

Development of electrochemical methods for field detection of trace metals in sediments

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Introduction: Electrochemical methods are widely used for the detection of trace metals (TM) in the different environmental matrixes. It offers a simple alternative to traditional analytical methods and provides a high degree of sensitivity with a lower cost and speciation possibility. One of the advantages is the device miniaturization that opens the possibility of developing a real time field detection system to overcome possible artefacts due to sample collection and handling and to provide immediate results for decision makers and/or early warning tools. In electrochemical community, the mercury electrode is widely used for the analyses of TM in natural samples, but toxicity makes it not desirable for the application in the field. An electrode surface that can enable the detection of the several metals simultaneously is still lacking. A variety of electrodes for *in situ* application have been developed during recent years to overcome these limitations [1-3]. The objective of the work is to develop a method for the electrochemical detection and quantification of TM in dredged sediments and to monitor the concentration of TM during the process of contaminated sediment remediation.

Methods: In our work, we focused on the detection of zinc (Zn), lead (Pb) cadmium (Cd) and copper (Cu) which are expected to have elevated concentrations in the samples. The aim was to develop and to test Bi modified glassy carbon electrode (Bi-GC) and the Au microwire electrode [1,3]. These electrodes have been used for detection of the TM with the stripping techniques, mostly in controlled laboratory conditions. Stripping techniques are two stage techniques in which metal is deposited on the electrode surface in the first stage, followed by oxidation of the deposit during a potential sweep what is used for quantification. For the field study a portable potentiostat was used associated to either a Bi-GC or an Au-microwire as the working electrode the working electrode, an Ag/AgCl, [KCl] = 3 M as the reference electrode and a Pt wire as the counter electrode (Fig 1). Samples were collected at a sediment disposal site near St. Omer (northern France) were digested on site in an acidic solution (1 M HCl, for 1 h) and filtered. For further analysis, samples were diluted and pH was adjusted (pH~2). Water samples were also taken and filtered during a granulometric treatment process of

sediment at CTP (Tournai, Belgium). ICP-AES and ICP-MS were also used in the laboratory for comparison.

Results: With the developed procedures, the detection and quantification of the TM are possible, but the sample matrix and applied experimental parameters have an impact on the observed responses. In the acid-digested sediment samples, Pb and Cu were detected at the Au microwire, while with the Bi-GC only Pb was detected. In the water samples from the industrial process only Zn was detected systematically. Depending on the electrode used and the degree of contamination of the samples, Cd and Cu were detected as well.

Discussion: The results indicate that the electrochemical methods for field and *in situ* measurements of TM have great potential. However, to apply in routine electrochemical techniques for TM determination in lixiviates and process water, experimental procedures should be adjusted according to the chosen target metals. The limits of their applicability will be discussed (limit of detection, interferences from the matrix, reproducibility...) as well as its advantages (portability, low-cost, rapidity...).

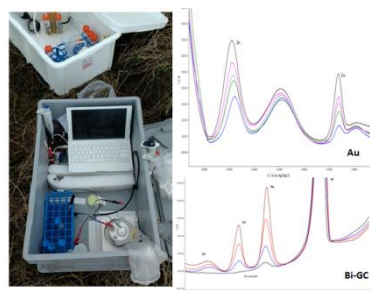


Fig. 1: Electrochemical setup and typical voltammograms obtained on Au and Bi-GC electrodes in the field.

References: [1] Jovanovski et al. (2017) *Curr. Opin. Electrochem.* **3**:114-122; [2] Li et al. (2017) *Curr. Opin. Electrochem.* **3**:137-143; [3] Alves et al. (2013) *Electroanalysis.* **25**:493-502.

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