



**HAL**  
open science

## Analysis of homemade peroxide-based explosives in water: A review

Pierre Michel, Jean-Luc Boudenne, Fabien Robert-Peillard, Bruno Coulomb

### ► To cite this version:

Pierre Michel, Jean-Luc Boudenne, Fabien Robert-Peillard, Bruno Coulomb. Analysis of homemade peroxide-based explosives in water: A review. Trends in Analytical Chemistry, 2023, 158, pp.116884. 10.1016/j.trac.2022.116884 . hal-03914456

**HAL Id: hal-03914456**

**<https://hal.science/hal-03914456>**

Submitted on 28 Dec 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Analysis of homemade peroxide-based explosives in water: A review

Pierre Michel, Jean-Luc Boudenne\*, Fabien Robert-Peillard, Bruno Coulomb  
Aix Marseille Univ, CNRS, LCE, Marseille, France

\* Corresponding author. Phone +33-(0)4-13551031; Fax +33-(0)4-13551060;  
e-mail: jean-luc.boudenne@univ-amu.fr

## Abstract

The detection of explosives is of paramount importance in the areas of internal security and military activities. Tracking down clandestine laboratories manufacturing homemade explosives, and in particular those made from organic peroxides (triacetone triperoxide TATP, methyl ethyl ketone peroxide MEKP, hexamethylene triperoxide diamine HMTD), is a major issue in the fight against terrorism worldwide. During the synthesis of these peroxide-based explosives, significant quantities of precursors or residues of explosives may be discharged into wastewater and then in environmental waters. Some of these precursors (e.g. acetone or hydrogen peroxide) are used for other applications (e.g. solvents, bleaching agents, medical and industrial products) and are therefore not specific of the manufacture of explosives. However, they can provide a first indication of the location of the production site through on-line monitoring of wastewater. Many analytical techniques exist for the trace analysis of explosives on post blast surfaces or for the quantification of traces of hydrogen peroxide in biological systems (topics already reviewed elsewhere). However, the application of these techniques to water and wastewater monitoring remains challenging. In this review, water sample preparation and instrumental methods applied (or at least adaptable) to water analysis for the quantification of peroxide-based explosives (PBEs) and of their major precursors are reviewed and discussed. Sample preparation by solid-phase extraction (SPE) is thoroughly investigated for organic peroxides and some precursors. Analytical methods such as electrochemistry, spectroscopy, chromatography coupled to mass spectrometry or flow injection techniques are presented for their application to PBEs. The advantages and disadvantages of the different analytical techniques show that some of these techniques could be combined to develop low-cost, easily transportable, and miniaturized methods for automated *in-situ* analyses of explosives and their major precursors.

## Abbreviations

APCI: atmospheric pressure chemical ionization; CFA: continuous flow analysis; CL : chemiluminescence; DADP: diacetone diperoxide; ECL : electrogenerated chemiluminescence; FIA: flow injection analysis; FTMS: Fourier transformation mass spectrometry; GC-MS: gas-chromatography coupled to mass spectrometry; HME: home-made explosive; HMTD: hexamethylene triperoxide diamine; HPLC: high performance liquid chromatography; HRMS: high-resolution mass spectrometry; HRP: horseradish peroxidase; LC-MS: liquid chromatography-mass spectrometry; LCMS-IT-TOF: liquid chromatography mass spectrometry – ion trap – time of flight; LOD: Detection limit; MEKP: methyl ethyl ketone peroxide; MIP: molecularly imprinted polymer; PBE: peroxide-based explosive; SFA: segmented flow analysis; SIA: sequential injection analysis ;SPE: solid phase extraction; TATP: triacetone triperoxide; TMDD: tetramethylene diperoxide dicarbamine; TNT: 2,4,6-trinitrotoluene.

## 1. Introduction

Explosive compounds can be classified according to their properties, chemical composition or use in explosive materials. The most widely used classification comes from the military field and is based on the velocity of detonation of the explosives: they are then classified in primary, secondary, and tertiary types [1,2]. Primary explosives are compounds that are very sensitive to small or moderate stimuli

(friction, heat, spark, impact) which means that a small amount of energy is required to detonate these materials. Primary explosives include peroxide-based explosives such as TATP, HMTD, diacetone diperoxide (DADP) and tetramethylene diperoxide dicarbamide (TMDD), lead-based explosives (lead styphnate, lead azide), tetrazene and nitroglycerin explosives. Among primary explosives, PBEs are unstable and have no industrial or military use and are thus often home-made explosives. Secondary explosives cannot be detonated without a strong stimulus. They often refer to nitro-based explosives such as royal demolition explosive (RDX), trinitrotoluene (TNT) or dynamite used in the military field. Usually, primary explosives are used in detonator in small quantities (in the milligram range) to initiate the detonation of a large quantity of secondary explosives. The most used primary explosive for transfer charge in the detonator is lead azide which is the most powerful of this class of explosives [3,4]. Tertiary explosives are based on ammonium nitrate and are the least sensitive type of explosives. They are safer to produce in large quantities than nitroglycerin-based explosives even though their pressure and detonation velocity are higher [1]. This additional group was created to separate and include insensitive explosives that are used in mining and demolition fields [2].

The last decade has witnessed a significant increase of terrorism and of the use of PBEs around the world. PBEs is a usual denomination for the most common and simple method of producing explosives: TATP, HMTD and MEKP. These organic peroxides can be synthesized from common household or sanitary products that are readily available on the market, such as acids, acetone, and hydrogen peroxide. The manufacturing process of these products can easily be found online by anyone, and the chemicals required are generally easily accessible (even though regulations have been put in place for some chemicals [5]).

These organic peroxides are all sensitive and unstable compounds and have a high detonation capacity, almost as powerful as the explosives commonly used in military applications such as 2,4,6-TNT [6]. Although these explosives are quite simple to synthesize, their detection in various environmental compartments raises major concerns due to the common household compounds used during their synthesis. In particular, the fact that these organic peroxides are nitrogen-free explosives means that they cannot be detected by most explosive detectors designed to detect nitrogenous molecules, especially nitroaromatic explosives. Therefore, in the early 2000s, terrorists have focused on these easy-to-synthesize and difficult-to-detect compounds and used them in terrorist attacks around the world. This constant threat therefore makes it crucial to identify and locate clandestine laboratories that synthesize home-made explosives (HMEs) before they can be used for terrorist purposes.

Since the late 2000s, wastewater has proven to be a good indicator matrix for the early detection of analytes in many fields. For example, the analysis of drugs in wastewater [7-10] provides an estimate of their nature and level of use in order to understand social and economic damage and to initiate targeted actions to reduce illegal drug use. The identification and quantification of pharmaceuticals or personal care products in wastewater [11,12] also enables a better understanding of their consumption and fate in order to develop or optimize removal processes. More recently, in the context of the COVID-19 pandemic, a wastewater analysis approach has been used to better understand the incidence, evolution and emergence of new variants [13-16].

The acid or thermal degradation of TATP and other PBEs has been extensively studied, and the relatively low log  $K_{ow}$  [17] and vapor pressure values at 25 °C (reported in Table 1) indicate that these compounds can be partially dissolved in water. However, the fate of these molecules in wastewater is not well known and their degradation in the wastewater system will depend on e.g. microbiological and physico-chemical parameters, the presence of other chemical compounds and the length of the wastewater system or residence time. Therefore, it is important to quantify these compounds as close as possible to the clandestine laboratories at the nanomolar level in order to increase the chances of detecting PBEs or their precursors in wastewater.

Some of the precursors or explosives themselves can thus be used as tracers of clandestine HMEs synthesis laboratories through wastewater monitoring [18]. Detection in wastewater of unusual concentrations of one PBE molecule or of either one unusual precursor (hexamine for HMTD, methyl ethyl ketone for MEKP) or of two general household chemicals simultaneously (acetone and hydrogen

peroxide for TATP) could be a strong indicator of HMEs production. A previous review conducted by R.M Burks and D.S. Hage in 2009 [19] focused on optical methods (luminescence, fluorescence, infrared and Raman spectroscopy), mass spectrometry and electrochemical techniques for PBEs and emphasized field measurements using portable instruments or assay kits. Another study by S. Caygill et al. in 2012 [20] focused mainly on the detection of many types of explosives and their precursors or degradation products on surfaces using commercial analytical devices or laboratory techniques. However, most of the techniques presented concerned the detection of analytes on surfaces or in the vapor phase and are therefore not always suitable for the analysis of these molecules in wastewater. This paper aims to focus on PBEs (the most frequently used HMEs over the last decade) and their precursors and to present a state of the art of current techniques and analytical methods for the on-line and off-line detection of PBEs and their precursors in water.

## 2. Peroxide-based explosives

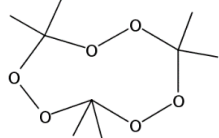
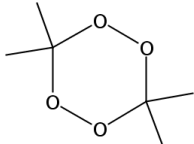
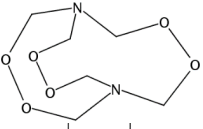
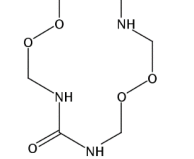
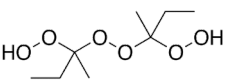
Acetone peroxide (also known as APEX) is a family of unstable nitrogen-free primary cyclic explosive compounds consisting of a mixture of hydrogen peroxide and acetone catalyzed by a strong acid (usually sulfuric acid) [21,22]. This PBE is mainly composed of the TATP trimer and the DADP dimer (DADP) [22-25]. DADP is often considered as the most dangerous and least stable form of the acetone peroxide, although a specific study on DADP has suggested that this form of acetone peroxide is less sensitive to friction and shock than its trimer form TATP [23].

