



FIRST TEST OF THE NEWLY DEVELOPED HEAVY METAL SENSORS FOR Cd AND Pb IN NATURAL SEAWATER SAMPLES

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TEST DONE AT THE INSTITUT DE CIÈNCIES DEL MAR (ICM-CSIC) IN THE AQUARIA AND EXPERIMENTAL CHAMBERS (ZAE) FACILITIES.

This area is designed to hold various aquatic organisms and to facilitate the study of different aspects of their biology. It occupies 650 m² and consists of a machine room, several rooms with aquariums, eleven thermo-regulated chambers, a wet laboratory and a dry laboratory. The water is obtained from an underwater intake 300 meters off the coast at 10 m depth. In addition a storage tank of 7 m³ ("flume") can be used to work with local water or from other areas. The facility is computer-controlled and monitored 24 hours a day by a system of sensors connected to alarms. The Mediterranean water can be customized to different treatments of filtration, temperature and salinity and can be supplied to 150 aquariums with capacities from 15 to 5000 liters.

Testing for heavy metals (Cd and Pb) sensor was performed *in situ* in the "flume" chamber. The "flume" consisted on a glass fiber tank, 20 m long with a square section of 60 cm side, full of filtered seawater that was left there for more than one month (Fig. 1). We have labelled this water as "old" seawater



Fig. 1 "Flume" chamber at the ZAE. Part of the "flume" can be seen on the right. The testing set-up for heavy metals is on the table at the end.



Sensor set-up for testing

Heavy metal sensors have been developed by Napcom (Institute of Material Science of Barcelona ICMAB-CSIC) and manufactured by DropSens (Fig. 2a). They are prepared to be connected to a potentiostat through a connexion box (Fig. 2b).



Fig. 2 Heavy metal sensors based on carbon –bismuth nanoparticles (a) and connecting box (b).

Sampling and testing procedure

Two samples of “old” seawater were taken in the “flume”, and another two “recent” samples were taken at the inlet of seawater, just recently pumped without any treatment.

Aliquots of 10 mL of seawater samples were diluted with 0.2 M acetate buffer pH 4.5, in a 1:1 volume ratio. Then, the sensor was submerged in the seawater sample (Fig. 3) and stripping square wave voltammetries were carried out at the optimized parameters.

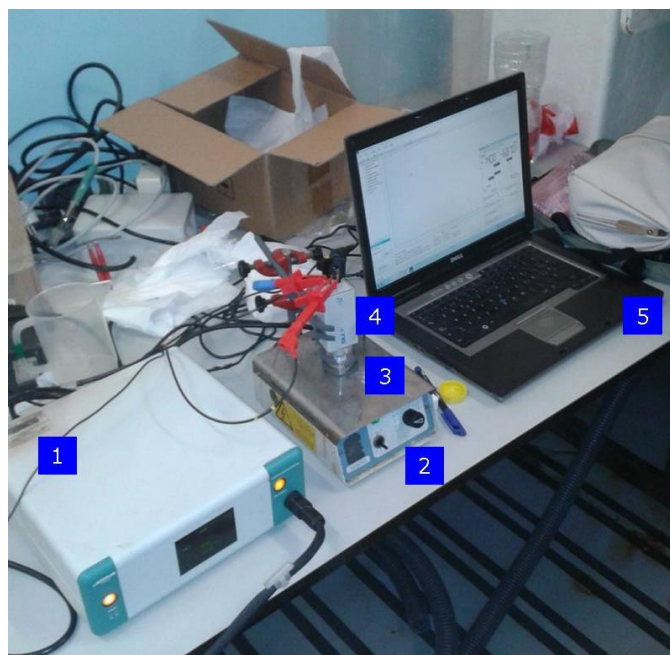


Fig. 3 Sensor set-up for Seawater analysis at ICM-ZAE: potentiostat (1), stirrer (2), sample (3), sensor box (4) and a PC for data processing, storing and display (5).

After stirring during 5 or 15 min, for the accumulation of the heavy metals on the surface of the sensor and applying a negative potential, the voltammetric response was recorded and displayed on the computer screen.

Finally, 25 ppb of Cd and Pb were added in one of the samples to check the testing accuracy.

Additional measurements were carried out later, in the laboratory at Institute of Microelectronics of Barcelona (IMB-CNM-CSIC). Longer accumulation times were used to increase the sensitivity of the device. Voltammetric measurements with screen-printed carbon electrodes (without Bismuth) were checked for the detection of Cu in the “old” seawater sample.

Results

Voltammetric measurements of both seawater samples showed no presence of Cd nor Pb (Fig. 4a & b) while in Cd and Pb spiked seawater samples, two oxidation peaks appeared corresponding to the two added analytes (Cd(II) at -0.75 V and Pb(II) at -0.43 V) (Fig. 4c).

