The **WMA System** is a platform able to detect, in real time, any metals in water samples. Has so far been applied in the assessment of the presence and concentration of some of the most common heavy metals that can be found in water, such as: Zinc, Chromium VI, Copper, Nickel. *Detection of Other pollutant metals will be soon available.*

The **WMA**

- compact, autonomous and low power consumption
- able to control both drinkable water and waste water
- data sending via GSM
Developed Applications

**Preliminary test on field:**

**Sensing platform** for real-time mapping of **water quality** in proximity of offshore hydrocarbon production sites mounted on an AUV (Autonomous Underwater Vehicle) equipped with wireless control and data transfer.

<table>
<thead>
<tr>
<th>Reference method</th>
<th>Chrome</th>
<th>Zinc</th>
<th>Nickel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylcarbazide</td>
<td></td>
<td>Zincon® at pH 8</td>
<td>Zincon® at pH 9</td>
<td>Zincon® at pH 4</td>
</tr>
<tr>
<td>Linearity</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
</tr>
<tr>
<td>Wavelength</td>
<td>520nm</td>
<td>638nm</td>
<td>600nm</td>
<td>665nm</td>
</tr>
</tbody>
</table>
Lab on chip

- Easy
- Low cost
- Miniaturized
- Portable

Embedding in a Payload

Lab process miniaturization

Final submarine drone
Traces of heavy metals can be detected with high precision, selectivity and sensitivity in water by spectrophotometric analysis making it competitive with more expensive and sophisticated techniques, like ICP-MS, GF-AAS, NAA, ISE.

**Lambert & Beer law**

The sample is mixed with reagents, reacting specifically with the element to be analyzed. In most cases a colored compound or complex is formed. The intensity of the color is a measure for the concentration and can be quantified using UV/Vis spectroscopy.

DFC solution is transparent while, in the form complexed by Cr(VI), it assumes a red-violet color, with a clear peak of absorbance at about 540 nm.

\[ A = \log_{10} \frac{I_0}{I} = \varepsilon lc \]

Cr(VI) solutions with increasing metal concentration. From left: 0.1 – 0.25 – 0.5 – 0.75 – 1 ppm
**Process optimization:**

- Choice of the ligand
- Laser source
- Limits of detection
- Critical parameters for miniaturization (pH, ligand solutions, dilutions, acidification, mixing, resting time...)
- Salted samples
- Aging of ligands solutions

**Sensitivity and accuracy** of the measurement (CV% and Standard deviation)

**Scale down** on a bench prototype

**Layout** definition to minimize dead volumes

**Integration on AUV**

1-5 Diphenylcarbazide for Cr(VI)

- Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) at suitable pH for Zn, Cu, Ni

Zincon chemical structure in its free form (left) and metal-chelated (right)
**Linearity of calibration curve** => $R^2 > 0.9$

**Deviation < 5%**

Cr (VI) calibration curves by DFC the standard method: absorbance at the peak of the spectra and at 520 nm.

**STANDARD METHOD:** Add to 100 mL of sample 1 mL of sulfuric acid diluted 1:1 and 2 mL of DFC solution 5g/L in acetone. Mix, wait for 10 min and finally read the peak adsorbance.

**OPTIMIZED METHOD:** Add to 100 mL of sample 1 mL of sulfuric acid diluted 1:30 and 2 mL of DFC solution 2g/L in methanol. Mix, wait for 3 min and finally read the adsorbance at $\lambda = 520$ nm.
### Chrome Zinc Nickel Copper

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Chrome</th>
<th>Zinc</th>
<th>Nickel</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>50mL of sample;</td>
<td>50mL of sample;</td>
<td>20mL of sample;</td>
<td>20mL of sample;</td>
<td>5mL of sample;</td>
</tr>
<tr>
<td>0.5mL H₂SO₄ (1:30);</td>
<td>0.5mL H₂SO₄ (1:30);</td>
<td>3mL of DFC dissolved in buffer at pH 8.5</td>
<td>10mL of a commercial buffer at pH 4;</td>
<td>5mL of Zincon solution; pH 9.5</td>
</tr>
<tr>
<td>1mL of DFC</td>
<td>1mL of DFC dissolved in Methanol</td>
<td></td>
<td>3mL of Zincon solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linearity</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
<td>10-0.1 ppm</td>
</tr>
<tr>
<td></td>
<td>100-5 ppb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength</td>
<td>520 nm</td>
<td>638 nm</td>
<td>600 nm</td>
<td>665 nm</td>
</tr>
</tbody>
</table>

**Specific wavelength for each method**

**Linearity till 0.1 ppm for an optical path of 10mm**

**Importance of pH control**

![Spectra of water, Cu or Zn solutions treated by Zincon](image1)

![Cu calibration curves by Zincon: water treated (orange) or untreated (blue) as blank](image2)
Automated microfluidic system. Sampling and mixing operations are exploited through automatic syringe systems. Bubble traps are set for a clear measurement.