HMTD is a heterocyclic amine peroxide which is less stable and more sensitive than TATP, with a low vapor pressure that makes it difficult to detect. HMTD is synthesized from a mixture of hexamine and hydrogen peroxide catalyzed by citric acid [6, 20, 26-29].

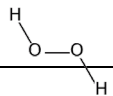
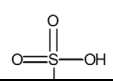
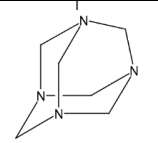
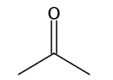
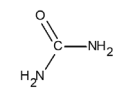
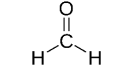
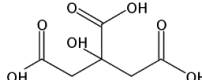
TMDD is also a cyclic organic peroxide known as a primary explosive, prepared from hydrogen peroxide, acetone, urea, and formaldehyde [30]. The exact molecular structure and sensitivity properties of this compound remained unknown for many years and were only confirmed by further structural investigation in 2015 using X-ray crystal structure analysis and new sensitivity tests [31-32]. These difficulties in characterizing this compound explain why there are few papers on TMDD and why most of its physical and chemical properties are unknown (mainly computed theoretical data available).

MEKP is a liquid organic peroxide with explosive properties. This family of peroxides is composed of at least seven peroxide species including a cyclic trimer, its most described species during MEKP preparation is the non-cyclic trimer  $C_8H_{18}O_6$  [33-34].

There are few databases and papers summarizing the experimental, physical and chemical properties of these peroxide-based explosives. Most of the data for these primary explosives are therefore theoretical data calculated by computation software. The results for the peroxide-based compounds are compiled in Table 1. The precursors of organic peroxides used to produce HMEs are simpler compounds and more data related to their experimental physical and chemical characteristics are therefore available (Table 2). The literature review therefore shows that primary explosives are still poorly described compounds that would require more physical and chemical experiments to establish and confirm their theoretical characteristics. Further studies on these molecules would allow a better understanding of their specificities in order to improve their detection and prevent potential future terrorist attacks involving these homemade explosives.

Compound	IUPAC Name	Molecular Structure	CAS Number	Molecular Weight (g mol <sup>-1</sup> )	pKa	Log K <sub>ow</sub> (25°C)	Solubility in water (25°C) (g L <sup>-1</sup> )	Vapor Pressure (mmHg, 25°C)
Triacetone triperoxide (TATP)	3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxacyclononane		17088-37-8	222.24	-	0.67	-	0.048
Diacetone diperoxide (DADP)	3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane		1073-91-2	148.16	-	1.47	-	0.185
Hexamethylene triperoxide diamine (HMTD)	3,4,8,9,12,13-Hexaoxa-1,6-diazabicyclo [4.4.4] tetradecane		283-66-9	210.18	2.66±0.20	1.3	-	2.9 x 10 <sup>-03</sup>
Tetramethylene diperoxide dicarbamide (TMDD)	1,2,8,9-tetraoxa-4,6,11,13-tetraazacyclotetradecane-5,12-dione		350581-77-0	236.18	11.66±0.20	-	-	-
Methyl ethyl ketone peroxide (MEKP)	2-hydroperoxy-2-(2-hydroperoxybutan-2-ylperoxy)butane		1338-23-4	210.22	11.27	-	1 - 5	<0.01

**Table 1. Physico-chemical properties of PBE compounds**

Compound	Molecular Structure	CAS Number	Molecular Weight (g mol <sup>-1</sup> )	pKa	Log K <sub>ow</sub> (25°C)	Solubility in water (25°C) (g L <sup>-1</sup> )	Vapor Pressure (mmHg, 25°C)	Henry Law constant (mol/m <sup>3</sup> .Pa)
Hydrogen peroxide		7722-84-1	34.01	11.65±0.10	-0.564±0.350	488	1.97	1.08 x 10 <sup>3</sup>
Sulfuric acid		7664-93-9	98.08	-3.19±0.15	-1.114±0.350	1000	0.0001	1.3 x 10 <sup>13</sup>
Hexamine		100-97-0	140.19	5.28±0.20	-0.169±0.736	853	6.1 x 10 <sup>-04</sup>	6.25 x 10 <sup>3</sup>
Acetone		67-64-1	58.08	20	-0.042±0.192	94.7	231	0,26
Urea		57-13-6	60.06	0.1	2.41	545	1.2 x 10 <sup>-05</sup>	5.7 x 10 <sup>6</sup>
Formaldehyde		50-00-0	30.03	13.27	0.35	400	3.890	3.2 x 10 <sup>1</sup>
Citric acid		77-92-9	192.12	2.93±0.28	-1.198±0.396	1330	1.7 x 10 <sup>-08</sup>	3 x 10 <sup>16</sup>

**Table 2. Physico-chemical properties of the main PBE precursors**

### 3. Analytical methods for PBEs determination

#### 3.1. Collection and preparation of water samples

This section focuses on the detection of PBEs in water and more precisely on the detection of the most common ones: TATP, HMTD, MEKP and their main precursors such as hydrogen peroxide and hexamine. Detection in aqueous media means that water samples from diverse origins should be collected and prepared properly before analysis. Sampling can be conducted through two different ways: continuously (passive or active) or discretely.

For example, discrete sampling has been chosen for river water samples, then stored at 4 °C for up to 24 h or longer at -20 °C. Samples were not acidified to avoid potential hydrolysis of the analytes [35]. Another discrete sampling has been performed for wastewater analysis by Ghosale et al. to test their method on real samples [36]. Authors collected samples in polyethylene bottles, filtered with Whatman® filter paper grade 42 and stored at 5 °C before analysis. However, discrete sampling is not advised for clandestine laboratories surveillance as it only allows a water sample to be collected at a specific time and at a specific location, and do not provide a large range of data.

In the case of the study of HMEs in wastewater, continuous methods should be chosen for an in-situ study, as it would permit an optimized temporal data sampling to avoid missing data. The choice of a passive or active sampling will depend on the techniques used and on the environmental matrices analyzed [37]. In this way, Rapp-Wright et al. sampled 24-h composites during eight days. After collection, samples were acidified at pH 2 with HCl to minimize microbial degradation and preserve stability, and stored at -20 °C. It should be noted that the potential hydrolysis of TATP was not considered in this study, this point should be further explored for sample conservation (advantages or disadvantages of acid preservation before analysis). Before being analyzed, the samples were defrosted and filtered under vacuum using grade GF/F glass microfiber filters [38]. These studies showed that the temperature control of the samples was crucial to avoid evaporation of the analytes.

In some studies, TATP quantification was performed after solid-phase microextraction (SPME) from sample headspace. However, analysis in the sample headspace or in the vapor phase is not sufficiently practical or sensitive for rapid in situ wastewater analysis [39]. Regarding sample preparation, SPE seems thus the method of choice for cleaning up and preconcentrating environmental samples. Different phases of SPE sorbent are available and have been used according to physical properties of PBEs. In a study on improved determination of femtogram-level of organic explosives in multiple matrices (including Thames River water in London and untreated wastewater from a major London wastewater plant) using dual-sorbent SPE and LC-HRMS [40], seven different sorbent cartridges were tested on 44 organic explosives (including TATP, HMTD and DADP). Among these, three sorbents showed sensitive results in the recovery of organic peroxides (model solutions fortified at 25 or 250 µg L<sup>-1</sup>): Oasis HLB (recoveries from 68 to 100 %), Isolute ENV+ (recoveries from 62 to 83 %) and HyperSep Retain PEP (recoveries from 82 to 115 %). In addition to the comparison of the efficiency of different sorbents used in SPE for the detection of explosives in water, the final purpose of that paper was to experiment a solid phase extraction step combining 2 different sorbent cartridges connected in series to study matrix removal in complex samples. The combination Hypersep NH<sub>2</sub>-Oasis HLB gave the best results for wastewater samples, both in term of matrix effects and recovery. For other matrices (soils, cooking oils, swabs), other combinations were found to be more effective, and therefore a universal combination of cartridges was not found to be suitable for all samples, depending on the nature of the matrix.

Another study conducted by the same research group aimed to detect different types of explosives (including organic peroxides such as TATP and HMTD) in London wastewater in 2017 [37]. The SPE was performed with a set of 34 different sorbents with 3 replicates. The most effective sorbent was HyperSep Retain PEP with recoveries of 85±1% and 89±11% for HMTD and TATP respectively. The results presented for the other sorbents exhibited recoveries with very high relative standard deviations (up to 100%), which limited the exploitation of the results for the various sorbents. Oasis HLB and Isolute ENV+ showed poor recoveries, which was contradictory with the previous study that showed good results for the same cartridges [40]. Volatility issues might explain these poor repeatabilities and recoveries for organic peroxides.

Recently, Irlam et al. [41] developed a low-cost 3D printed block for solid-phase extraction of trace explosives. The miniaturized piece was 3D-printed in a commercial methacrylate-based resin using a cost-effective stereolithography printer. The frit-free configuration of the 3D-printed SPE column allowed the packing of various commercially available sorbent particles. Although the extraction efficiency with Isolute Env+ for TATP and especially HMTD in different matrices was not fully satisfactory, the device allowed SPE with low back pressure and could thus be coupled to alternative miniaturized analytical systems.

Another study concerning the detection of trace amounts of HMEs and precursors by SPE LC-MS in Thames River in London in 2017 showed results of the efficiency of different sorbent cartridges: Bond Abs Elut Nexus, Oasis HLB, Telos ENV and Telos Neo PRP. These sorbents were tested for TATP, HMTD and hexamine [18]. SPE was used to clean the samples and extract the analytes for LC-MS analysis. The conclusion of this paper was that Telos ENV exhibited the best efficiency. This SPE cartridge worked perfectly for HMTD, showed good rates for hexamine but had a rather poor analyte removal rate with TATP. Among other sorbents, only Bond Elut Nexus cartridge showed a good recovery rate (66.5%) for TATP, the other tests were all ineffective for the extraction of organic peroxides and precursors. The washing step with methanol 60% might explain these poor SPE performances.

