and wastes from mining plants has been studied. High concentrations of TNT were found in sewage water samples in the case of underground mining of iron ore.
3. The presence of TNT in surface water was established.
4. 2-amino-4,6-dinitrotoluene and 2,4,-dinitrotoluene, which can be considered as products of TNT metabolism, were also identified in the studied samples.
5. The developed method and results of the present study make it possible to introduce the quantitative determination of TNT and its metabolites into the programs for monitoring of surface water, sewage water and wastes in the mining plant sites in different countries as well in Russia, namely in Kuzbass.

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