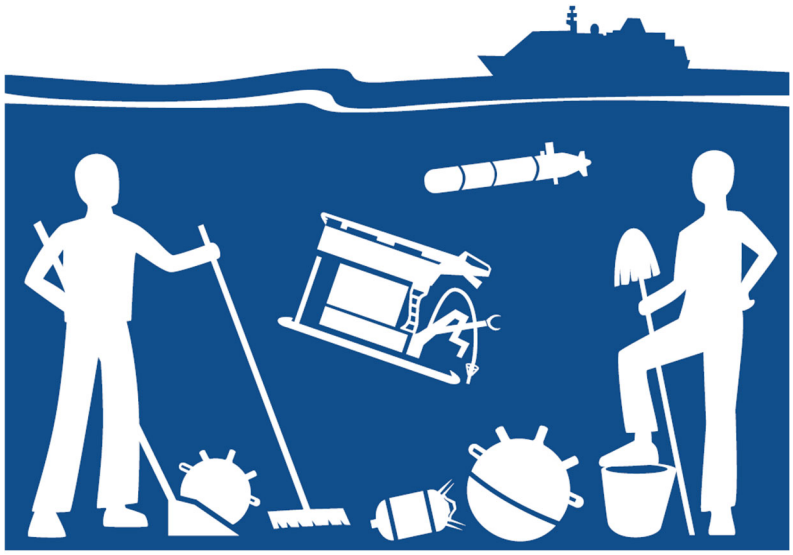

MMinE-SwEEPER

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Abstract

Coastal European waters are contaminated ubiquitously with unexploded ordnance (UXO) and munitions from intentional disposal, especially resulting from the two World Wars (WWI and WWII). In addition to the explosion and security risks, these munitions contain cytotoxic, genotoxic, and carcinogenic chemicals associated with conventional explosives, chemical warfare agents (CWA), and munition structural components. There is a critical need to clear undersea munitions due to the hazards associated with accidental detonation and leakage of toxic chemicals. Recent studies have demonstrated the ubiquitous contamination of EU marine waters with munitions, and have shown conclusively that chemical leakage from underwater munitions is evident in the environment and biota. The enormous potential of offshore development and the Blue Economy, coupled with the nearly ubiquitous presence of relic munitions on the European seafloor, make explosive detection capabilities all the more urgent. Chemical monitoring within regulatory and scientific programs is critical for recognizing and responding to changes in the environmental release of hazardous substances. However, traditional monitoring efforts decouple sampling (at-sea, shipboard) and measurement (land-based laboratories) activities, typically relying on grab samples collected at long time intervals. This results in delays in data availability and likely failure to account for discontinuous chemical release events, as well as the fundamental follow-on effect that such events can therefore not be addressed or managed. Modern technology development is slowly changing this paradigm, with powerful analytical instruments that are portable and robust enough for use in the field. Fieldable instrumentation and methods have the potential to lower sampling and analytical costs, allow analysis of more samples to provide higher spatial or temporal coverage, permit redesign of sampling strategies in response to data generated on-the-fly, and avoid sample handling problems associated with sample preservation, storage, and laboratory processing. The goal of the current review is to provide an overview of the state-of-the-art with regard to fieldable technologies and techniques for analysis of dissolved explosive compounds in seawater. This will provide a background to evaluate the best technologies for different deployment scenarios, and to set targets for chemical detection technology planned in the MMinE-SwEEPER project.

1. Introduction

The European Commission has developed a dedicated strategy to realize the enormous potential of Blue Growth (BG) for Europe. BG is an instrument that could help drive job creation and promote stability in Europe as it represents over five million jobs and a gross added value of nearly €500 billion per year (European Union, 2012). Relic munitions and UXO on the seafloor are a major impediment to the development and exploitation of off shore resource potential represented by Blue Growth (Frey, 2018). This threat broadly affects offshore energy, aquaculture, shipping, and tourism. Maritime Spatial Planning (MSP) and Integrated Coastal Zone Management (ICZM) promote sustainable development and facilitate cross-sector and cross-border planning of marine waters and management of coastal zones. Within the Integrated Maritime Policy, the 2008 Marine Strategy Framework Directive (MSFD) aims to achieve good environmental status (GES) for EU marine waters by 2020, and toxic chemical release from corroding and deteriorating munitions directly challenges efforts to achieve GES.

Coastal European waters are contaminated ubiquitously with unexploded ordnance (UXO) and munitions from intentional disposal (Fig. 1; Beck et al., 2018). Coastal waters are particularly impacted by relic munitions resulting from the two World Wars (WWI and WWII), and the German portions of the North Sea and Baltic Sea alone contain some 1.6 million metric tons of munitions (Böttcher et al., 2011). In addition to the explosion and security risks, these munitions contain cytotoxic, genotoxic, and carcinogenic chemicals associated with conventional explosives, chemical warfare agents (CWA), and munition structural components. Explosives in underwater munitions tend to undergo slow alteration during exposure to seawater, making them more sensitive to detonation and therefore even more hazardous (Müller, 2017; Pfeiffer, 2012). There is a critical need to clear undersea munitions due to the hazards associated with accidental detonation and leakage of toxic chemicals. Explosion risk particularly applies to dredging and development of offshore infrastructure associated with aquaculture, wind farms, cables, and oil or gas pipelines, as well as increasing ship traffic in general. In Europe, investment in the offshore wind sector alone was expected to exceed €9 billion in 2018 (WindEurope, 2018), and UXO encounters have caused unexpected delays and costs in pipeline projects exceeding tens of million euros (Cooke, 2015; Griggs, 2014). In addition to the safety hazard of detonation, underwater munitions also pose a major environmental and ecological risk (Craig and Taylor, 2011; Greenberg et al., 2016; Missiaen et al., 2006), and munition clearance is also increasingly recognized as necessary on environmental grounds (Campana, 2016).