In order to assess the consistency between these different studies, we tried to summarize the published results for the SPE of TATP, HMTD and hexamine, depending on the sorbent phase used (Table 3). High discrepancies between the published results can be easily noticed, for example regarding TATP and Oasis HLB, with recoveries ranging from 16 to 100 %. Modified polystyrene-divinylbenzene sorbent phases appeared to provide the most consistent results for TATP and HMTD with recoveries between 72 and 99%. The data in Table 3 show that the sample volume collected was between 6 and 100 mL and that an enrichment factor of 20 to 40 was achieved (except in the case of evaporation under N<sub>2</sub> where the enrichment factor can reach 1000). However, it should be taken into consideration that the quantification methods used in these studies were based on LC-MS systems and that the use of less sensitive analytical methods will require higher enrichment factors and therefore larger sample volumes. Further studies are required to confirm these results and better study recoveries of organic peroxides during SPE step are also needed.



Manufacturer	Sorbent tradename	Sorbent	Sample matrix <sup>1</sup>	Analyte	Eluent <sup>2</sup>	Removal or recovery (%)	Sample vol (mL)	Eluent vol (mL)	EF <sup>3</sup>	Ref
Agilent	Bond Elut Abs Nexus	Polymeric sorbent, non-polar retention mechanism	River water	Hexamine	ACN	6.1	6	4	-	[18]
			River water	TATP	ACN	66±3	6	4	-	[18]
			Wastewater	TATP	ACN	49±11	100	1	1000**	[37]
			River water	HMTD	ACN	1.1	6	4	-	[18]
			Wastewater	HMTD	ACN	50±18	100	1	1000**	[37]
Agilent	Bond Elut PPL	S-DVB <sup>4</sup> modified with proprietary nonpolar surface	Wastewater	TATP	ACN :MeOH	78±86	100	5	400*	[38]
			Wastewater	HMTD	ACN :MeOH	72±84	100	5	400*	[38]
Agilent	Bond Elut ENV	Unmodified PS-DVB <sup>5</sup>	Wastewater	TATP	ACN :MeOH	96±105	100	5	400*	[38]
			Wastewater	TATP	ACN :MeOH	106±8	100	5	20	[38]
			Wastewater	HMTD	ACN :MeOH	37±42	100	5	400*	[38]
			Wastewater	HMTD	ACN :MeOH	149±4	100	5	20	[38]
Biotage	Isolute ENV+	Hydroxylated PS-DVB	River water, wastewater	TATP	ACN	83±3	100	2.5	40	[40]
			Wastewater	TATP	MeOH	282±4	100	5	400*	[38]
			Wastewater	TATP	MeOH	97±18	100	5	20	[38]
			Wastewater	TATP	MeOH	122±8	100	2	1000**	[37]
			Soil extract, blood, oil	TATP	ACN	60±15	10	0.5	20	[41]
			River water, wastewater	HMTD	ACN	81±8	100	2.5	40	[40]
			Wastewater	HMTD	MeOH	53±16	100	5	400*	[38]
			Wastewater	HMTD	MeOH	43±3	100	5	20	[38]
			Wastewater	HMTD	MeOH	103±12	100	2	1000**	[37]
			Soil extract, blood, oil	HMTD	ACN	15±8	10	0.5	20	[41]
Biotage	Evolute ABN	Modified PS-DVB	Wastewater	TATP	MeOH	99±24	100	5	20	[37]
			Wastewater	HMTD	MeOH	82±17	100	5	20	[37]
Kinesis	TELOS ENV	Hydroxylated PS-DVB	River water	Hexamine	ACN	82.9±6	6	8	-	[18]
			River water	TATP	ACN	38	6	8	-	[18]
			Wastewater	TATP	MeOH	132±5	100	2	1000**	[37]
			River water	HMTD	ACN	109±5	6	8	-	[18]
			Wastewater	HMTD	MeOH	21±17	100	2	1000**	[37]
Kinesis	TELOS neo PRP	Polar-modified reversed phase	River water	Hexamine	ACN	0.3	6	8	-	[18]
			River water	TATP	ACN	0	6	8	-	[18]
			River water	HMTD	ACN	0.4	6	8	-	[18]

ThermoFisher Scientific	HyperSep Retain PEP	Urea PS-DVB modified	Wastewater	TATP	ACN	115±11	100	2.5	40	[37]
			Wastewater	TATP	MeOH	89±11	100	5	400*	[37,38]
			River water, Wastewater	HMTD	ACN	97±10	100	2.5	40	[40]
			River water, Wastewater	HMTD	MeOH	85±1	100	5	400*	[38,40]
Waters	Oasis HLB	DVB-N-vinylpyrrolidone	River water	Hexamine	ACN	14	6	4	-	[18]
			River water	TATP	ACN	16	6	4	-	[18]
			River water, Wastewater	TATP	ACN	100±22	100	2.5	40	[40]
			Wastewater	TATP	MeOH	35±36	100	5	400*	[38]
			Wastewater	TATP	MeOH	70±14	100	5	20	[38]
			River water	HMTD	ACN	0.4	6	4	-	[18]
			River water, Wastewater	HMTD	ACN	89±22	100	2.5	40	[40]
			Wastewater	HMTD	MeOH	59±62	100	5	400*	[38]
Wastewater	HMTD	MeOH	116±13	100	5	20	[38]			

<sup>1</sup> Spiked river water and wastewater samples

<sup>2</sup> ACN : Acetonitrile; MeOH : Methanol

<sup>3</sup> Enrichment Factor

<sup>4</sup> Styrene-DivinylBenzene

<sup>5</sup> PolyStyrene-DivinylBenzene\* Eluate was evaporated to dryness under N<sub>2</sub> before reconstitution in 250 µL of MeOH, \*\* Eluate was evaporated to dryness under N<sub>2</sub> before reconstitution in 100 µL of MeOH

**Table 3. Summary of SPE results published for organic peroxides and hexamine**

### 3.2. Liquid chromatography-mass spectrometry (LC-MS) analysis

A large number of military explosives are usually analyzed by GC-MS methods. However, PBEs are unstable compounds and some studies have noted that repeated injections quickly lead to problems of activation of the stationary phase of GC column resulting in the deterioration of the quality of chromatographic peaks [42]. To overcome this problem, analytical techniques based on LC-MS have been developed for HMTD [38] and for TATP [43] using atmospheric pressure chemical ionization (APCI) in positive mode. These first studies allowed the quantification of HTMTD and TATP with detection limits of 20 and 100  $\mu\text{g L}^{-1}$  (90 nM and 476 nM), respectively.

On this basis, a number of other studies have led to the development of various LC-MS methods. One example is the study conducted by Xu et al. in 2014 [44] who quantified TATP from 13  $\mu\text{g L}^{-1}$  (59 nM) and HMTD from 4.9  $\mu\text{g L}^{-1}$  (23 nM) among twenty organic explosives using a hybrid mass spectrometer combining a linear ion trap detector and an orbitrap detector with Fourier transformation. Another example concerns the use of a high-resolution time-of-flight mass spectrometer (Q-ToF) for the analysis of TATP and HMTD [45] sampled on swabs in indoor and outdoor surfaces. This method enabled sensitive and robust quantification of HTMD and TATP (detection limits of 0.5 and 10 ng on column, respectively). Ions with an m/z ratio of 209.0766 ( $[\text{HMTD}+\text{H}]^+$ ) and 207.0973 ( $[\text{C}_7\text{H}_{15}\text{O}_5\text{N}_2]^+$ , by reaction between HMTD and methanol) are reported in the literature as characteristics of the presence of HMTD in a sample. The high-resolution mass spectra obtained in this study showed that the m/z 207.0614 ion observed corresponds in practice to tetramethylene diperoxide diamine dialdehyde, a degradation product of HMTD. Concerning TATP, the study confirmed the major ion used in LC-MS with a m/z ratio of 240.1443 ( $[\text{TATP}+\text{NH}_4]^+$ ).

All these methods were however only performed with analytical standards or cotton swabs extracted with different solvents. Very few LC-MS methods have been directly applied for PBEs determination in environmental samples such as wastewater, natural waters or other environmental matrices. Therefore, Gamble et al. developed in 2017 an analytical method based on a SPE step followed by LC-MS-Ion Trap-Time of Flight detection (LC-MS-IT-ToF) for the quantification of TATP, HTMD and its main precursor, namely hexamine [18]. This method was applied to their monitoring during the different steps of the treatment chain applied in wastewater treatment plants. The SPE step used herein was optimized to clean up the samples prior to LC-MS analysis and the detection limits obtained for TATP, HMTD and hexamine were 252, 44 and 35  $\mu\text{g L}^{-1}$  (1.1, 0.2 and 0.25  $\mu\text{M}$ ), respectively. Another research group in London also published two papers on the combination of SPE and LC-HRMS (high-resolution mass spectrometry) detection, for the determination of various explosives including TATP and HMTD in 24-h composite wastewater samples. The study of the SPE step was first carried out on with 34 different sorbents for the whole compounds tested [38], the results concerning PBEs were presented previously in section 3.1. SPE not only allowed sample clean-up but also the ability to reach a pre-concentration factor of 20 to 400, contributing to lower the detection limit of TATP and HMTD to 2 and 5  $\mu\text{g L}^{-1}$  (9 nM and 23 nM), respectively. The second study concerned the development of a similar method with a dual-sorbent SPE to limit matrix effects in wastewater and river water samples. The detection limits were then slightly lowered to 1.2 and 1.4  $\mu\text{g L}^{-1}$  (6 nM and 7 nM) for TATP and HMTD [40].

These methods enable selective detection of PBEs, however the detection limits determined in these studies seem high for monitoring application in wastewater. It would be necessary to couple these methods with a pre-concentration procedure allowing a high enrichment factor.

