Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Development, validation and comparison of three methods of sample preparation used for identification and quantification of 2,4,6-trinitrotoluene and products of its degradation in sediments by means of GC-MS/MS.

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Spiking of sediment samples

The matrix can have a considerable effect on the way in which the analysis is conducted and the quality of the obtained results. For example, as you can see in Figure S2†, when extraction is carried out without the matrix, the recoveries obtained immediately after the preparation of the sample as well as recoveries after 1, 2 and 3 days are similar. So we can say that the time between spiking and extraction of the sample does not affect the analysis recovery. The situation changes when we spike a sediment sample. The analytical signal from the sample analysed immediately after the preparation is close to that without the presence of a matrix. On the other hand, a sample analysed after 1 day gains about 10% less recovery and stays constant over time. Probably during the passage of time TNT and its degradation products penetrate the porous and enter into the structure of the mud, which is then harder to extract. For this reason, it is necessary to leave the prepared sample for at least one day before proceeding with the analysis to optimize the sample preparation conditions. Such accepted conditions should be repeatable and stable.

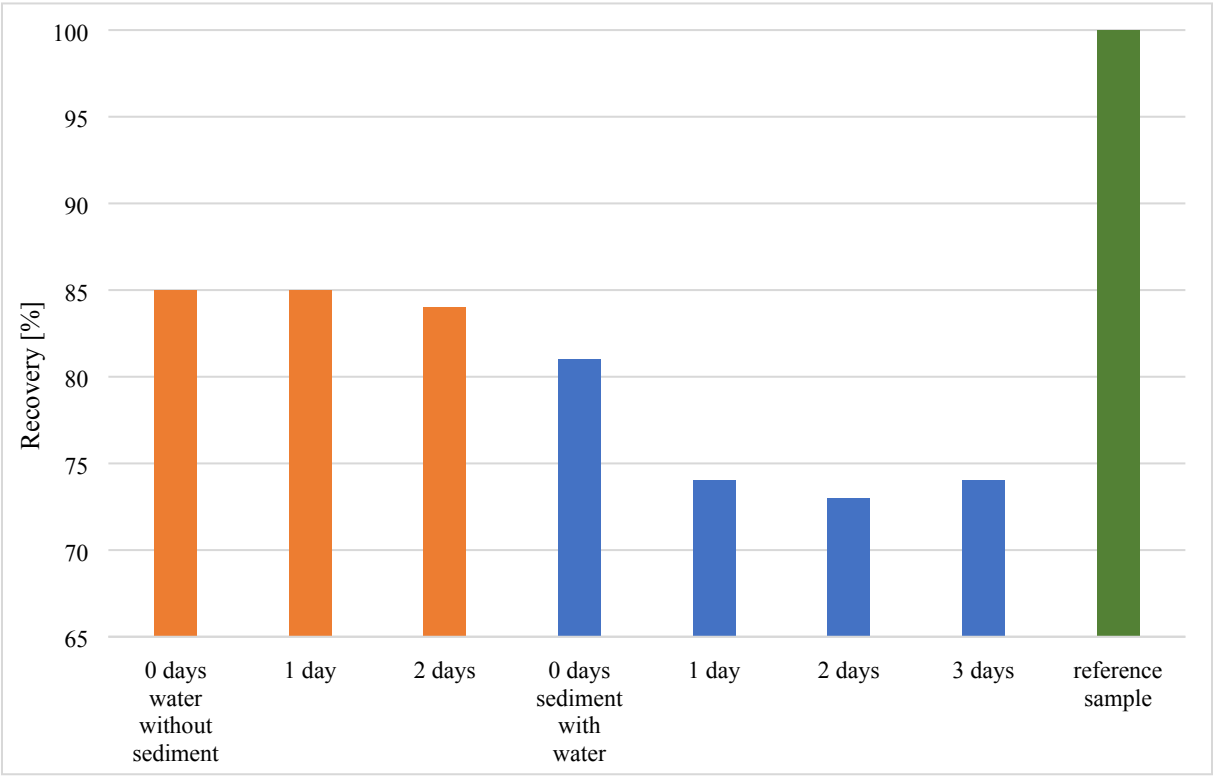

Fig. S1†. TNT recovery depending on the time between spiking and analysis.