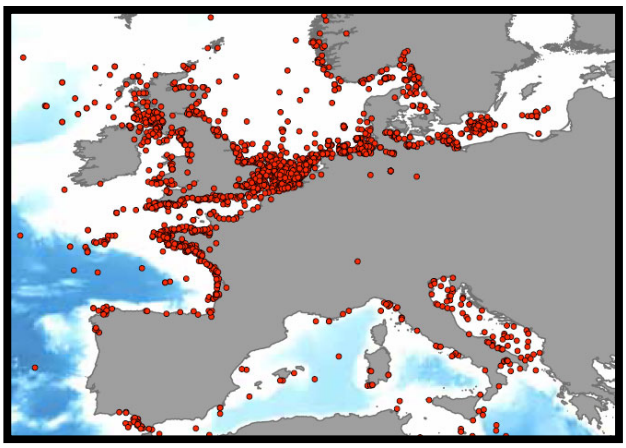

Figure 1. Known munitions dumpsites and reported munitions encounters in EU waters.

The EU context

A NATO pilot study initiated in 1992 identified conventional explosives and chemical warfare agents as primary trans-border contaminant risks associated with defense activities, and the HELCOM committees CHEMU and MUNI were formed to examine the issue subsequently (HELCOM, 1995, 2013). Since 2002, a number of EU- and national-funded research projects have been directed towards identifying underwater

munitions, and characterizing the spread and ecological impact of munition-associated chemicals. Chemical warfare agents have historically been the primary focus of these efforts, including the European programs REDCOD (2002-2005, Research on Environmental Damage Caused by Chemical Ordnance Dumped at Sea)(Amato et al., 2006), MERCW (2003-2008, Modelling of Ecological Risks Related to Sea-Dumped Chemical Weapons) (Missiaen et al., 2006), CHEMSEA (2011-2013, Chemical munitions search and assessment) (Bełdowski et al., 2016), and MODUM (2013-2016, Monitoring of Dumped (chemical) Munitions Threat) (Beldowski et al., 2018). A broader approach in two current projects includes also chemical contaminants associated with conventional explosives, EU-funded DAIMON (2016-2019, Decision Aid for Marine Munitions) and Germany-funded UDEMM (2016-2019, Environmental monitoring for the delaboration of conventional munitions) (Greinert, 2019). These studies have demonstrated the ubiquitous contamination of EU marine waters with UXO and discarded munition material (DMM), and have shown conclusively that chemical leakage from underwater munitions is evident in the environment and biota.

Existing methods for munition search and clearance

Given the lack of constraint surrounding the extent and quantity of munitions disposed in the marine environment, as well as the type of explosives and their condition, direct inspection is always required in order to evaluate the risk. Geophysical techniques have been successful in mapping the local distribution of munitions on the seafloor (10 - 1000 meter scale) and represent the most common survey tools employed by military and EOD service companies. Towed or remote/autonomously-operated vehicle-mounted magnetometers identify metal objects including munitions but also marine litter on and immediately below the seafloor. Sub-bottom profilers identify dense objects buried in the seafloor, but are also non-specific for munitions and often provide false positives (Wolf, 2017). Optical imagery or direct video inspection by ROV produces high resolution images and can be used to accurately identify munitions objects, but requires expert guidance and is limited to individual objects. Sidescan sonar and multibeam echo sounder images of objects exposed on the seafloor are often difficult to distinguish from rocks and marine litter. In addition, many geophysical techniques work well in shallow water, but are more challenging in deep water, leading to higher risk scores for deep water hazards (Sayle et al., 2009). Multiple techniques applied in combination improve confidence in detection and identification, but currently available methods remain unable to universally identify munitions on the seafloor.

Field methods for chemical detection

A variety of EOD tasks require sensing and detection of underwater munition, or discrimination and identification of UXO already detected by other means. Underwater munitions are extensively and virtually ubiquitously corroded (OSPAR Commission, 2016; Silva and Chock, 2016), and this breaching leads to slow release of a munition chemical plume to the water column (Wang et al., 2013; Beck et al., 2025). Direct sensing of explosive and CWA compounds provides the most direct approach to identify munitions, and is an unequivocal signature for objects requiring clearance. Chemical signatures are likely to be strongest and most persistent in near bottom waters, especially at deep sites where such chemical detection could help reduce the high risk scores. In addition, chemical fingerprints based on detection of multiple munition compounds (MCs) could help identify the specific types of munition present.

Chemical monitoring within regulatory and scientific programs is critical for recognizing and responding to changes in the environmental release of hazardous substances. However, traditional monitoring efforts decouple sampling (at-sea, shipboard) and measurement (land-based laboratories) activities, typically

relying on grab samples collected at long time intervals. This results in delays in data availability and likely failure to account for discontinuous chemical release events, as well as the fundamental follow-on effect that such events can therefore not be addressed or managed. Modern technology development is slowly changing this paradigm (Arndt et al., 2022), with powerful analytical instruments that are portable enough for transport to the field (e.g., Stravs et al., 2021). Field monitoring of chemical release from underwater munitions is particularly challenging given harsh conditions at sea.

Despite the clear need for in situ chemical detection technology, successful methods for broad application remain unrealized. The US military has spent more than US$400M on UXO sensing technologies (Seminar, 2015), which includes numerous approaches for chemical sensing of MC. Similar technologies have been developed in parallel in EU programs, and the most promising include amplifying fluorescent polymer sensors (Dock et al., 2010), displacement-based immunosensing technology (Veitch et al., 2011), square wave voltammetry (Fu et al., 2005), Raman spectroscopy (HMEs and Howe, 2016), and neutron analysis (Valkovic et al., 2009), among others to be discussed in this review. These methods all have strengths and weaknesses with regard to fieldability and appropriateness for detection of environmental levels of explosive compounds (typically ng/L levels).