### 3.3. Electrochemical Methods

Organic peroxides such as TATP and HMTD can be easily converted by UV irradiation [46] or acid degradation [47] to their precursor  $\text{H}_2\text{O}_2$ , which is an electroactive molecule detectable by electrochemical methods. The application of these analytical methods to PBEs and their major precursors in natural waters or wastewater can therefore be considered. However, while there are many references in the literature on the detection of  $\text{H}_2\text{O}_2$  by electrochemical methods, very few studies have demonstrated an application to natural waters or wastewater on real samples. Indeed, most studies

concern the detection of  $\text{H}_2\text{O}_2$  in biological systems. Advances in this field will therefore not be considered here (they can be found in other reviews including Chen et al.'s research works in 2012 [48] or more recently by Yu et al. in 2022 [49]), this section will focus on the electrochemical detection of PBEs. Nevertheless, it is interesting to present here Ghosale et al.'s works (2017) who developed a low-cost way to detect  $\text{H}_2\text{O}_2$  in wastewater using a paper electrode functionalized by silver nanoparticles-based ink [36]. This paper electrode was prepared by direct writing with a pen filled with a nano ink made of silver nanoparticles capped with octylamine (AgNPs-OA) and sintered to make it conductive.  $\text{H}_2\text{O}_2$  was then detected by cyclic voltammetry using the paper electrode with a detection limit as low as  $0.5 \mu\text{M}$ , with a linear range up to  $10 \text{ mM}$  and a relative standard deviation below 2%. Real wastewater samples from the city of Bilaspur in India were tested with the developed method. The results showed that the  $\text{H}_2\text{O}_2$  concentration was below the detection limit, but spike levels of  $\text{H}_2\text{O}_2$  between  $0.6$  and  $5 \text{ mM}$  in samples resulted in recovery rates close to 100%. Stability of the prepared electrode was checked for 60 days, and the same analytical responses were found during this period.

Various analytical systems were developed for the direct or indirect (after conversion to hydrogen peroxide) detection of PBEs. A first study in 2006 reported the results for the monitoring of liquid traces of PBEs such as TATP and HMTD. This method was based first on the photochemical degradation of organic peroxides and then on the preferential electrocatalytic activity of Prussian blue towards the reduction of  $\text{H}_2\text{O}_2$ . Amperometric measurements provided a highly selective and sensitive peroxide sensing. The results of this study showed low detection limits of  $50 \text{ nM}$  for TATP with photochemical  $\text{H}_2\text{O}_2$  generation using an Nd:YAG laser, or  $0.25$  and  $0.30 \mu\text{M}$  for TATP and HMTD respectively with simple UV irradiation using a high intensity UV lamp [50].

In 2008 and 2009, a research group from the University of Idaho proposed a low-cost electrochemical detection method for TATP [51] and HMTD [52] using the electrocatalytic reaction of Fe(II/III)-ethylene diamine tetraacetate (EDTA) complex and hydrogen peroxide. The difference between the two methods depended on the way in which PBEs standards were treated. For TATP, the method involved acid decomposition with  $1.08 \text{ M HCl}$  to release  $\text{H}_2\text{O}_2$  or hydroperoxides, and then buffering with acetic acid at  $\text{pH } 3.7$ . The peroxides then underwent an electrocatalytic reduction by the Fe(II)-EDTA complex on a glassy carbon electrode. The method showed a detection limit of  $0.89 \mu\text{M}$  for TATP. The authors also showed that there was an electrocatalytic response even without acid treatment of the samples, probably due to the residual  $\text{H}_2\text{O}_2$  from the TATP synthesis [51]. For HMTD, hydrolysis was carried out by direct acidification with the Fe(III)-EDTA reagent at  $\text{pH } 2.1$ . The results showed a detection limit of  $30 \mu\text{M}$  for HMTD [52]. Simultaneous analysis of HMTD and TATP was therefore possible, depending on the hydrolysis step.

In 2013, the University of Mississippi developed a method for the determination of TATP using electrogenerated chemiluminescence (ECL). This method was based on the generation of hydroxyl radicals ( $\bullet\text{OH}$ ), from peroxide functional groups present in TATP, able to oxidize electrogenerated  $\text{Ru}(\text{bpy})_3^+$  cations into  $\text{Ru}(\text{bpy})_3^{2+*}$  cations in the excited state, return to the fundamental state being accompanied by a light emission. The study compared three detection methods, with prior UV irradiation of TATP, with prior acid hydrolysis of TATP by  $0.12 \text{ mM HCl}$ , or by direct ECL analysis of TATP. The same detection limit of  $2.5 \mu\text{M}$  TATP was obtained in the three cases, the direct method allowing a faster and easier analysis. The authors also considered  $\text{H}_2\text{O}_2$  that may be present in household products. Its interference has been able to be eliminated by the addition of a catalase enzyme to the sample prior to analysis, the excess catalase being then removed by the addition of sodium azide which had no effect on ECL detection. The results also showed that the responses of TATP and HMTD were additive, and that this method was therefore not able to quantify the two compounds separately [53]. A similar approach was described by Cui et al [54] with a 2-D ECL using gold nanoparticles, providing a detection limit of approximately  $10 \mu\text{M}$  for TATP.

Similarly, Mamo and Gonzalez-Rodriguez [55] have also developed an electrochemical method that did not require sample treatment by UV irradiation or acid hydrolysis. In this study, they used a molecularly imprinted polymer (MIP) that allowed the selective extraction of TATP and its detection by electrochemistry. The MIP was polymerized on the surface of a glassy carbon electrode by cyclic voltammetry. The detection of TATP by differential pulse voltammetry with  $\text{LiClO}_4$  as supporting

electrolyte resulted in a detection limit of 0.12  $\mu\text{M}$  with a good selectivity towards other types of explosives such as nitro-aromatics [55].

The different systems presented above could be relevant for monitoring traces of TATP or HMTD, because they usually do not require a large amount of energy or bulky equipment. However, most of them have only been tested on standard solutions of TATP or HTMD in acetonitrile or in a water/acetonitrile mixture and have not been tested on natural water or wastewater real samples. Moreover, the detection limits obtained were not adapted for the quantification of TATP or HMTD traces in water and these systems would benefit from being coupled with SPE methods presented in part 3.1.

### 3.4 Spectroscopy-based methods

Like electrochemical methods, studies related to  $\text{H}_2\text{O}_2$  detection in biological samples by spectroscopic methods will not be considered in this review, as it is focused on methods potentially applicable to environmental water samples.

Qian et al. [56] synthesized a quinoline-based fluorescent probe for  $\text{H}_2\text{O}_2$  quantification in aqueous solutions. The method was based on the cleavage of the boronate group of the probe by  $\text{H}_2\text{O}_2$  which led to an increase of the fluorescence intensity at 480 nm. The probe showed a good chemoselectivity for  $\text{H}_2\text{O}_2$  over other reactive oxygen species or halogenated anions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>), however the concentrations tested did not reflect environmental concentrations and the method has not been tested on real water samples. A similar approach was described with an anthracene boronate probe for  $\text{H}_2\text{O}_2$  detection, exhibiting significant fluorescent quenching in the presence of triethylamine and  $\text{H}_2\text{O}_2$ , with detection limit below 17 nM [57]. The interference study was only limited to TATP and organic solvents.

Another study [58] focused on TATP and  $\text{H}_2\text{O}_2$  determination by oxidative deboronation and fluorescence detection. A prochelator bearing a boronate group was synthesized and demonstrated a fluorescence increase ( $\lambda_{\text{em}} = 440 \text{ nm}$ ) upon addition of  $\text{H}_2\text{O}_2$  and  $\text{Zn}^{2+}$ . As TATP could not be quantified directly, it was first degraded in a 1 M acetic acid solution for 5 min to release  $\text{H}_2\text{O}_2$ . The method resulted in a limit of detection below 10 nM for TATP. However, this method was described in methanol solution and the authors mentioned that it worked only in the presence of low levels of water. The potential for application to real aqueous samples seems thus quite limited.

Dansyl-modified  $\beta$ -cyclodextrin derivatives have been proposed for the detection of TATP and DADP in aqueous solutions [59]. The sensing was based on the displacement of the dansyl moiety from the cavity of the cyclodextrin by the peroxide guest resulting in a decrease of the intensity of the fluorescence of the dye. Although this strategy brings a new methodology for peroxide sensing, sensitivity and selectivity were rather low and applications to real water samples are not possible.

Sella and Shabat [60] presented a self-immolative dendritic probe for TATP direct detection. These probes, made of self-immolative dendrimers, directly detected TATP through amplification of a single cleavage event initiated by one molecule of  $\text{H}_2\text{O}_2$  by spontaneously releasing all their end-groups (reporters). A single molecule of  $\text{H}_2\text{O}_2$  releases 3 molecules of free fluorogenic reporters which should provide a fluorescence response. This new probe allowed the measurement of  $\text{H}_2\text{O}_2$  at a concentration of 1  $\mu\text{M}$  and TATP in micrograms scale in aqueous buffer (pH=8) without any pretreatment.

In Can et al.' study [61], a spectrophotometric detection method was developed, based on the acidic hydrolysis of TATP into  $\text{H}_2\text{O}_2$  mixed with magnetite nanoparticles. The TATP determination consisted in 3 steps. First, TATP was hydrolyzed into  $\text{H}_2\text{O}_2$  by a strong acid (HCl). Then  $\text{H}_2\text{O}_2$  formed was degraded with  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles (NMPs) into reactive oxygen species. Finally, *N,N*-dimethyl-*p*-phenylene diamine (DMPD) was added to react with the reactive oxygen species and oxidized into a colored cationic radical ( $\text{DMPD}^+$ ) which was then retained on a Nafion membrane. Quantification of TATP was carried out by spectrophotometric measurements at 554 nm on the membrane and resulted in a detection limit of 0.4  $\mu\text{M}$ . This method was shown to be highly selective over possible interferents existing in household detergents, reducing sugars or even soil extracts.