Optical analyser designed and built at Politecnico di Torino. An electronical driver was designed and built to control laser source and to read photodiode detector.
The automated microfluidic system was **finally integrated on an AUV** for marine water analysis, through a **cylindrical plastic Payload**. This vehicle is able to sail in deep water (up to 300 meters) near any interesting site. Some field tests were carried out near Genova Port, equipping the AUV with control and data transfer systems.

**Any relevant problem occurred during the test:** the wireless control of the system was reactive and precise, data were collected by the integrated Raspberry, stored in the internal memory and also wireless transferred to a PC on the seaside location.
Scientific Production


- M. Periolatto, F. Catania, C.F. Pirri, L. Scaltrito, S. Ferrero, “Spectrophotometric monitoring system, integrated in an autonomous underwater vehicle, for continuous heavy metal detection near offshore sites” Offshore Mediterranean Conference and Exhibition 2019, March 27-29, 2019 (Published on international Conference Proceeding);

- F. Catania, M. Periolatto, L. Scaltrito, Matteo Cocuzza, C.F. Pirri, S. Ferrero, “Spectrophotometric monitoring system, integrated in an autonomous underwater vehicle, for continuous heavy metal detection near offshore sites”, AIV XXIV CONFERENCE, Conference Center Hilton/RG Hotel Giardini Naxos, Sicily (IT), May 7 - 10, 2019 (Poster)


- F. Catania, A. Piscitelli, S. Ferrero, M. Cocuzza, C. F. Pirri, L. Scaltrito, M. Periolatto, “Cr(VI) in water: continuous, on site spectrophotometric determination”, Sixth Intl. Conf. Advances in Bio-Informatics, Bio-Technology and Environmental Engineering-ABBE 2018 (Published on international Conference Proceeding);
Developed Applications

DOWSE

Monitoring of urban water supply and waste water

Vision
To make the environment a wholesome place

Mission
Committed to provide and exploit water analyses in order to increase efficiency of chemical laboratories
The technical domain of this proposal is industrial IOT and smart sensing

**Smart sensor**
This device enables more accurate and automated collection of environmental data with less erroneous noise amongst the accurately recorded information. Moreover due to the fastness of the measurement and due to the low volumes needed, many data can be collected in short time and with cost effectiveness.

**Data availability and sharing**
The system software must allow the transmission of data to monitoring units and laboratories LIMS and possibly to a cloud server via the cellular network.
Each system follows a specific calibration procedure and a calibration curve is released.

### Technical data

<table>
<thead>
<tr>
<th>FEATURES</th>
<th>QTY</th>
<th>UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>538x406x211</td>
<td>mm</td>
</tr>
<tr>
<td>Weight</td>
<td>21</td>
<td>kg</td>
</tr>
<tr>
<td>Battery capacity</td>
<td>20</td>
<td>A/h</td>
</tr>
<tr>
<td>Supply Voltage</td>
<td>24</td>
<td>V</td>
</tr>
<tr>
<td>Maximum current consumption</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Reagents life</td>
<td>30</td>
<td>days</td>
</tr>
<tr>
<td>Limit of detection</td>
<td>5</td>
<td>ppb</td>
</tr>
<tr>
<td>Measuring range</td>
<td>5 – 300</td>
<td>ppb</td>
</tr>
<tr>
<td>Resolution (range 0- 100 ppb)</td>
<td>5</td>
<td>ppb</td>
</tr>
<tr>
<td>Resolution (range 100- 300 ppb)</td>
<td>5</td>
<td>%</td>
</tr>
</tbody>
</table>

- 3 different measure modes: Fast, Laboratory, On-site.
- Touchscreen display
- FTP Upload data
- Fast USB data download
- Intelligent interface with residual battery life/reagents quantities
- Selectable sampling frequency
- Reduced analysis volumes and reagents quantities, with measuring chamber up to 1 ml
- Two reagents / complexing agents with fast charging mode
- Replaceable measuring chamber with 10-100 mm optical path range
- Customizable heavy metal detection (Cr(VI), Ni, Zn, Cu, As, etc..)
- Additional modules