Fieldable instrumentation and methods have the potential to lower sampling and analytical costs, allow analysis of more samples to provide higher spatial or temporal coverage, permit redesign of sampling strategies in response to data generated on-the-fly, and avoid sample handling problems associated with sample preservation, storage, and laboratory processing. The goal of the current review is to provide an overview of the state-of-the-art with regard to fieldable technologies and techniques for analysis of dissolved explosive compounds in seawater. This will provide a background to evaluate the best technologies for different deployment scenarios, and to set targets for chemical detection technology planned in the MMinE-SwEEPER project.

2. Critical characteristics

Previous studies of chemical patterns from underwater relic munitions have shown that dissolved explosive gradients are sharp and vary over time (e.g., Dock et al., 2010; Beck et al., 2019; Rosen et al., 2021), making measurement speed of great importance. Deployment of sensors on moving platforms also requires high sampling frequency (Dock et al., 2010). Low concentrations at relatively short distances from munition targets also indicates that detection capabilities must include high sensitivity. Munitions often contain mixtures of explosives, and it is advantageous to be capable of simultaneously measuring multiple target compounds (Lotufo et al., 2018). This specificity of detection is furthermore important to avoid interferences from one compound on another. Taken together, the most important technological aspects for the current evaluation are sensitivity, specificity, and analysis speed.

3. Existing technologies

Numerous mature portable technologies are available for detection of trace amount sof explosives in non-aquatic systems (e.g., airports), including desorption electrospray ionization (DESI-MS; Mulligan et al., 2005), GC-MS, and ion mobility spectrometry (IMS). These typically reply on gas-phase analytes or thermal desorption of particulate samples, although ESI interfaces for liquids are also possible (Wells et al., 2008).

A recent review of in situ technologies suggested that IMS may have future applications in aquatic systems (Raupers et al., 2023), but we are only aware of one study employing this technology. In that study, Rodacy et al. (2000, 2001, 2002) analyzed explosives in seawater after preconcentration by solid-phase micro-extraction, followed by thermal desorption and IMS detection. Despite the latter success, many of these techniques are challenging to deploy in the field due to their need for solvents and pressurized gas (Forbes and Cisco, 2017).

Laboratory-based analyses for explosives detection have improved greatly in specificity and sensitivity in recent decades (Gledhill et al., 2019; Bünning et al., 2021; Meany and McGuffin, 2008; Singh, 2007). However, many laboratory systems are not portable or robust enough to be field-deployable. Nonetheless, recent work has adapted many explosive detection systems for field use, including IMS (Rodacy et al., 2000, 2001, 2002), electrochemical sensors (e.g., Wang and Thongngamdee, 2003; Fu et al., 2005; Trammell et al., 2008), and immunosensors (e.g., Bromage et al., 2007a, 2007b; Charles et al., 2014) all have shown promise, but have not yet been used long-term for monitoring dissolved explosives. These and other novel, not commercially-available methods are discussed in detail below, and the critical characteristics identified in Section 2 for the various methods are compiled in Table 1.

Table 1. Compiled method characteristics for select studies representative of different fieldable method types.

Method	Detection limit (µg/L)	Specificity	Matrix influence	Analysis rate	Reference
Immunosensor	0.05	High (some cross-reactivity, esp. with Tetryl)	Low	7-8 min, including sensor regeneration	Bromage et al., 2007
	1	Medium (cross reactivity with DNT and ADNT)	n.d. (tests in seawater)	~6 min	Charles et al., 2010
Amplifying fluorescent polymer	80	High (using PCA for discrimination)	n.d. (tests in seawater)	15-30 s	Woodka et al., 2012
	0.008			minutes-hours with preconcentration	Woodka et al., 2012
	2	n.d.	n.d. (tests in seawater)	10s of seconds	Dock et al., 2010
Electrochemical	10	Medium (interference by DNT)	Low to moderate	few min.	de Sanoit et al., 2009
	0.8	High (using PCA for discrimination)	n.d. (tests in seawater)	n.r.	Rabenecker and Pinkwart, 2009
	25	n.r.	Low	30 s.	Wang and Thongngamdee, 2003
HPLC-UV	<1	High	Low	Hours	US EPA, 2007
	n.d.	High	Low	15 min.	This work
HPLC-MS	0.001-0.01	High	Low	10-15 min.	Esposito et al., 2023
SPME-IMS	qualitative	High	Low	Min. to hours	Rodacy et al., 2001
GC-MS	n.r.	High	Low	Min. to hours	Kirgan et al., 2008
	1	High	Low	9 min.	Splichal et al., 2011

n.r.: not reported

n.d.: not determined

3.1 Immunosensors

Immuno-enzymatic assays (e.g., "ELISA: Enzyme Linked Immunosorbent Assay") have become a well-established diagnostic tool, e.g., for the detection of amino acids, and have been used as early as 2003 for detection of TNT (Wilson et al., 2003). The detection principle relies on labelled antibody-antigen couples that can be detected by various methods, but typically, fluorescence. One of the couples is immobilized on a solid substrate, while the other is free in solution with the target compound of interest (Fig. 2). Binding competition at the immobilized reaction sites produces a response in the fluorescent label proportional to the concentration of the target compound. Substrate-immobilized systems require an additional step to remove bound moieties and regenerate the substrate (Bromage et al., 2007b).