More recently, Duong and Rhee [62] reported the fabrication of a hydrogen peroxide sensing membrane based on HRP immobilized on a sol-gel membrane, synthesized from carboxyl groups functionalized with CdSe/ZnS quantum dots and aminofluorescein. This membrane allowed fluorescence measurement of H<sub>2</sub>O<sub>2</sub> concentrations in the range 0.1–10 mM with a detection limit of 11 μM. However, the method was only applied to artificial wastewater prepared from standard ions, which did not allow the evaluation of possible interferences and matrix effects of real wastewater samples.

### 3.5 Flow Injection techniques

Many on-line analysis systems have been developed for the detection of H<sub>2</sub>O<sub>2</sub> in different media but very few systems have been applied to the detection of explosives. As with electrochemical systems or spectroscopic methods, H<sub>2</sub>O<sub>2</sub> can be considered both as a precursor or as a degradation product of peroxide-based explosives (after acid hydrolysis or UV irradiation). This section will only focus on flow analytical systems applied to the detection of PBEs or to their precursors in water samples. Analytical features of the different flow systems described below are compared in Table 4.

Some flow analytical systems have been reported for the quantification of H<sub>2</sub>O<sub>2</sub> in natural waters or wastewater. Lazrus et al. [63] proposed in 1985 a fluorescence detection method based on the reaction of H<sub>2</sub>O<sub>2</sub> with horseradish peroxidase (HRP) in the presence of *p*-hydroxyphenylacetic acid. This method was adapted to a segmented flow analyzer (SFA) and was applied to H<sub>2</sub>O<sub>2</sub> quantification in atmospheric precipitations. This method was also adapted by Schick et al. [64] in 1996 to a continuous flow analysis procedure (CFA). They applied this automated analytical procedure to H<sub>2</sub>O<sub>2</sub> measurements in environmental samples (snow, rain, surface water, spring water) and drinking water samples and compared the method with two commonly used spectrophotometric methods respectively based on titanium-H<sub>2</sub>O<sub>2</sub> complex formation and DPD (*N,N*-diethyl-*p*-phenylenediamine) oxidation. The method resulted in a low detection limit (6 nM) and measurement capacity of approximately 12 samples per hour. The method was however interfered by chlorine, organic peroxides, and other oxidants, and dissolved organic matter; although the analytical performances obtained were better than those obtained by spectrophotometric methods; these interferences limit its applicability to environmental samples or wastewater. More recently, the reaction of H<sub>2</sub>O<sub>2</sub> with HRP was adapted in a Flow Injection Analysis (FIA) system by Tang et al. [65] using near-infrared spectrofluorimetric detection of tricarbochlorocyanine dye (Cy.7.Cl). The detection limit obtained after optimization of the operating conditions was 55 nmol and the method was applied to the quantification of H<sub>2</sub>O<sub>2</sub> in real rainwater samples. However, the interference of nitrates for a molar ratio higher than 1000 can pose analytical difficulties for the quantification of H<sub>2</sub>O<sub>2</sub> at low concentrations in wastewater.

In 2019, Jones & Lee [66] presented a sequential injection analysis (SIA) system for ultra-sensitive quantification of H<sub>2</sub>O<sub>2</sub> in coastal seawater samples. The analytical procedure was based on chemiluminescence detection of H<sub>2</sub>O<sub>2</sub> using luminol and iron interference was masked by complex formation with ferrozine. The SIA system enabled sensitive measurements of H<sub>2</sub>O<sub>2</sub> down to 0.14 nM with an autonomy of 48h.

Concerning the analysis of PBEs, two flow systems have been reported. In the first one, Mahbub et al [67] optimized the conditions for the acid degradation of PBEs (HMTD, MEKP, TATP) with concentrated HCl and developed a method for the detection of H<sub>2</sub>O<sub>2</sub> thus generated by chemiluminescence with luminol and Cu<sup>2+</sup> as catalyst, after neutralization with 18% sodium hydroxide. The method was adapted in a flow injection system allowing the quantification of HMTD, MEKP or TATP in less than 3 minutes at concentrations in the μM range. The use of concentrated HCl implied the modification of traditional FIA systems based on the use of a peristaltic pump (rapid deterioration of tubings and equipment) which was replaced by pneumatically driven flow control. The low acid degradation efficiency of MEKP (9% under optimized conditions) was reported as a limitation of the system.

In the second one, a flow analysis system was directly coupled to mass spectrometers. In this case, the column compartment was bypassed, and the FIA system allowed then direct injection into the ionization source. Ostrinskaya et al. [68] developed a FIA system coupled to a tandem mass spectrometer for the

detection and quantification of ten inorganic or organic explosives including TATP and HMTD with a quantification limit of 0.43 and 0.04  $\mu\text{g L}^{-1}$  (1.9 nM and 0.19 nM) respectively and with an analysis time of less than 1 minute.

**Table 4. Summary of flow systems performance for the detection of HMEs and their precursors.**

Analyte	Flow system	Method	Detection limit ( $\mu\text{M}$ )	Linear Range ( $\mu\text{M}$ )	RSD (%)	Reference
H <sub>2</sub> O <sub>2</sub>	SFA fluorometry	POPHA	0.012	0.012 – 15	0.66	[63]
H <sub>2</sub> O <sub>2</sub>	CFA fluorimetry	POPHA	0.006	0.024 – 0.29	2.19	[64]
H <sub>2</sub> O <sub>2</sub>	FIA NIR	Cy7 Dye	0.056	0.186 – 7.19	1.3	[65]
	Spectrofluorometry					
H <sub>2</sub> O <sub>2</sub>	SIA CL	Luminol		0.25x10 <sup>-3</sup> - 0.9	2.2	[66]
TATP/HMT	FIA CL	Luminol/Cu <sup>2</sup>	0.5	1-200	-	[67]
D	FIA CL	+	10	20-200	-	[67]
MEKP		Luminol/Cu <sup>2</sup>				
		+				
TATP	FIA MSMS	APCI (Pos)	1.9x10 <sup>-3</sup>	1.9x10 <sup>-3</sup> – 0.9	0.92	[68]
HMTD	FIA MSMS	APCI (Pos)	1.9x10 <sup>-4</sup>	1.9x10 <sup>-4</sup> – 0.48	3.82	[68]

### 3.6 Handheld methods

The tracking of clandestine PBEs synthesis laboratories can be facilitated using easily portable or transportable analytical procedures. In the last decade, some studies have been carried out for the development of handheld methods allowing the rapid and on-site quantification of explosives or their precursors.

Stewart et al [69] showed that a portable Raman spectrometer could be used to quickly determine the concentration of H<sub>2</sub>O<sub>2</sub> in aqueous solutions on site, without complex calibration procedures. The method resulted in a semi-quantification of H<sub>2</sub>O<sub>2</sub>, and the concentrations detected were quite high (range from 5 to 30% w/w), thus limiting its applicability to measurements in suspected improvised explosive manufacturing sites.

On-site measurements can also be performed with paper-based analytical devices. Salles et al [70] developed a colorimetric paper sensor for the identification of five explosives (TATP, HMTD, 4-amino-2-nitrophenol, nitrobenzene and picric acid). The method was based on the formation of 3 spots on the sensor paper with three different reagents (creatinine, acidified potassium iodide, aniline) which reacted differently with the targeted explosives. The quantification was performed after acquisition of an image and determination of the RGB (Red-Green-Blue) values of each spot using a smartphone. Looking specifically at PBEs, the method was able to semi-quantify TATP and HMTD from concentrations of 0.2 and 1.0  $\mu\text{g}$  per 10  $\mu\text{L}$  drop respectively, i.e. concentrations of 100 and 400  $\mu\text{M}$ . In a similar way, Peters et al [71] developed a paper-based microfluidic analytical device ( $\mu\text{PAD}$ ) for the on-site detection of improvised explosives and H<sub>2</sub>O<sub>2</sub>. The detection of H<sub>2</sub>O<sub>2</sub> was based on the reaction of the sample on a spot of ammonium titanium oxalate leading to the formation of a yellow color. Quantification could be performed with the naked eye, but the analytical characteristics could be improved by using a color scanner and ImageJ software. In this latter configuration, H<sub>2</sub>O<sub>2</sub> could be detected from 400  $\mu\text{M}$ . Although simple, these paper-based devices have poor detection limits and seems not applicable for trace measurements of PBEs in water.

A more promising approach was developed by Climent et al. with a test-strip assay based on a TATP-selective polyclonal antibody associated with mesoporous silica nanoparticles loaded with the fluorescent dye sulforhodamine B [72]. An hapten derivating from TATP was used to trigger the release of the fluorescent dye. Presence of TATP in the tested sample released the fluorescent chemical probe

with large signal amplification. TATP could be detected at concentrations as low as 15  $\mu\text{g L}^{-1}$  (68 nM), without prior acid or UV decomposition and without interference from other organic peroxides or  $\text{H}_2\text{O}_2$ . The results showed a slight interference of nitropenta (PETN) and nitroguanidine and the method was able to detect TATP in real conditions, in drinking water and in wastewater (influent and effluent). This approach was further optimized in 2020 by the same research group with an improved hapten and smartphone detection coupled to a home-made excitation source, which gave a detection limit lowered to 4 nM [73]. The authors described their method as semi-quantitative, as the dynamic response range was very narrow (one or two orders of magnitude, depending on the detection mode).

