



Development of analytical methods used for the study of 2,4,6-trinitrotoluene degradation kinetics in simulated sediment samples from the Baltic Sea

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ARTICLE INFO

Keywords:

Baltic Sea
Bottom sediments
Dumped munitions
2,4,6-Trinitrotoluene
Degradation pathways
Chromatographic analysis

ABSTRACT

Large amounts of ammunition containing 2,4,6-trinitrotoluene (TNT) and other substances were dumped in the Baltic Sea after WWII. Considering progressive corrosion processes, studying the transformation of TNT occurring in the environment constitutes an important aspect of a possible associated risk. This study focused on the transformations of TNT in simulated conditions of the Baltic Sea bottom sediment. Methods of analysis of TNT and selected products of its transformations were developed for that purpose. The developed methods allowed for the determination of selected compounds below 1 ng/g. Systematic monitoring of TNT transformations in the environment of the bottom sediment was performed. This allowed for the determination of the kinetics of TNT degradation and identification of degradation reaction products. Based on the obtained results, the TNT decay half-time in conditions present in the Baltic Sea was estimated to be 16.7 years for the abiotic environment and 5.6 for the biotic environment.

1. Introduction

Studies of explosives and their transformations in the natural environment constitute an important aspect of the assessment of danger posed by those materials for the natural environment, both on exercise field and in storage facilities. Ammunition dumped in seas and oceans, including the Baltic Sea, is an example of this problem. The subject goes back to 1945 when the Potsdam Conference decided to eliminate Germany's war potential. As a result of this, ammunition units, among other bombs and artillery shells containing explosives and chemical warfare agents, were dumped in the relatively shallow Baltic Sea (Szarejko and Namieśnik, 2009).

Studies carried out within the framework of the CHEMSEA project (Chemical Munitions Search & Assessment) demonstrated that the dumped chemical ammunition was often located out of the official designated dumping areas (the Gotland deep, the Bornholm deep), with precise localisation unknown (Knobloch, 2013). As seen in Table 1, the main explosive materials deposited in the Baltic Sea were 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen, RDX). Among the mixtures listed, the composition named Torpex is the most abundantly present in the Baltic Sea. That is because the mixture was most commonly used for elaboration of torpedoes. Besides TNT and

RDX, the mixture contains approximately 18% aluminium in the form of dust and < 1% waxes (Juhász and Naidu, 2007; Walsh and Jenkins, 1992).

Due to corrosive processes and the resulting possibility of release of hazardous substances into the water and bottom sediments, dumped ammunition has become an issue due to the potential effects on the environment and sea users (Pennington and Brannon, 2002). Besides the environmental risk, the economic aspect associated with danger and limitations of maritime works in the Baltic Sea must also be taken into account (Knobloch, 2013). For that reason, the determination of precise localisation of the ammunition on the bottom of the Baltic Sea, as well as the determination and assessment of the associated environmental risk, are of utter importance.

The basic requirement of conducting reliable research on explosives and particularly on environmental hazards they generate is to apply comprehensive and modern methods of analysis of all analysed compounds. Currently, chromatographic techniques, such as thin layer chromatography (Błądek et al., 1995), high-performance liquid chromatography (Sener et al., 2017), gas chromatography (Thomas et al., 2018; Rahal and Moussa, 2011) coupled with various detectors, and nuclear magnetic resonance (NMR) spectroscopy (Salter-Blanc et al., 2013) are the most extensively applicable to the analysis of explosives.

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Table 1

Explosive composition used during World War II. Data presented in the table was retrieved from the literature (Juhász and Naidu, 2007; Walsh and Jenkins, 1992; Glasby, 1997).

No.	Name	Composition	Notes
1	Amatol	Ammonium nitrate and TNT	Extensively used in bombs, shells, depth charges, and naval mines
2	Baronal	Barium nitrate, TNT, and powdered aluminium	–
3	Baratol	Barium nitrate and TNT	Used in British hand grenades
4	Composition A	88.3% RDX and 11.7% plasticizer	–
5	Composition B	RDX, TNT, and wax	–
6	Composition H6	45% RDX, 30% TNT, 20% powdered aluminium, and 5% wax	Replaced Torpex for use in naval applications
7	DBX (Depth Bomb Explosive)	21% RDX, 21% ammonium nitrate, 40% TNT, and 18% powdered aluminium	An alternative for Torpex, which used less of the strategic material RDX
8	Minol	40% TNT, 40% ammonium nitrate, and 20% powdered aluminium (Minol-2)	Developed by the British Royal Navy and used in torpedoes, depth charges, and naval mines. Unsuitable for shells because of a risk of detonation if subjected to very high accelerations
9	Pentolites	50% pentaerythritol tetranitrate (PENT) and 50% TNT	–
10	Picratol	52% ammonium picrate and 48% TNT	Used in armour-piercing shells and bombs insensitive to shock
11	PIPE	81% PETN and 19% oil	–
12	PTX-1	30% RDX, 50% tetryl, and 20% TNT	–
13	PTX-2	41–44% RDX, 26–28% PETN, and 28–33% TNT	–
14	PVA-4	90% RDX, 8% poly(vinyl alcohol) (PVA), and 2% dibutyl phthalate	–
15	RIPE	85% RDX and 15% oil	–
16	Tetrytols	70% tetryl and 30% TNT	–
17	Torpex	42% RDX, 40% TNT, and 18% powdered aluminium	Developed for use in torpedoes, it was especially effective at producing destructive, underwater explosions
18	Trialen 105	15% RDX, 70% TNT, and 15% powdered aluminium	Used by the Luftwaffe
19	Explosive “D”	Ammonium picrate	US Army/Navy
20	Type 91 Explosive	Trinitroanisol (TNA)	Japanese Army/Navy