Selection of solvent and drying method

In order to carry out the correct and efficient extraction it is necessary to select appropriate solvent for this process. The type of solvent plays a major role in extraction efficiency. The results presented in Figure S2† show that the best solvent for the analysis of TNT and its degradation products is chloroform. This compound will be used as the extracting substance for all the subsequent analyses. In the absence of this solvent, it may be possible to use methylene chloride or ethyl acetate, although a lower yield of extraction is to be expected. Only hexane is not suitable as a solvent because it did not give any analytical signal of 2,4-DNA and also gave about 2 times lower recoveries of all the compounds than recoveries obtained from chloroform. With regard to the drying technique, there was no difference which one we chose. Both techniques i.e., drying with magnesium sulfate and drying with a stream of inert gas gave almost the same results. The difference between them was in limit of error, below 1%. As using magnesium sulfate is faster and more economical, it was chosen for drying the extracts.

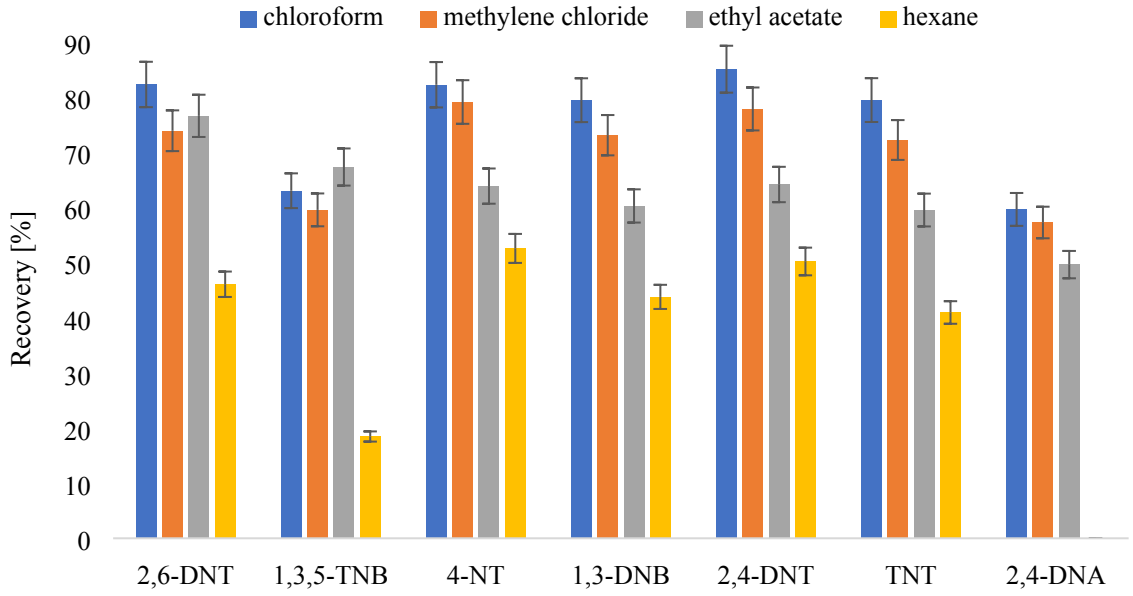

Fig. S2†. Dependence of extraction recovery on the type of solvent used for TNT and its degradation products.