Many other handheld methods have been described for the detection of  $\text{H}_2\text{O}_2$  or TATP in the vapor phase or for organic solutions of TATP powder. Detection of  $\text{H}_2\text{O}_2$  in saturated vapor with portable organic-inorganic hybrid fluorescent probes has been demonstrated with detection limit in the vapor phase as low as 184 ppt [74]. However, no potential application of this type of analytical method has been demonstrated for the direct detection in real aqueous samples. A method with a portable luminometer has been proposed for the handheld detection of organic solutions of TATP and HMTD after acidic degradation, reaction with HRP and detection with luminol [75]. Detection limits of 0.2  $\mu\text{M}$  were obtained, but selectivity issues limited the application of the method for the identification of unknown powders.

Globally, only the method based on the polyclonal antibody seems to have the potential for application to the detection of PBEs in real water samples with handheld devices. Sensitivity and selectivity with multiple potential interferents are still a challenge for these type of devices, and detection in real complex liquid samples needs to be validated in further studies.

#### 4. Conclusion and perspectives

Many current studies on other compounds (COVID-19, pharmaceuticals, drugs) have proven that wastewater and rivers could serve as proxies for the study of these contaminants, highlighting that the choice of these aqueous matrices applied to explosives or their precursors would be very relevant. However, while there are many references in the literature for the detection of explosives in the gas phase or on surfaces, only a few articles and reviews focusing on the detection of HMEs and their precursors in water and wastewater have been conducted.

Several methods have been applied for the detection of PBEs or their precursors. Most of these methods have detection limits in the micromolar range and are therefore not applicable for wastewater or other real water samples. Methods with lower detection limits are listed in Table 5. For PBEs, mass spectrometry-based methods seem to be the only methods with sufficient sensitivity and proven selectivity for complex real samples. However, the fluorescent test strips based on polyclonal antibodies could have the potential for rapid and on-site alert device for the presence of low levels of PBEs. Validation in real complex samples is still required for a reliable deployment of this type of devices.

Analyte	Method	LOD (nM)	Comment	Ref
TATP		6		
HMTD	SPE – LC/HRMS	7	Complex and expensive material	[40]
TATP	MIP / cyclic voltammetry	120	No test on real water samples, interference study limited to other explosives	[55]
TATP	Fluorescence	10	Only demonstrated with low level of water, interference with $\text{H}_2\text{O}_2$	[58]



TATP		1.9		
HMTD	FIA-MS/MS	0.19	Complex and expensive material	[68]
TATP	Antibody- Fluorescence test strips	4	Portable, narrow dynamic range, selectivity not demonstrated in complex samples	[73]
H <sub>2</sub> O <sub>2</sub>	Fluorescence	17	Lack of interference study, no test on real water samples	[57]
H <sub>2</sub> O <sub>2</sub>	SIA-CL	0.14	Demonstrated only on seawater samples	[66]

**Table 5. Summary of methods for the detection of PBEs and their precursors with nanomolar detection limits**

Flow systems would benefit from the implementation of SPE to improve the detection limits and selectivity. Although only a few studies have been conducted on SPE of PBEs from water, a few sorbents appear to be effective for the extraction of TATP (Agilent Bond Elut Nexus) and HMTD (Kinesis TELOS® Env) or both (Thermo Scientific™ HyperSep™ Retain PEP). Further studies should make it possible to integrate these sorbents into flow analysis systems. The extraction and pre-concentration of PBEs could also be ensured by a passive sampling step that would allow accumulation and concentration over long-term exposure [76,77]. However, this type of device is also difficult to calibrate in order to obtain reliable quantitative results and this might be the reason why no passive sampling in the water phase for PBEs has been described yet.

Few studies have been conducted with real samples of wastewater or river water. Table 5 presents the different works reported with applications on real environmental samples. The most comprehensive overview was conducted by Rapp-Wright et al. in 2017 [38], representing a large screening study of explosives in wastewater from a major European city. Although only one type of explosive of the 29 analyzed was found in the wastewater (2,4-dinitrotoluene at a maximum concentration of 303 ng L<sup>-1</sup>), this type of study could be expanded to precursors and continuous measurement of the concentrations of PBEs and their precursors.

There is thus still a real need to develop low-cost, easily transportable, and miniaturized methods for automated in-situ analyses of explosives and their main precursors. As wastewater networks form a mesh in a city, such an analytical system could be deployed at several locations in the wastewater network, which would enable a rough location of the sources of their releases into the sewer system. This alert function could thus circumscribe the geographical scope and time span of the investigation of clandestine laboratories by the security forces. The discrimination between these precursors and their presences in household products remains challenging, so the analytical system needs to be able to carry out several measurements per hour to observe an accurate time trend. Reaching detection limits in the nM range is also a challenge to be applied to detect low concentrations (or variations) in real water samples. Combining SPE of PBEs to efficient optical detection (chemiluminescence, fluorescence) could provide an ideal tool to reach low detection limits and selectivity in complex matrices such as wastewater. For in-situ detection of HMEs, another technical obstacle is the wastewater matrix, which limits the possibility of using traditional SPE methods that are prone to column clogging. Therefore, new pre-concentration methods for these molecules, suitable for miniaturized flow systems, must be developed.

#### Acknowledgement

This work is funded by the French Defense Innovation Agency (AID #2021451) and Aix-Marseille university.

## References

- [1] E. G. Mahadevan, Ammonium Nitrate Explosives for Civil Applications: Slurries, Emulsions and Ammonium Nitrate Fuel, Oils in Wiley-VCH, 1 Classification of Explosives, 2013, pp. 1-4.
- [2] F. Zapata, C. García-Ruiz, Chemical Classification of Explosives, Critical Reviews in Analytical Chemistry. (2020) 1–18. <https://doi.org/10.1080/10408347.2020.1760783>.
- [3] M. Marshall, J.C. Oxley, Chapter 2 – Explosives: The Threats and the Materials, 2009, pp. 11-26. <https://doi.org/10.1016/B978-0-12-374533-0.00002-7>
- [4] N. Mehta, K. Oyler, G. Cheng, A. Shah, J. Marin, K. Yee, Primary Explosives: Primary Explosives, Z. Anorg. Allg. Chem. 640 (2014) 1309–1313. <https://doi.org/10.1002/zaac.201400053>.
- [5] Regulation (EU) 2019/1148 of the European parliament and the council of 20 June 2019 on the marketing and use of explosives precursors; <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32019R1148>
- [6] E. Espinosa, A. Peña-Quevedo, L. Pacheco-Londono, R. Infante, S. Hernández-Riveral, Explosive Materials: Classification, Composition and Properties, in T.J. Janssen (Eds.), A Review of Peroxide Based Homemade Explosives: Characterization and Detection, Huppauge Inc., New York, 2010, pp. 259-282.
- [7] E. Zuccato, C. Chiabrando, S. Castigloiono, R. Bagnati, and R. Fanelli, Estimating Community Drug Abuse by Wastewater Analysis, EHP, Environ. Health Perspect. 116 (2008) 1027-1032. <https://dx.doi.org/10.1289%2Fehp.11022>.
- [8] R. Irvine, C. Kostakis, P. Felgate, E. Jaehne, C. Chen, J. White, Population drug use in Australia: A Wastewater Analysis, Forensic Sci. Int. 210 (2011) 69-73. <http://dx.doi.org/10.1016/j.forsciint.2011.01.037>.
- [9] M. Alda, C. Postigo, S. Castiglioni, Illicit drug consumption estimations derived from wastewater analysis: A critical review, Sci. Total Environ. 409 (2011) 3564-3577. <https://doi.org/10.1016/j.scitotenv.2010.05.030>.
- [10] F. Lai, C. Ort, C. Gartner, S. Carter, J. Prichart, P. Kirkbride, R. Bruno, W. Hall, G. Eahlesham, J. Mueller, Refining the estimation of illicit drug consumptions from wastewater analysis: co-analysis of prescription pharmaceuticals and uncertainty assessment, Water Res. 45 (2011) 4437-4448. <https://doi.org/10.1016/j.watres.2011.05.042>.
- [11] J. Radjenovic, M. Petrovic, D. Barcelo, Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor, Anal Bioanal Chem. 387 (2007) 1365-1377. <https://doi.org/10.1007/s00216-006-0883-6>.
- [12] A. Shraim, A. Diab, A. Alsuhaime, E. Niazy, M. Metwally, M. Amad, S. Sioud, A. Dawoud, Analysis of some pharmaceuticals in municipal wastewater of Almadinah Almunawarah, Arabian J. Chem. 10 (2017) S719-S729. <https://doi.org/10.1016/j.arabj.2012.11.014>.
- [13] S. Shah, S. Gwee, J. Ng, N. Lau, J. Koh, J. Pang, Wastewater surveillance to infer COVID-19 transmissions: A systematic review, Sci. Total Environ. 804 (2022) 150060. <https://doi.org/10.1016/j.scitotenv.2021.150060>.
- [14] K. Arkas, L. Hillary, S. Malham, J. McDonald, D. Jones, Wastewater, and public health: the potential of wastewater surveillance for monitoring COVID-19, Curr Opin Environ Sci Health. 17 (2020) 14-20. <https://doi.org/10.1016/j.coesh.2020.06.001>.
- [15] S. Wang, H. Green, M. Wilder, Q. Du, B. Kmush, M. Collins, D. Larsen, T. Zeng, High-Throughput Wastewater Analysis for Substance Use Assessment in Central New York during the COVID-19 Pandemic, Environ. Sci.: Processes Impacts, 22 (2020) 2147-2161. <https://doi.org/10.1039/D0EM00377H>.
- [16] W. Randazzo, E. Guesvas-Ferrando, R. Sanjuan, P. Domingo-Galap, G. Sanchez, Metropolitan wastewater analysis for COVID-19 epidemiological surveillance, Int. J. Hyg. Environ. Health, 230 (2020) 113621. <https://doi.org/10.1039/D0EM00377H>.
- [17] P.L. Damour, A. Freedman, J. Wormhoudt, Knudsen effusion measurement of organic peroxide vapor pressures, Propellants Explos. Pyrotech, 35 (2010) 514-520. <https://doi.org/10.1002/prop.200900083>
- [18] S.C. Gamble, L.C. Campos, R.M. Morgan, Detection of trace peroxide explosives in environmental samples using solid phase extraction and liquid chromatography mass spectrometry, Environmental Forensics. 18 (2017) 50–61. <https://doi.org/10.1080/15275922.2016.1263901>.