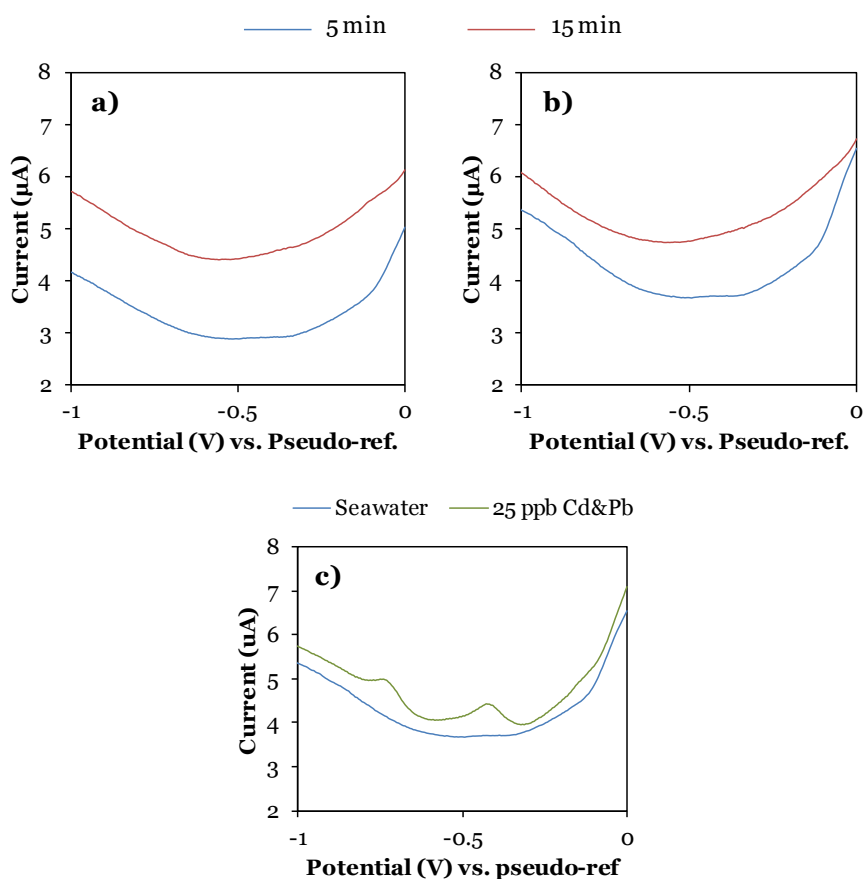


Fig 4. Graphs of the analyses: “old” seawater(a), “recent” seawater(b) and with Pb and Cd added (c).

Additional experiments, carried out in the laboratory, applying longer accumulation times, showed no signals for the detection of these heavy metals in the two seawater samples. Nevertheless, the detection of copper in the “old” seawater sample was positive (Fig. 5). The copper peak was identified by performing measurements in the same sample by adding known concentrations of a solution of Cu (II). When using a blank sample of artificial seawater supplied by TellLab no Cu(II) was detected.

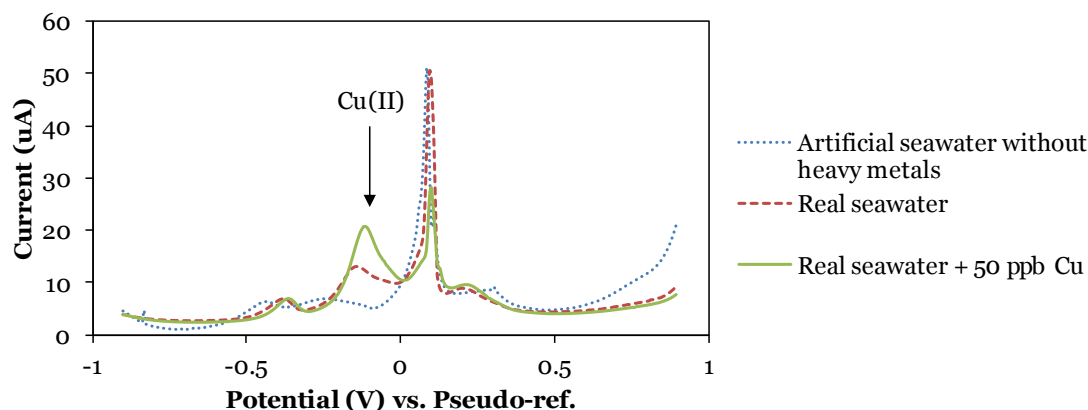


Fig 5. Graphs of the analysis of copper in “old” real seawater and its comparison with artificial seawater and spiked “old” real seawater.

Conclusions and future tests

This first test using natural Mediterranean seawater has shown that the method and electrode worked correctly.

The water salinity of the samples was ~38, that is, nearly the highest values (40) that can be found in open seas worldwide. Neither “recent” nor “old” seawater analysed has shown significant values of Cd and Pb. However, Cu has been detected in the “old” seawater. These results are in accordance to the periodic control analyses carried out in the ZAE.

System setup performed correctly for laboratory work on land, and would also be adequate for an oceanographic ship but for routine tests in other sea platforms it should be compacted by using smaller components. Tests will be done as soon as the new prototype be available.

Since other heavy metals such as Zn can be present in the ZAE, according to the above mentioned periodic monitoring, new tests will soon be done for this metal.

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