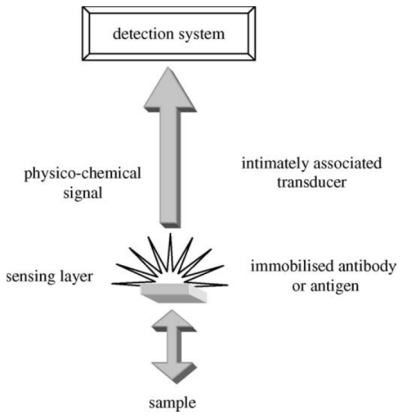

Figure 2. General principle of the immunosensor assay (from Marquette and Blum, 2006).

Immunoassay systems have been used successfully to detect dissolved TNT at environmentally-relevant concentrations (high ng/L to µg/L levels) in various aquatic matrices (Bromage et al., 2007a, 2007b; Charles et al., 2010). The rapid response of immunoassays (minutes or faster) makes them capable of detecting temporal variations in TNT plumes, such as those caused by tidal currents (Charles et al., 2014). These sensors have also been mounted on autonomous underwater vehicle platforms (AUV) for spatial mapping of TNT plumes from point sources (Fig. 3; Veitch et al., 2011, Adams et al., 2011).

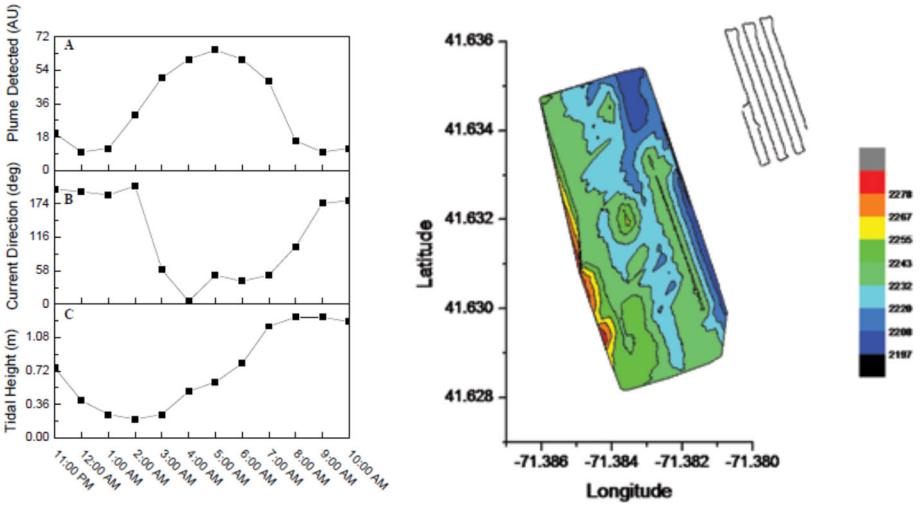

Figure 3. a) Time series of a simulated TNT plume over a tidal cycle at an estuary inlet (from Charles et al., 2014). b) Contour plot of a TNT plume measured with an immunosensor mounted on a REMUS100 AUV (from Adams et al., 2011).

Immunoassay sensors show substantial promise for in situ detection of explosives emitted from relic munitions. Immunosensors show especially fast response, and detection limits should be sufficient for the medium range of levels typically found in marine systems (Beck et al., 2025; Rosen et al., 2022; den Otter et al., 2023). Such sensors are limited thus far to TNT, limiting their potential for detecting multiple explosive chemicals emitted from mixed munition fills. In addition, preparation of the immobilized assay substrate is complex and requires specialized expertise to manufacture.

3.2 Amplifying Fluorescent Polymers

Amplifying fluorescent polymer (AFP) sensors operate on a similar principle to immunosensors, but use instead a fluorescing conjugated polymer substrate that is quenched by interaction with target chemicals. Water is passed over the substrate, and the fluorescence response measured by spectrometer. The AFP method can achieve very fast analysis rates (10s of seconds; e.g., Dock et al., 2010), but this has the tradeoff of lower sensitivities. AFP has a detection limit higher than immunosensors, on the order of 2 µg/L (Dock et al., 2010) or higher (Woodka et al., 2012). The rapid analysis rate makes AFP sensors suitable for mapping high concentration underwater plumes with AUVs, as demonstrated by Dock et al. (2010; Fig. 4).

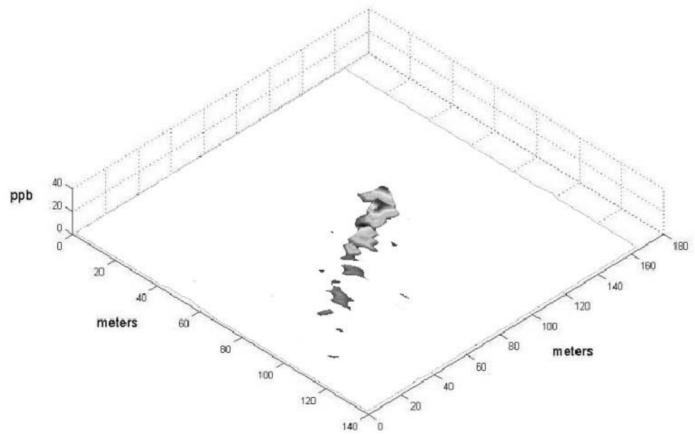

Figure 4. TNT plume from a synthetic source mapped with an AUV-mounted AFP sensor (from Dock et al., 2021).

Low concentration sources require analyte preconcentration to increase signals sufficiently for detection by AFP. Woodka et al. (2012) used Tenax resin to preconcentrate TNT from seawater, followed by thermal desorption and AFP detection. This method reduced the detection limit from 80 µg/L to 8 ng/L, but required long loading time (up to 4 h at the lowest concentration level). Preconcentrating systems are probably not appropriate for deployment on fast-moving AUVs, but have application on remotely-operated vehicles that move more slowly and can collect stationary samples. This trade-off between sample analysis frequency and detection limit is one of the greatest challenges to making real-time measurements at environmentally-relevant concentrations.

