# Novel ship-based and submersible Membrane Inlet-Photo-Ionization Mass Spectrometer (MI-PIMS) for on-line detection of fuel spills, environmental contaminants and TNT in sea water

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## Abstract

The trace analysis of anthropogenic pollutants in seawater, such as Polycyclic Aromatic Hydrocarbons (PAH) from oil spills and TNT from dumped ammunition, is crucial in marine sciences. After the World Wars, large quantities of ammunition were dumped in European coastal waters, posing a threat to marine ecosystems. Continuous monitoring is necessary. A new online analysis method combines direct water sampling via a membrane inlet with a mobile Photoionization Mass Spectrometer (MI-PIMS). The system samples seawater into a membrane extraction unit, where organic contaminants penetrate a PDMS membrane and are transported to a TOFMS. Laser pulses ionize target molecules using Resonance-Enhanced Multiphoton Ionization (REMPI), enabling real-time measurements of pollutants at ng/L levels.

The mobile MI-PIMS system was initially tested in the Warnow Estuary in Rostock, Germany, and showed high sensitivity in detecting PAH in sea water. This allows the detection of e.g., oil spills or other pollution sources. The approach was also used to detect PAH and other aromatic xenobiotics in process water from marine sulfur scrubbers, with pollutant transfer highly dependent on operating conditions. For explosive detection at ammunition dump sites, TNT and other explosives need to be detected. The target molecules penetrate the PDMS membrane and are guided via a capillary in the MS system. 226 nm Nd:YAG-OPO-laser pulses or 213 nm laser pulses (quintupled Nd:YAG) are inducing a photolytic formation of $NO_2$ from any nitroorganic explosive. The $NO_2$ molecule subsequently undergoes instantaneous predissociation, forming nitrous oxide molecules (NO) which are efficiently ionized by the same laser pulse in a 1+1-REMPI process. The $NO^+$ signal serves as sensitive markers for explosives.

A shipborne MI-PIMS system was developed. The system for on-line testing of sea water can be operated onboard ships in a ship deck-based container. On a research cruise with the German Research Vessel “Littorina” bottom water from ammunition dump sites in the Baltic Sea was tested. The bottom water was pumped up by a submersible probe or a small remotely operated underwater vehicle (ROV). Explosives (TNT) were successfully detected by MI-PIMS at ppb concentrations, indicating that the shells are already disintegrating.

Finally, a submersible, underwater MI-PIMS system was developed to test for PAH from oil spills and TNT traces at ammunition dump sites. The MI-PIMS system, consisting of a pressure resistant

membrane inlet, a compact reflectron TOF mass spectrometer and a fully tunable Nd:YAG-OPO laser system, was setup in an aluminums pressure housing (max. depths: 100m). The submersible MI-PIMS system is battery powered. For underwater operation it is mounted on a large ROV unit. Data communication is running via the surface connection line of the ROV. A first test of the submersible MI-PIMS/ROV system was conducted on a Baltic Sea research cruise with the German Research Vessel “Alkor”. The system was operable and able to detect trace of PAH in sea water.

Within the outlook, future development perspectives of the MI-PIMS approach are discussed.

## Biography - R. Zimmermann

1995 Graduation (Dr. rer. nat.), TU Munich/Weihenstephan, 1999 Research sojourn University of Antwerp, Belgium, 2001 Professorship in analytical chemistry (C3), University of Augsburg; division manager at bifa-Umweltinstitut in Augsburg and team leader GSF (at the research centre), 2001 state doctorate (environmental chemistry and analysis), TU Munich/Weihenstephan, since 2008 Chair in analytical chemistry (W3) and head of the Joint Mass Spectrometry Centre of the University of Rostock and the Helmholtz Zentrum München, since 2022 Head of Department Life, Light & Matter (LLM)

## Keywords

Underwater mass spectrometer, Photoionization, Membrane inlet, TOF, TNT, PAH