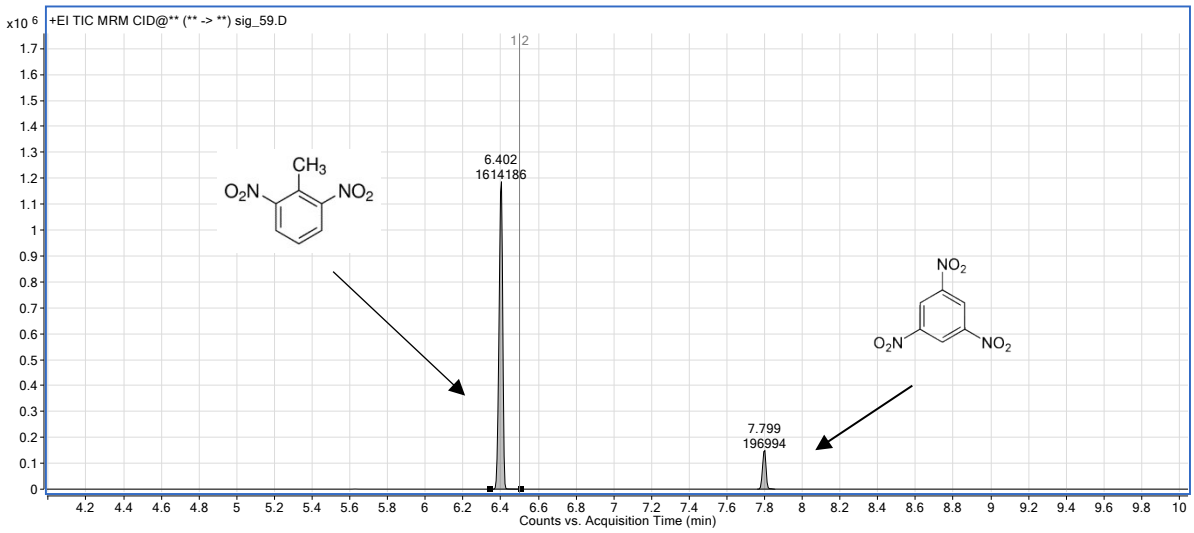

Fig. S3†. Chromatogram obtained during analysis of the Baltic sediments spiked with target chemicals (2,6-DNT and 1,3,5-TNB) with GC-MS/MS.

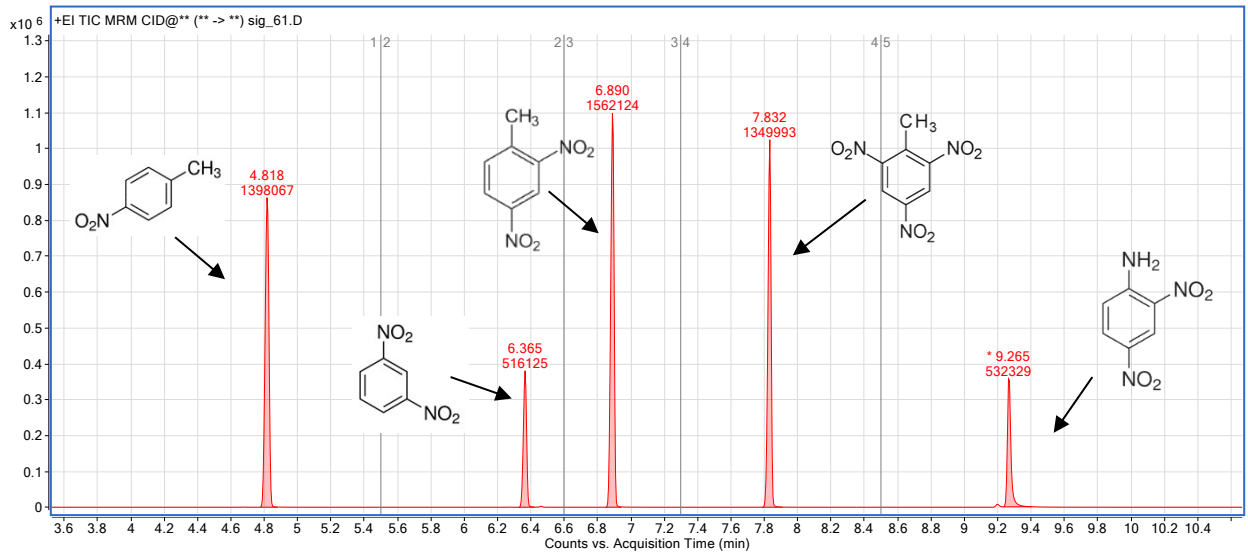

Fig. S4†. Chromatogram obtained during analysis of the Baltic sediments spiked with target chemicals (4-NT, 1,3-DNB, 2,4-DNT, TNT and 2,4-DNA) with GC-MS/MS.