3.3 Electrochemical Detection

Electrochemical sensors represent a major class of sensors and are widely employed for chemical monitoring in aquatic systems (Baranwal et al., 2022). In these sensor systems, a varying electrochemical potential is applied between two electrodes, resulting in an electrical current proportional to the chemical concentration due to electrochemical reactions at the electrode surface. The potential at which this current is observed differs depending on the reaction, and gives

information about the chemical type reacting at the electrode. Electrochemical detection of TNT relies on the reduction of nitro groups to the amino form, giving three characteristic peaks at -0.85, -0.7, and -0.55 V (Au electrode vs. Ag/AgCl reference electrode; Rabenecker, 2019).

Early electrochemical systems indicated a detection limit on the order of 1000 mg/L (e.g., Krausa et al 1997), although newer electrode types such as boron-doped diamond electrodes have improved the detection limits to 1 mg/L (Goh and Pumera, 2010) and as low as 10 µg/L (de Sanoit et al., 2009). Electrochemical detection appears to work well in seawater (Rabenecker and Pinkwart, 2009), making such sensors promising for detection of chemicals from relic munitions. Indeed, an electrochemical sensor developed by the Fraunhofer ICT (Pfinztal) has been deployed on both AUV and ROV platforms (Fig. 5), and successfully detected TNT near test explosive sources (Rabenecker, 2019). Wearable electrochemical sensors for TNT have even been proposed to protect divers from environmental contaminants and safety hazards (Malzahn et al., 2011).

Figure 5. Fraunhofer electrochemical sensor deployed on a SeaCat AUV (Atlas Electronics; images from Fraunhofer ICT, 2018). (Left) Sensor (white box) mounted on the AUV head. (Right) Deployment of AUV with sensor in the Baltic Sea.

3.4 Portable HPLC

The most common traditional method of detecting dissolved explosives replies on separation by high performance liquid chromatography (HPLC) and detection by ultraviolet (UV) spectrometry (EPA method 8330A; US EPA, 2007). This method has been widely used (Guarav et al., 2007), and forms the basis for analysis by mass spectrometry (e.g., Gledhill et al., 2019). Explosive compounds are separated by liquid chromatography on an appropriate HPLC column (commonly reverse-phase C8 or C18), followed by UV detection. Most explosives absorb light in the UV region (190−400nm), but detection at 254 nm is often chosen due to the low incidence of interference at this wavelength (Crockett et al., 1999).

Laboratory-based HPLC systems are generally non-portable and unsuitable for field deployment. However, recent advances in portable HPLC technology are making it possible to perform such measurements in the field (Rahimi et al., 2020; Hemida et al, 2023). To our knowledge, such systems have not yet been used for detection of explosives in seawater. Our tests with the Axcend FocusLC portable HPLC system (Hemida et al., 2023) show good separation and detection of seven explosive compounds (Fig. 6). Explosive analysis based on HPLC was also used by Esposito et al. (2023), coupled with mass spectrometric detection instead of UV (see Section 3.5). HPLC-based approaches have excellent selectivity for target compounds, and gradients can be optimized to resolve compounds of particular interest. In addition, sample preparation and preconcentration methods can be added to eliminate the seawater matrix prior to analysis (see Section 3.6). The greatest drawback to HPLC based methods is the time required for chromatographic separation. HPLC methods are typically on the order of 10-20 minutes (Fig. 6; Gledhill et al., 2019; Esposito et al., 2023), and it seems unlikely that this can be reduced to less than several minutes.

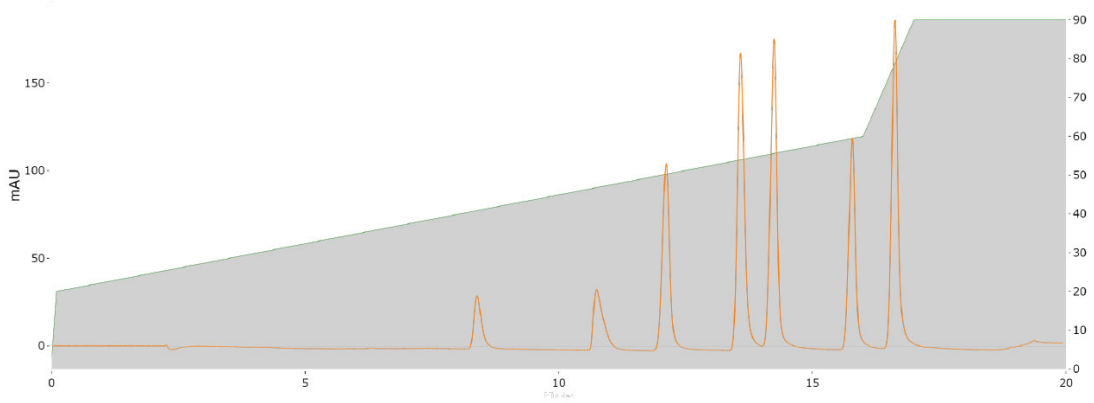

Figure 6. Chromatogram of a multi-compound explosive chemical mixture on an Axcend FocusLC portable HPLC. Peak identification from retention at 7 min include: HMX, RDX, Nitrobenzene, 1,3-Dinitrobenzene, 2,4-Dinitrotoluene, 1,3,5-Trinitrobenzene, and 2,4,6-Trinitrotoluene. The grey shading indicates the methanol solvent gradient (right y-axis scale).

