Suspect screening and quantification of trace organic explosives in wastewater using solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry

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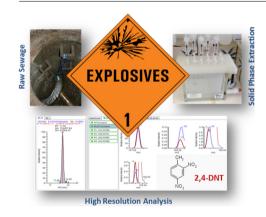
HIGHLIGHTS

- 34 sorbents tested for SPE of multiple classes of trace explosives.
- Recoveries between 56 and 124% achieved using mixed polarity polymeric sorbents.
- Determination of 29 explosives possible at the ng–μg L^{-1} level in wastewater matrix.
- 2,4-dinitrotoluene detected in London composite wastewater samples ($\leq$303 ng L^{-1}).
- Both suspect screening and quantitative analysis possible with LC-HRMS.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The first comprehensive assessment of 34 solid phase extraction sorbents is presented for organic explosive residues in wastewater prior to analysis with liquid chromatography-high resolution accurate mass spectrometry (LC-HRMS). A total of 18 explosives were selected including nitramines, nitrate esters, nitroaromatics and organic peroxides. Three polymeric divinylbenzene-based sorbents were found to be most suitable and one co-polymerised with n-vinyl pyrrolidone offered satisfactory recoveries for 14 compounds in fortified wastewater (77–124%). Limits of detection in matrix ranged from 0.026–23 μg L^{-1} with $R^2 \geq 0.98$ for most compounds. The method was applied to eight 24-h composite wastewater samples from a London wastewater works and one compound, 2,4-dinitrotoluene, was determined over five days between 332 and 468 g day^{-1} (225–303 ng L^{-1}). To further exploit the suspect screening capability, 17 additional explosives, precursors and transformation products were screened in spiked wastewater samples. Of these, 14 were detected with recoveries from 62 to 92%, highlighting the broad applicability of the method. To our knowledge, this represents the first screen of explosives-related compounds in wastewater from a major European city. This method also allows post-analysis detection of new or

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1. Introduction

In recent years, sewage epidemiology has been successfully applied to estimations of community pharmaceuticals and illicit drugs usage across several cities [1]. In the same way, the detection and monitoring of explosive residues, their precursors and degradation products in wastewater could represent useful intelligence for policing and security services regarding clandestine activity in a specific location.

To date, a number of studies have focused on the presence of toxic nitroaromatic and nitramine explosive compounds in industrial wastewaters and receiving waters such as rivers, lakes, seawater and groundwater to evaluate environmental and human exposure and subsequent health hazards. 2,6-dinitrotoluene (2,6-DNT) was detected at up to $6 \mu g \, L^{-1}$ in a mixture of industrial effluent and raw domestic sewage from Finland and trinitrotoluene (TNT) was measured at high $mg \, L^{-1}$ concentrations in wastewater effluent sourced from a Brazilian TNT manufacturing plant [2,3]. Other explosives detected in surface waters include octahydro-1,3,5,7-tetranitro-1,3,5,7-triazine (HMX) and cyclotrimethylene-trinitramine (RDX) at low $\mu g \, L^{-1}$ concentrations in groundwater from a military base and HMX, RDX and pentaerythritol tetranitrate (PETN) at sub $ng \, L^{-1}$ concentrations in lake and river water used for military activities [2,4,5]. The detection of a broad range of such chemically unstable compounds in highly complex matrices at trace concentrations has proven to be extremely difficult, especially for influent wastewaters.

Organic explosives in aqueous samples are generally analysed using gas chromatography (GC) or liquid chromatography (LC) with ultra-violet (UV) and/or mass spectrometry (MS) detection [6,7]. More recently, the high resolving power (up to 100,000) and mass accuracy provided by high resolution accurate mass spectrometry (HRMS) has been shown to provide high selectivity and sensitivity even in highly complex environmental matrices for targeted, suspect screening and untargeted analysis [8]. Although sensitivities have greatly improved using HRMS, more complex matrices such as wastewater still result in ion suppression. More focus is needed on improving sample pre-treatment and clean-up. Prior to explosive analysis, several extraction and pre-concentration techniques have been applied to wastewater effluent, seawater, surface waters, groundwater and drinking water and include salting-out solvent extraction [9], solid phase extraction (SPE) [4,10–14] solid phase micro-extraction [5,15] dispersive liquid–liquid micro-extraction [16,17] and direct ultra-sound assisted dispersive liquid–liquid micro-extraction [18]. Overall, SPE is the most commonly applied technique for aqueous sample extraction given its simplicity, concentration/cleanup ability and low solvent consumption [19]. Previously used SPE sorbents for explosives have mainly been composed of styrene and/or (alkyl)vinylbenzene and are often with additional polar or ion exchange functionalities for added selectivity [4,14,20–25]. Silica and graphitic carbon have also been successfully applied [13,26]. Most extraction methods focused on a very limited number and range of explosive chemistries, and, in terms of sample complexity, most have been applied to surface and ground waters with very few tackling more complex wastewater matrices.