- [19] R.M. Burks, D.S. Hage, Current trends in the detection of peroxide-based explosives, *Anal Bioanal Chem.* 395 (2009) 301–313. <https://doi.org/10.1007/s00216-009-2968-5>.
- [20] J.S. Caygill, F. Davis, S.P.J. Higson, Current trends in explosive detection techniques, *Talanta*. 88 (2012) 14–29. <https://doi.org/10.1016/j.talanta.2011.11.043>.
- [21] M. Fitzgerald, D. Bilusich, Sulfuric, Hydrochloric, and Nitric Acid-Catalyzed Triacetone Triperoxide (TATP) Reaction Mixtures: An Aging Study: Triacetone Triperoxide reaction mixtures, *Journal of Forensic Sciences*. 56 (2011) 1143–1149. <https://doi.org/10.1111/j.1556-4029.2011.01806.x>.
- [22] L.C. Pacheco-Londono, A.J. Pena, O.M. Primera-Pedrozo, S.P. Hernandez-Rivera, N. Mina, R. Garcia, R.T. Chamberlain, R.T. Lareau, An experimental and theoretical study of the synthesis and vibrational spectroscopy of triacetone triperoxide (TATP), in: E.M. Carapezza (Ed.), Orlando, FL, 2004: p. 279. <https://doi.org/10.1117/12.542851>.
- [23] P. Bowden, B. Tappan, V. Manner, D. Preston, B. Scott, Characterization of Diacetone Diperoxide (DADP), *AIP Conf. Proc.*, 1793 (2017) 040010. <https://doi.org/10.1063/1.4971504>.
- [24] R. Matyas, J. Pachman, Study of TATP: Spontaneous Transformation of TATP to DADP – Full Paper, *Propellants Explos. Protech.*, 34 (2009) 484-488. <https://doi.org/10.1002/prop.200800043>.
- [25] H. Félix-Riviera, M. Ramirez-Cedeno, R. Sanchez-Cuprill, S. Hernandez-Rivera, Triacetone triperoxide thermogravimetric study of vapor pressure and enthalpy of sublimation in 303-338 K temperature range, *Thermochim. Acta*, 514 (2011) 37-43. <https://doi.org/10.1016/j.tca.2010.11.034>.
- [26] A. Pena-Quevedo, S. Hernandez-Rivera, Mass Spectrometry Analysis of Hexamethylene Triperoxide Diamine by its Decomposition Products, *Proc. SPIE*, 7303 (2009). <https://doi.org/10.1117/12.819080>.
- [27] J.C. Oxley, J.L. Smith, M. Porter, L. McLennan, K. Colizza, Y. Zeiri, R. Kosloff, F. Dubnikova, Synthesis and Degradation of Hexamethylene Triperoxide Diamine (HMTD), *Propellants, Explosives, Pyrotechnics*. 41 (2016) 334–350. <https://doi.org/10.1002/prop.201500151>.
- [28] R. Matyas, J. Pachman, *Primary Explosives*, Springer-Verlag, Berlin, and Heidelberg, 2013.
- [29] Office of the director of National Intelligence: Joint Counterterrorism Assessment Team First Responders toolbox, Hexamethylene Triperoxide Diamine HMTD Survey, 2020.
- [30] A.J. Peña-Quevedo, N. Mina-Calmide, N. Rodríguez, D. Nieves, R.B. Cody, S.P. Hernández-Rivera, Synthesis, characterization and differentiation of high energy amine peroxides by MS and vibrational microscopy, in: E.M. Carapezza (Ed.), Orlando (Kissimmee), FL, 2006: p. 62012E. <https://doi.org/10.1117/12.666202>
- [31] M. Fitzgerald, M. Gardiner, D. Armitt, G. Dicoski, C. Wall, Confirmation of the Molecular Structure of Tetramethylene Diperoxide Dicarbamide (TMDD) and Its Sensitiveness Properties, *J. Phys. Chem. A*, 119 (2015) 905-910.
- [32] A. Pedroza Zarate, F. Colpas-Castillo, D. Franco, W. Cabrera-Lafaurie, E. Espinosa-Fuentes, A Fragmentation Mechanism of Homemade Explosive TMDD Using DART-MS and Isotopic Labeling, *Chin. J. Explos. Propellants*, 41 (2018) 16-20. <http://dx.doi.org/10.14077/j.issn.1007-7812.2018.01.003>.
- [33] N. Milas, A. Golubovic, Studies in organic peroxides XXV: preparation, separation and identification of peroxides derived from methyl ethyl ketone and hydrogen peroxide. *J. Am. Chem. Soc.*, 81 (1959) 5824-5826. <https://doi.org/10.1021/ja01530a068>.
- [34] S. Graham, R. Hodgson, L. Vechot, M. Essa, Calorimetric studies on the thermal stability of methyl ethyl ketone peroxide (MEKP) formulations, *Process Saf. Environ. Prot.*, 89 (2011) 424-433. <https://doi.org/10.1016/j.psep.2011.08.005>.
- [35] J. Pachman, R. Matyas, Study of TATP: stability of TATP solutions, *Forensic Science International* 207 (2011) 212-214. <http://dx.doi.org/10.1016/j.forsciint.2010.10.010>
- [36] A. Ghosale, K. Shrivastava, R. Shankar, V. Ganesan, Low-Cost Paper Electrode Fabricated by Direct Writing with Silver Nanoparticle-Based Ink for Detection of Hydrogen Peroxide in Wastewater, *Anal. Chem.* 89 (2017) 776–782. <https://doi.org/10.1021/acs.analchem.6b03512>.
- [37] S. Gamble, *Forensic Detection of Explosives in the Wastewater System*, University College London, 2016.
- [38] H. Rapp-Wright, G. McEneff, B. Murphy, S. Gamble, R. Morgan, M. Beardah, L. Barron, Suspect screening, and quantification of trace organic explosives in wastewater using solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry, *Journal of Hazardous Materials* 329 (2017) 11–21. <https://doi.org/10.1016/j.jhazmat.2017.01.008>.

- [39] W. Fan, M. Young, J. Canino, J. Smith, J. Oxley, J.R. Almirall, Fast detection of triacetone triperoxide (TATP) from headspace using planar solid-phase microextraction (PSPME) coupled to an IMS detector *Analytical and Bioanalytical Chemistry* 403 (2012) 401-408. <https://doi.org/10.1007/s00216-012-5878-x>
- [40] R.C. Irlam, M.C. Parkin, D.P. Brabazon, M.S. Beardah, M. O'Donnell, L.P. Barron, Improved determination of femtogram-level organic explosives in multiple matrices using dual-sorbent solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry, *Talanta* 203 (2019) 65-76. <https://doi.org/10.1016/j.talanta.2019.05.047>.
- [41] R.C. Irlam, C. Hughes, M.C. Parkin, M.S. Beardah, M. O'Donnell, D. Brabazon, L.P. Barron, Trace multi-class organic explosives analysis in complex matrices enabled using LEGO®-inspired clickable 3D-printed solid phase extraction block array, *Journal of Chromatography A* 1629 (2020) 461506. <https://doi.org/10.1016/j.chroma.2020.461506>
- [42] A. Crowson, M.S. Beardah, Development of an LC/MS method for the trace analysis of hexamethylenetriperoxidodiamine (HMTD), *Analyst*. 126 (2001) 1689-1693. <https://doi.org/10.1039/b107354k>.
- [43] L. Widmer, S. Watson, K. Schlatter, A. Crowson, Development of an LC/MS method for the trace analysis of triacetone triperoxide (TATP), *Analyst*. 127 (2002) 1627-1632. <https://doi.org/10.1039/B208350G>.
- [44] X. Xu, M. Koeberg, C.-J. Kuijpers, E. Kok, Development and validation of highly selective screening and confirmatory methods for the qualitative forensic analysis of organic explosive compounds with high performance liquid chromatography coupled with (photodiode array and) LTQ ion trap/Orbitrap mass spectrometric detections (HPLC-(PDA)-LTQ Orbitrap), *Science & Justice*. 54 (2014) 3-21. <https://doi.org/10.1016/j.scijus.2013.08.003>.
- [45] L. Dunn, H.S.A. Al Obaidly, S.E. Khalil, Development and validation of fast liquid chromatography high-resolution mass spectrometric (LC-APCI-QtoF-MS) methods for the analysis of hexamethylene triperoxide diamine (HMTD) and triacetone triperoxide (TATP), *Forensic Chemistry* 10 (2018) 5-14. <https://doi.org/10.1016/j.forc.2018.06.003>
- [46] J. Hong, J. Maguhn, D. Freitag, A. Kettrup, Determination of H<sub>2</sub>O<sub>2</sub> and organic peroxides by high-performance liquid chromatography with post-column UV irradiation, derivatization and fluorescence detection, *Fresenius J. Anal. Chem.* 361 (1998) 124-128. <https://doi.org/10.1007/s002160050847>
- [47] Y. B. Tsaplev, Decomposition of cyclic acetone peroxides in acid media, *Kinetics and Catalysis*, 53 (2012) 521-524. <https://doi.org/10.1134/S0023158412050163>
- [48] Chen W., Cai S., Ren Q.-Q., Wen W., Zhao Y.-D., Recent advances in electrochemical sensing for hydrogen peroxide: a review, *Analyst* 137 (2012) 49-58. <https://doi.org/10.1039/C1AN15738H>
- [49] Yu Y., Pan M., Peng J., Hu D., Hao Y., Qian Z., A review on recent advances in hydrogen peroxide electrochemical sensors for applications in cell detection, *Chin. Chem. Lett.* 33 (2022) 4133-4145. <https://doi.org/10.1016/j.ccllet.2022.02.045>
- [50] D. Lu, A. Cagan, R.A.A. Munoz, T. Tangkuaram, J. Wang, Highly sensitive electrochemical detection of trace liquid peroxide explosives at a Prussian-blue 'artificial-peroxidase' modified electrode, *Analyst*. 131 (2006) 1279. <https://doi.org/10.1039/b613092e>.
- [51] D.F. Laine, C.W. Roske, I.F. Cheng, Electrochemical detection of triacetone triperoxide employing the electrocatalytic reaction of iron(II/III)-ethylenediaminetetraacetate and hydrogen peroxide, *Analytica Chimica Acta*. 608 (2008) 56-60. <https://doi.org/10.1016/j.aca.2007.12.003>.
- [52] D.F. Laine, I.F. Cheng, Electrochemical detection of the explosive, hexamethylene triperoxide diamine (HMTD), *Microchemical Journal*. 91 (2009) 125-128. <https://doi.org/10.1016/j.microc.2008.08.015>.
- [53] S. Parajuli, W. Miao, Sensitive Determination of Triacetone Triperoxide Explosives Using Electrogenerated Chemiluminescence, *Anal. Chem.* 85 (2013) 8008-8015. <https://doi.org/10.1021/ac401962b>.
- [54] Y. Cui, Y. Jin, X. Chen, J. Wu, Two-Dimensional Electrochemiluminescence on Porous Silicon Platform for Explosive Detection and Discrimination, *ACS Sens.* 3 (2018) 1439-1444. <https://doi.org/10.1021/acssensors.8b00113>