3.5 Portable mass spectrometry

Mass spectrometry is the gold standard for analysis of organic explosive compounds, and has been used extensively for laboratory-based measurements (Badjagbo and Sauvé, 2012). Both gas- and liquid-chromatography mass spectrometry (GCMS and LCMS, respectively) have been applied. High mass resolution spectrometers can avoid isobaric interferences and greatly reduce interferences from other compounds (Xu et al., 2014). This leads to a substantial reduction in the detection limit, and coupled with preconcentration methods, makes the detection of explosives in seawater extremely sensitive (detection limits approaching pg/L; Gledhill et al., 2019). The latter method has also been used with GCMS detection to achieve low detection limits (Bünning et al., 2021). We are aware of only one study that has undertaken the challenge of bringing a high-resolution mass spectrometer into the field (Stravs et al., 2021), and this is unlikely to be implemented more widely in the near future.

Compact mass spectrometers have low mass resolution (typically 0.5-1 amu), but have the advantage of portability. Hemida et al. (2021) list 12 miniature mass spectrometers compatible with HPLC systems (e.g., Fig 7). Most of these have electrospray or atmospheric chemical ionization sources, which are appropriate for explosive compounds. One of these mass spectrometers (the Mini-10; Purdue University) was also used with a membrane inlet system for direct analysis of dissolved explosives (Kirgan et al., 2008). Methods based on GCMS detection have also been used for in-field measurements of explosives in groundwater (Splichal et al., 2011; Kirgan et al., 2008).

Mass spectrometry measurements are highly specific and generally very fast. However, they typically require sample pre-treatment to eliminate the seawater matrix (see Section 3.6), and both gas and liquid chromatography add additional time to each analysis cycle. Even the direct measurement by membrane inlet mass spectrometry (MIMS)requires 30 minutes of equilibration time (Kirgan et al., 2008). A more recent system developed in the AMMOTRACe project (Raupers et al., 2023) uses a membrane inlet coupled to a resonance-enhanced multiphoton ionization (REMPI) source and mass spectrometer, but also requires 10s of minutes per analysis (AMMOTRACe, 2025).

Figure 7. Commercially-available compact or miniature mass spectrometers. From left: 4500 MiD (Microsaic), expression CMS (Advion Interchim Scientific), Portability (BaySpec), and Mini12 (Purdue University).

3.6 Preconcentration of explosives from seawater

A variety of methods are available to preconcentrate explosive compounds from seawater, including especially solid-phase (micro-)extraction of discrete water samples and passive samplers that accumulate chemicals from the free water column. Solid phase extraction (SPE) is a common method for quantitative extraction of dissolved explosives from up to 1 L of seawater (e.g., Maskarinec et al., 1984; Lee et al., 1996; Craig et al., 2019; Gledhill et al., 2019). A range of commercial SPE resins have been used, including Chromabond EASY, BondElut ENV, Waters Oasis HLB, Porapak R, and Porapak RDX (see compilation by Esposito et al., 2023). After extraction, target analytes are eluted for analysis, sometimes following additional preconcentration by evaporation of the eluate to a smaller volume. Explosive extraction by SPE is also frequently performed online, with pumped samples and reagents, and switching valves altering fluidic pathways (Sun et al., 2011; Esposito et al., 2023). Automated online SPE has the advantage of reducing both human handling error and sample preparation and analysis time. Solid-phase micro-extraction has a similar operating principle, with target compounds adsorbed on a fiber sampler that then undergoes thermal desorption and introduction into a detector such as a mass spectrometer (Rodacy et al., 2002; Jonsson et al., 2007). Methods using SPME can often improve on SPE by ease of use, lower detection limits, and use of smaller solvent volumes (e.g., Jonsson et al., 2007).

Passive samplers operate on a similar principle to SPE and SPME, but are deployed in the water column and passively accumulate dissolved chemicals (Belden et al. 2015; Rosen et al. 2016, 2018; Lotufo et al. 2018, 2019; Estoppey et al., 2019). Polar Organic Chemical Integrative Samplers (POCIS) have been successfully deployed at a number of marine munitions sites (Belden et al. 2015; Rosen et al. 2016, 2018; Lotufo et al., 2018, 2019). While discrete grab samples preconcentrated by SPE only capture an instantaneous snapshot of the contamination at a location, passive samplers have the advantage of integrating concentration fluctuations over time (Rosen et al., 2021). Other materials also sorb dissolve explosives, and alternative passive samplers have also been developed (e.g., Warren et al., 2018). Passive samplers are generally not appropriate for field analysis because they are specifically designed to provide time-averaged information, and generally require more intensive preparation for analysis.

4. Outlook for the future

The approaches discussed in Section 3, and especially hyphenated techniques combining preconcentration, chromatographic separation, and mass spectrometric detection are well-established for automated monitoring in land-based laboratories (Elpa et al., 2019), and is capable of detecting a wide range of organic contaminant compounds (Köke et al., 2022). Fieldable versions of this technology expands the possibilities for environmental monitoring of underwater munitions, as well as rapid response mapping after environmental disasters.

Future release of MCs from underwater munitions in the southwest Baltic Sea is certain to increase as corrosion advances, and contamination levels will most likely rise if no action is taken to remove munitions from the sea. In the first such action globally, at the end of 2021, the German federal government allocated 100 million Euro for a pilot program to begin test removal and on-land disposal of munitions from underwater dumpsites (Mergener, 2024). In comparison with blow-in-place disposal (e.g., Maser et al., 2023), this method of remediation is likely to have low negative environmental impact, although there is a potential for heightened chemical release due to munition disturbance. The clearance will begin in Lübeck Bay, which has some of the highest levels of environmental MC contamination. This will provide a proof-of-concept for remediating underwater munitions, and allow cost-benefit evaluation in comparison with the “monitored no action” approach proposed in a US military SERDP/ESTCP workshop in 2021 (Lotufo et al., 2021).