For the first time, a method for trace detection of multiple classes of explosives in raw wastewater using SPE, high performance liquid chromatography (HPLC) and HRMS is presented. The main objectives were to develop a broadly applicable SPE method based on the extraction of 18 high-order organic explosives, including nitramines, nitrate esters, nitroaromatics and peroxides (Table 1) at the $ng \, L^{-1}$ concentration range; and to exploit the capability of HRMS further via application to suspect screening of several additional explosives in wastewater influent sampled from one of the largest wastewater treatment plants (WWTP) in the EU, based in London, UK. With continual monitoring of explosive components in influent wastewater, deviations from any measured background concentration could produce intelligence on the catchment area in which explosives may be illegally manufactured.

2. Experimental

2.1. Reagents, chemicals and consumables

HPLC grade methanol, acetonitrile, ethyl acetate, isopropyl alcohol, dichloromethane and dimethyldichlorosilane were purchased from Fisher Scientific (Loughborough, UK). For optimisation of the analytical method for a set of $n = 18$ prioritised explosives, standard solutions of hexahydro-1,3,5-trinitroso-1,3,5-triazine (R-salt, 99.8%), HMX (99.1%), RDX (98.6%), nitrobenzene (NB, 99.8%), nitroglycerine (NG, 99.4%), 3,4-dinitrotoluene (3,4-DNT, 100%), 2,4-dinitrotoluene (2,4-DNT, 100%), 2,6-DNT (100%), 2-nitrotoluene (2-NT, 99%), 3-nitrotoluene (3-NT, 98.7%), 4-nitrotoluene (4-NT, 99.2%), erythritol tetranitrate (ETN, 99.9%), tetryl (98.6%), TNT (100%) and PETN (99.4%) at $1000 \, mg \, L^{-1}$, and triacetone triperoxide (TATP, 99.1%), hexamethylene triperoxide diamine (HMTD, 89.1%) and ethylene glycol dinitrate (EGDN, 96.2%) at $100 \, mg \, L^{-1}$ were sourced from Accustandard (New Haven, CT, USA). For testing of the developed method for semi-targeted analysis, a second set of explosives, precursors and transformation products were selected ($n = 17$). These included 1,3,5-trinitrobenzene (TNB, 100%) at $2000 \, mg \, L^{-1}$, 1,2-dinitrobenzene (1,2-DNB, 100%), 1,3-dinitrobenzene (1,3-DNB, 97.0%), 4-amino-2,6-dinitrotoluene (4-Am-2,6-DNT, 100%), 2-amino-4,6-dinitrotoluene (2-Am-4,6-DNT, 100%), diphenylamine (DPA, 100%) at $1000 \, mg \, L^{-1}$, and nitroguanidine (NQ, 100%), 2,6-diamino-4-nitrotoluene (2,6-DA-4-NT, 99.7%), 2,4-diamino-6-nitrotoluene (2,4-DA-6-NT, 100%), 1,3-dinitroglycerin (1,3-DNG, 99.6%), 1,2-dinitroglycerin (1,2-DNG, 99.3%), picric acid (PA, 99.1%), triethylene glycol dinitrate (TEGDN, 97.4%), 3,5-dinitroaniline (3,5-DNA, 99.3%) at $100 \, mg \, L^{-1}$ were also sourced from Accustandard. 2,3-dimethyl-2,3-dinitrobutane (DMDNB, 98%) was purchased from Sigma-Aldrich (Gillingham, Dorset, UK) and 1,3-dimethyl-1,3-diphenylurea (DMDPU) and 1,3-diethyl-1,3-diphenylurea (DEDPU) were prepared in methanol at $1000 \, mg \, L^{-1}$ and obtained from the UK Forensics Explosives Laboratory (FEL). Working solutions were prepared in HPLC grade methanol for each stock solution at $10 \, mg \, L^{-1}$ and $100 \, \mu g \, L^{-1}$ and stored in the dark at $-20 \, °C$.

Ultrapure water was supplied by a Millipore Synergy-UV water purification system at $18.2 \, M\Omega \, cm$ (Millipore, Bedford, USA). Ammonium acetate (>99% purity), ammonium chloride (>99% purity) and hydrochloric acid solution (37% w/v) were purchased from Sigma-Aldrich.

2.2. Sample collection

Influent wastewater was collected from a wastewater facility located in the greater London (population equivalent = 3.5 mil-