- [55] S. K. Mamo, J. Gonzalez-Rodriguez, Development of a molecularly imprinted polymer-based sensor for the electrochemical determination of triacetone triperoxide (TATP), *Sensors* 14 (2014) 23269-23282. <https://doi.org/10.3390/s141223269>
- [56] Y.-Y. Qian, L. Xue, D.-X. Hu, G.-P. Li, H. Jiang, Quinoline-based fluorescent probe for ratiometric detection of hydrogen peroxide in aqueous solution, *Dyes and Pigments*. 95 (2012) 373–376. <https://doi.org/10.1016/j.dyepig.2012.05.013>.
- [57] Y. Zhang, Z. Jiao, W. Xu, Y. Fu, D. Zhu, J. Xu, Q. He, H. Cao, J. Cheng, Design, synthesis and properties of a reactive chromophoric/fluorometric probe for hydrogen peroxide detection, *New J. Chem.* 41 (2017), 3790-3797. <https://doi.org/10.1039/c7nj00851a>
- [58] M.E. Germain, M.J. Knapp, Turn-on Fluorescence Detection of H<sub>2</sub>O<sub>2</sub> and TATP, *Inorg. Chem.* 47 (2008) 9748–9750. <https://doi.org/10.1021/ic801317x>.
- [59] E. Almenar, A. M. Costero, P.Gaviña, S. Gil, M. Parra, Towards the fluorogenic detection of peroxide explosives through host–guest chemistry, *R. Soc. Open Sci.* 5 (2018) 171787. <http://dx.doi.org/10.1098/rsos.171787>
- [60] E. Sella, D. Shabat, Self-immolative dendritic probe for direct detection of triacetone triperoxide, *Chem. Commun.* (2008) 5701. <https://doi.org/10.1039/b814855d>.
- [61] Z. Can, A. Üzer, K. Türkekul, E. Erçağ, R. Apak, Determination of Triacetone Triperoxide with a N,N-Dimethyl-p-phenylenediamine Sensor on Nafion Using Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles, *Anal. Chem.* 87 (2015) 9589–9594. <https://doi.org/10.1021/acs.analchem.5b01775>.
- [62] H.D. Duong, J.I. Rhee, Development of Ratiometric Fluorescence Sensors Based on CdSe/ZnS Quantum Dots for the Detection of Hydrogen Peroxide, *Sensors*. 19 (2019) 4977. <https://doi.org/10.3390/s19224977>.
- [63] A.L. Lazrus, G.L. Kok, S.N. Gitlin, J.A. Lind, S.E. McLaren, Automated Fluorometric Method for Hydrogen Peroxide in Atmospheric Precipitation, *Anal. Chem.* 57 (1985) 917-922. <https://doi.org/10.1021/ac00281a031>
- [64] R. Schick, I. Strasser, H.-H. Stabel, Fluorometric Determination Of Low Concentrations Of H<sub>2</sub>O<sub>2</sub> In Water: Comparison With Two Other Methods And Application To Environmental Samples And Drinking-Water Treatment, *Wat. Res.* 31 (1997) 1371-1378. [https://doi.org/10.1016/S0043-1354\(96\)00410-1](https://doi.org/10.1016/S0043-1354(96)00410-1)
- [65] B. Tang, L. Zhang, K. Xu, FIA–near-infrared spectrofluorimetric trace determination of hydrogen peroxide using tricarchlorobocyanine dye (Cy.7.Cl) and horseradish peroxidase (HRP), *Talanta*. 68 (2006) 876–882. <https://doi.org/10.1016/j.talanta.2005.06.053>.
- [66] M.R. Jones, K. Lee, Determination of environmental H<sub>2</sub>O<sub>2</sub> for extended periods by chemiluminescence with real-time inhibition of iron interferences, *Microchemical Journal*. 147 (2019) 1021–1027. <https://doi.org/10.1016/j.microc.2019.04.027>.
- [67] P. Mahbub, P. Zakaria, R. Guijt, M. Macka, G. Dicoski, M. Breadmore, P.N. Nesterenko, Flow injection analysis of organic peroxide explosives using acid degradation and chemiluminescent detection of released hydrogen peroxide, *Talanta*. 143 (2015) 191–197. <https://doi.org/10.1016/j.talanta.2015.05.052>.
- [68] A. Ostrinskaya, R.R. Kunz, M. Clark, R.P. Kingsborough, T. Ong, S. Deneault, Rapid Quantitative Analysis of Multiple Explosive Compound Classes on a Single Instrument via Flow-Injection Analysis Tandem Mass Spectrometry, *J Forensic Sci.* 64 (2019) 223–230. <https://doi.org/10.1111/1556-4029.13827>.
- [69] S.P. Stewart, S.E.J. Bell, D. McAuley, I. Baird, S.J. Speers, G. Kee, Determination of hydrogen peroxide concentration using a handheld Raman spectrometer: Detection of an explosives precursor, *Forensic Science International*. 216 (2012) e5–e8. <https://doi.org/10.1016/j.forsciint.2011.08.002>.
- [70] M.O. Salles, G.N. Meloni, W.R. de Araujo, T.R.L.C. Paixão, Explosive colorimetric discrimination using a smartphone, paper device and chemometrical approach, *Anal. Methods*. 6 (2014) 2047–2052. <https://doi.org/10.1039/C3AY41727A>.
- [71] K.L. Peters, I. Corbin, L.M. Kaufman, K. Zreibe, L. Blanes, B.R. McCord, Simultaneous colorimetric detection of improvised explosive compounds using microfluidic paper-based analytical devices (μPADs), *Anal. Methods*. 7 (2015) 63–70. <https://doi.org/10.1039/C4AY01677G>.
- [72] E. Climent, D. Gröninger, M. Hecht, M.A. Walter, R. Martínez-Mañez, M.G. Weller, F. Sancenón, P. Amorós, K. Rurack, Selective, Sensitive, and Rapid Analysis with Lateral-Flow Assays Based on

Antibody-Gated Dye-Delivery Systems: The Example of Triacetone Triperoxide, *Chem. Eur. J.* 19 (2013) 4117–4122. <https://doi.org/10.1002/chem.201300031>.

[73] E. Climent, M. Biyikal, D. Gröninger, M.G. Weller, R. Martinez-Mañez, K. Rurack, Multiplexed detection of analytes on single test strips with antibody-gated indicator-releasing mesoporous nanoparticles, *Angew. Chem. Int.* 59 (2020) 23862-23869. <https://doi.org/10.1002/anie.202009000>

[74] H. Mu, Y. Zhang, P. Zheng, M. Zhang, Ultrafast fluorescence probe to H<sub>2</sub>O<sub>2</sub> vapor based on organic-inorganic hybrid silica nanoparticles, *Talanta* 237 (2022) 122914. <https://doi.org/10.1016/j.talanta.2021.122914>

[75] S. Girotti, E.N. Ferri, E. Maiolini, L. Bolelli, M. D’Elia, D. Coppe, F.S. Romolo, A quantitative chemiluminescent assay for analysis of peroxide-based explosives, *Anal. Bioanal. Chem.* 400 (2011) 313-320. <https://doi.org/10.1007/s00216-010-4626-3>

[76] G.L. McEneff, A. Richardson, T. Webb, D. Wood, B. Murphy, R. Irlam, J. Mills, D. Green, L.P. Barron, Sorbent film-coated passive samplers for explosives vapor detection Part B : deployment in semi-operational environments and alternative applications *Scientific Reports* 8 (2018) 5816, <https://doi.org/10.1038/s41598-018-24245-x>

[77] N. Estoppey, J. Mathieu, E. Gascon Diez, E. Sapin, O. Delémont, P. Esseiva, L.F. de Alencastro, S. Coudret, P. Folly, Monitoring of explosive residues in lake-bottom water using Polar Organic Chemical Integrative Sampler (POCIS) and chemcatcher: determination of transfer kinetics through Polyethersulfone (PES) membrane is crucial, *Environ. Poll.* 252 (2019) 767-776. <https://doi.org/10.1016/j.envpol.2019.04.087>