Such remediation will require continuous monitoring to ensure that the activity does not worsen chemical release during munition disturbance. Fieldable monitoring platforms can provide the near-continuous data required for rapid response to release events. Furthermore, hybrid technologies allow leveraging of and linking the positive aspects of different methods to achieve systems capable of deployment in novel platforms and scenarios.

One objective in the MMinE-SwEEPER project is to further develop and text integration of the GEOMAR Xplotector system and the Fraunhofer ICT electrochemical sensor system. The goal of this work is to improve the analysis speed of the Xplotector system while also increasing the sensitivity of the electrochemical sensor. Hybridization may also produce an improved and complete system capable of being deployed in situ. Details of the planned development are discussed briefly below.

4.1 GEOMAR "Xplotector" Lab-in-a-Box System

Figure 8. Final version of the Xplotector prototype.

The shipboard analytical system dubbed the "Xplotector" is a standalone unit for preconcentration and analysis of a suite of dissolved explosive compounds (Fig. 8). The system comprises a fluidics module with online solid-phase extraction (SPE; Porapak RDX) preconcentration of target compounds coupled to an analytical module with compound separation by high performance liquid chromatography (HPLC; reversed-phase C8) and detection with electrospray ionization mass spectrometry (ESI-MS; Microsaic 4500 MiD; Fig. 7). The prototype system was detailed in Esposito et al. (2023) and demonstrated during multiple research campaigns in the Baltic Sea (Fig. 9). Successful detection and quantification were shown for dissolved TNT, RDX, DNB, and ADNT in natural seawater (e.g., Sanderson, 2023; Raupers et al., 2023). The Xplotector achieves relatively fast analysis time (less than 15 min., primarily limited by the preconcentration and chromatography separation times), low detection limits (down to 2 ng L^{-1}), and automated operation, which make the system ideal for on-site monitoring, search, and identification of common conventional munition compounds in seawater.

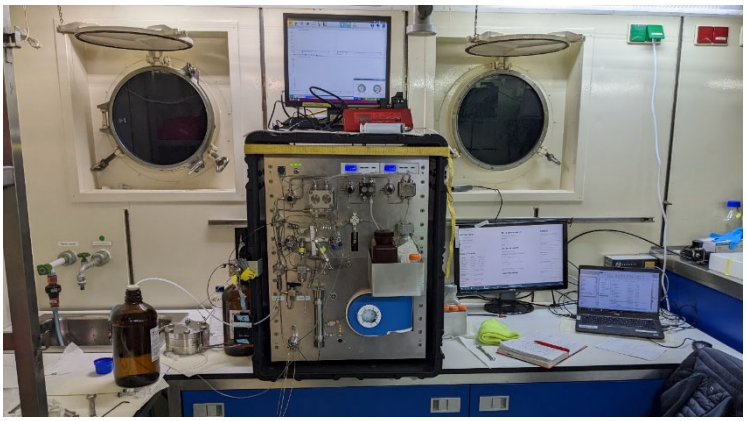

Figure 9. The Xplotector in the wet lab on R/V ALKOR during cruise AL583 (Oct. 2022).

The Xplotector system is a field-deployable platform that achieves high sensitivity and unequivocal identification of a suite of munitions compounds in seawater, and represents a major step change in technology for at-sea chemical analysis. The mass spectrometer was upgraded in 2023 to the expression CMS (Fig. 7; APCI source, Advion Interchim Scientific), which offers the possibility to detect a wider array of target substances than currently possible with the Xplotector, including other explosives and chemical warfare agents, and with better sensitivity.

4.2 Fraunhofer ICT electrochemical sensor

The Fraunhofer ICT electrochemical sensor is based on the cyclic voltammetry (CV) principle (Section 3.3), developed through more than 20 years of experience (Rabenecker and Pinkwart, 2009). The

sensor itself consists of entirely custom-designed and built hardware, including the 3-D printed body, sensor head, electronics, and software. The electrochemical sensor relies on micro-fluidics and high sensitivity electronics.

Two different formats of the Fraunhofer system were developed. One variant of the electrochemical sensor system was set up as an autonomous, stand-alone system in which the sensor system is completely self-sufficient. In this case, the power supply, communication and data evaluation are all within the self-contained sensor system so that it can work autonomously and independently of any type of carrier vehicle (e.g., a crawler; Fig. 10). The evaluation of the data is carried out by custom-developed software.

Figure 10. Fraunhofer ICT electrochemical sensor mounted on a seafloor crawler. The righthand image shows the sensor head extended on a metal "arm" in front of the crawler. A water sampling probe for discrete sample collection is mounted next to the sensor for cross-comparison and validation.

The second system was implemented as an integrated concept where power and communication are integrated with the carrier vehicle. The control of the sensor system and the evaluation of the measurement data are carried out by an operator on board the accompanying ship. Current trials also involve the application of a more sensitive electrochemical technique called Square Wave Voltammetry (SWV). SWV promises to increase the sensitity of the electrochemical system compared to CV (Bozic et al., 2008).

Both electrochemical sensor systems underwent extensive practical testing during several sea trials in the North and Baltic Seas, and both were successfully used to check suspicious objects for the presence of explosive traces.

4.3 System integration within MMinE-SwEEPER

The Fraunhofer electrochemical sensor may also serve as a rapid detection system for integration with the Xplotector fluidic preconcentration system. Discrimination between the voltammograms of TNT and other nitroaromatics (Rabenecker and Pinkwart, 2009) would eliminate the need for chromatographic separation of the target analytes, potentially speeding the rate of analysis. This would also improve the sample matrix at analysis, and voltametric detection of TNT in solutions with

acetonitrile has already been demonstrated (de Sanoit et al., 2009). Given the current Technology Readiness Level of both systems (>TRL 4), integration of the two systems should be possible without major development requirements of either system. Physical connections and fluidic methods will need to be developed and optimized, and the software of the two systems must communicate with one another. Finally, once an operational system is realized, the physical construction will be reconceptualized to allow deployment on as wide range of shipboard and in situ platforms as possible.