Table 2

TNT solubility (g/100 g) in selected solvents at 20 °C (Ryon, 1987).

Solvent	Solubility
Water	0.013
Pyridine	137
Acetone	109
Toluene	55.0
Benzene	67.0
Methyl acetate	72.1
Chlorobenzene	33.9
Chloroform	19.0
Carbon disulphide	0.48
Diethyl ether	3.29
Trichloroethylene	3.04
Ethanol (95%)	1.23
Carbon tetrachloride	0.65
1,2-Dichloroethane	18.7
Ethylene dichloride	18.7

Among these techniques used in the analysis of explosives, liquid chromatography is becoming increasingly important (Sener et al., 2017). The key advantage of this method is that analysed compounds are not exposed to high temperatures, as in the case of gas chromatography. That is particularly important in the analysis of explosives, most of which undergo thermal decomposition at high temperature. TNT and its decomposition products are an exception, as they may be successfully analysed by both liquid and gas chromatography (Thomas et al., 2018). This is due to their high thermal stability, for example, the melting point of TNT is 81 °C (Huang et al., 2016), the boiling point is 240 °C (Giannoukos et al., 2015), and the decomposition point is 295 °C (Huang et al., 2016). Additionally, the relatively low molar weight of 227.13 g/mol and good solubility in the majority of organic solvents (Table 2) allows for the direct analysis of the compound with gas chromatography with no need for a previous derivatisation reaction (Rahal and Moussa, 2011). On the other hand, poor water solubility favours efficient liquid-liquid extraction from aqueous matrices or

solid-liquid extraction from soil or sediments to organic solvents in the process of preparation of samples for the chromatographic analysis.

The main reactions that TNT undergoes in the natural environment are oxidation and reduction of its functional groups that are substituents in the benzene ring (Walsh and Jenkins, 1992; Glasby, 1997). Under the effect of oxidative factors, the methyl group in TNT may be oxidised to the carboxyl group, which subsequently is removed in the process of decarboxylation, forming trinitrobenzene (Ayoub et al., 2010). TNT may also undergo reactions of denitration, leading to 2,6-dinitrotoluene and 1,3-dinitrobenzene (Ayoub et al., 2010). Other important products of TNT degradation are amines, formed as the result of reduction of one of three nitro groups in the amine group (Wang et al., 2010).

The purpose of this study was to develop sensitive and precise methods for the analysis of TNT and its decomposition products using modern methods of liquid and gas chromatography, as well as the analysis of transformations of the compound in bottom sediments from the Baltic Sea under biotic and abiotic conditions. The study was divided into two stages. The first stage involved the development and optimisation of the method for determination of TNT and selected products of its decomposition, including the following: 4-nitrotoluene; 1,3-dinitrobenzene; 1,3,5-trinitrobenzene; 2,4-dinitrotoluene; 2,6-dinitrotoluene; 2,4-dinitroaniline; 2,6-dinitro-4-aminotoluene; and 4,6-dinitro-2-aminotoluene, with the use of a gas chromatograph coupled with tandem mass spectrometry (GC–MS/MS) working in the selected reaction monitoring (SRM) mode. Additionally, methods for the determination of TNT, 2,4,6-trinitrobenzoic acid (TNBA), and 1,3,5-trinitrobenzene with the use of a liquid chromatograph coupled with the Orbitrap type mass analyser (LC-Orbitrap) were developed and optimised. The second stage of the study involved systematic monitoring of transformations of TNT in the environment of the bottom sediment from the Baltic Sea, the determination of kinetic curves of those transformations, and the identification of reaction products with the use of the developed methods of chromatographic analysis. Additionally, the correctness of the identification of substances formed during the decomposition of TNT in the bottom sediment was confirmed with

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