

**DAIMON Toolbox Fact Sheets:**

*Methods for measurement of warfare agents' pollution in sediments*

**Assessment category: Hazardous substances**

**Toolbox component: Sediment chemistry**

**Fact Sheet 2.2: Chemical analysis of CWAs and degradation products in sediment with GC-MS/MS**

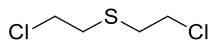
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**What is it?**

Chemical analysis of chemical warfare agents in sediment samples is based on gas chromatography-tandem mass spectrometry technique (GC-MS/MS) utilizing multiple reaction monitoring (MRM). Identification criteria of detected chemicals are based on European Union guidelines of ion ratios.<sup>1</sup>

Target chemicals are sulfur mustard and its degradation products,  $\alpha$ -chloroacetophenone, tabun, and variety of arsenic containing compounds (Clark I, PDCA, etc). Full list of analytes are listed in the DAIMON Report on Chemical Analysis of Sea-Dumped Chemical Warfare Agents and Conventional Munitions in Sediment Samples.<sup>2</sup>

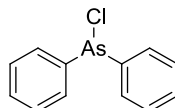
Example compound structures:



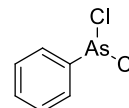
Sulfur mustard



1,4-Dithiane



Clark I



Phenyldichloroarsine (PDCA)

**What does it tell you?**

Chemical analysis of CWAs in sediment indicates if dumped munitions are present and leaking. A positive analysis result is a specific indicator for leakage of specific CWA.

**Type of Indicator** (tick box)

- non-specific stress indicator
- specific for groups of contaminants incl. CWA or explosives
- CWA-specific indicator
- specific for substances related to explosives (e.g. TNT)

### How to measure it?

Detailed sample preparation and analytical techniques are available in the DAIMON Report on Chemical Analysis of Sea-Dumped Chemical Warfare Agents and Conventional Munitions in Sediment Samples.<sup>2</sup>

**Species:** CWA-chemicals and their degradation products in sediment samples.

**Matrix:** Sediment

**Equipment:** For measurement of CWAs in sediment samples, special laboratory equipment for sample preparation and analysis is required.

**Measurements and units:** Frozen sediment samples are thawed, and specific sample preparation techniques are applied prior to quantitative analysis utilizing GC-MS/MS technique in MRM-mode. This includes derivatization procedure to allow for analysis of the arsenic containing compounds. Calibration standards (~ 0.5-50 pg/μl) are run prior and post the sample batch. Hexachlorobenzene (HCB) is used as an internal standard. The results of the analyses are finally presented as μg/kg dry weight in original sediment (μg/kg dw). Only values above the lower limit of quantitation (LLOQ) are reported.

### How to analyze and assess the data?

The identification of the detected chemicals are based on EU guidelines.<sup>1</sup> In case of selected scan techniques (like MRM), reliable compound identification requires relative intensities of the detected ions, expressed as a percentage of the intensity of the transition, to correspond to those of the reference standard, at comparable concentrations, measured under the same conditions. For each target chemical detected from the samples, ion ratio between the qualifier ion (q) and the quantifier ion (Q) is calculated (q/Q –ratio) and compared to that of the reference standard. The calculated ion ratios must fall in a certain tolerance window. If the q/Q–ratio does not fulfill the tolerance criteria, the identification is not considered reliable and the data will be rejected.

Concentrations of the target compounds are calculated based on the calibration standard curves. The LLOQ values for target chemicals typically vary between 0.5-2.5 pg/μl.

### Contact information of the analyzing laboratory

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### References

<sup>1</sup> COMMISSION DECISION of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results, Official Journal of the European Communities, 2002, 2002/657/E, pp. 36

<sup>2</sup> DAIMON report *Chemical Analysis of Sea-Dumped Chemical Warfare Agents and conventional Munitions in Sediment Samples*