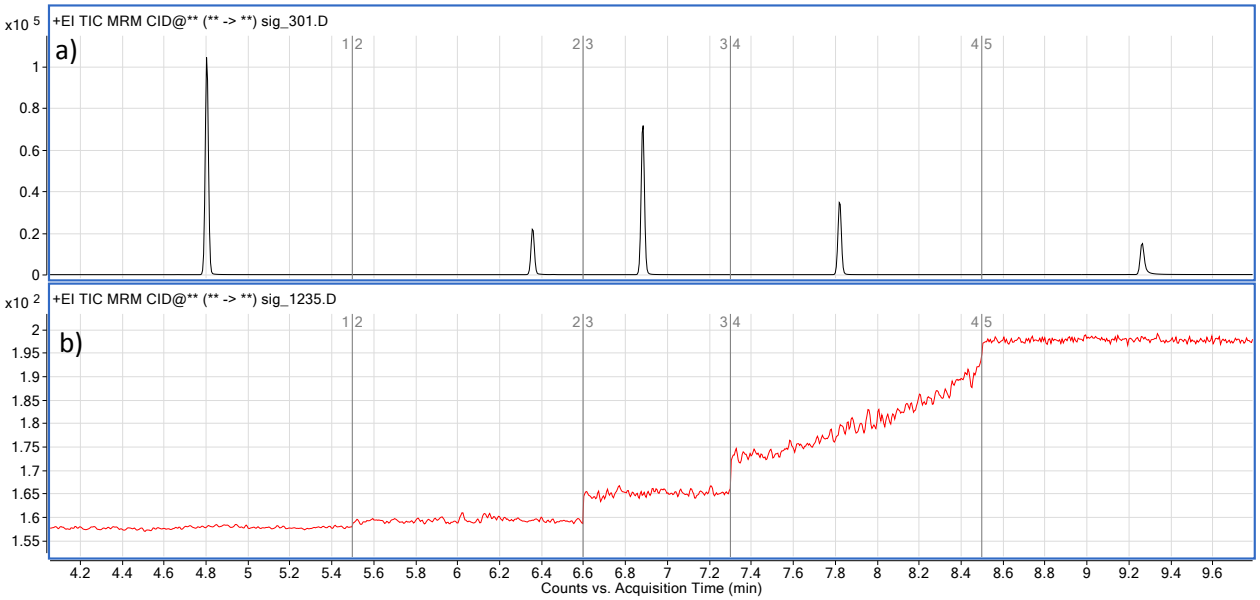

Fig. S5† Set of chromatograms obtained during the analysis of a) contaminated sediment spiked with target chemicals (4-NT, 1,3-DNB, 2,4-DNT, TNT and 2,4-DNA) and b) blank sediment.

Table 1†. SRM transition used in the analysis of TNT and its degradation products with GC-MS/MS coupled with electron ionization. 70 ms of dwell time was used for all SRM transition.

Analyte	Precursor Ion	Product Ion	Colision cell energy [eV]

Analyte	Precursor Ion	Product Ion	Colision cell energy [eV]
TNT	210	210	0
		193	8
		164	5
		90	15
1,3,5-TNB	213	213	0
		167	10
		120	21
1,3-DNB	168	75	24
		122	8
		92	13
2,4-DNT	165	165	0
		119	5
		118	9
2,6-DNT	165	165	0
		148	9
		90	15
4-NT	137	107	4
		91	17
		79	12
2,4-DNA	183	183	0
		153	10
		107	16
C12	170	85	2
		71	3
		57	9
		43	15