5. Conclusions

There is a critical and growing need for fieldable technologies that allow detection and monitoring of dissolved explosive chemicals in seawater. The enormous potential of offshore development and the Blue Economy, coupled with the nearly ubiquitous presence of relic munitions on the European seafloor, make explosive detection capabilities all the more urgent. Existing technologies are capable of performing such analyses, but differences in sensitivity, selectivity, and analysis speed mean that no single method represents a perfect solution. Highly sensitive and selective systems based on mass spectrometry tend to be both large and have slow measurement rates. There are therefore suited well to long-term monitoring or site assessment where chemical concentrations may be low and accuracy is required. In contrast, immunosensors, amplifying fluorescence polymers, and electrochemical sensors can be much faster, smaller, and agile. These sensors are ideal for deployment on dynamic platforms such as autonomous underwater vehicles, although their lower sensitivity limits application to such tasks as mapping high concentration chemical plumes.

Hybridization of technologies, namely the mass-spectrometry based Xplotector and the Fraunhofer electrochemical sensor will be developed and tested within the MMinE-SwEEPER project. The goal is to combine the best characteristics of each to simultaneously achieve high sensitivity and fast sample analysis. The outcome of this development has the potential to advance the state of the art for explosive chemical detection in marine systems and become the standard for monitoring chemical release during interaction with relic munitions during offshore development.

In conclusion, existing technologies can fulfill needs for monitoring chemical release from underwater munitions. This includes both monitoring ongoing chemical contamination under a “monitored, no-action” scenario or Enhanced Monitored Natural Recovery (e.g., as recommended by Lotufo et al., 2021), or monitoring chemical release during active removal and remediation. Although existing methods and instrumentation are capable of performing such monitoring tasks, they are typically only in demonstrator or prototype stages, with Technology Readiness Level (TRL) lower than required for general commercial manufacture and application. Planned development in the EU PPPA-funded CAMMera project (cammera-munition.eu) will advance the TRL for the Xplotector system, but additional technical advancements may be necessary before regular, semi-automated monitoring is feasible.

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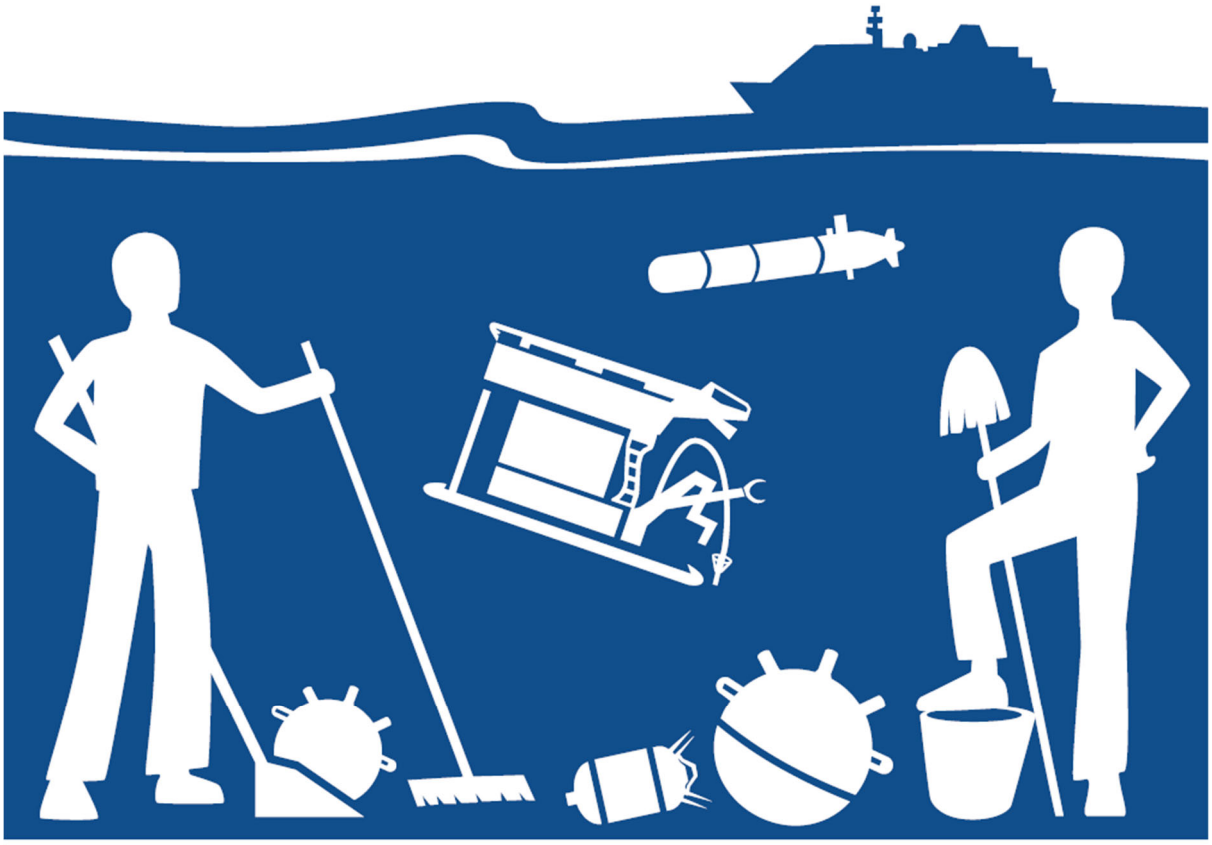

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