

# Towards electrochemical measurements in the field of labile Cu, Pb and Zn in sedimentary particles

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## Introduction:

Determining the overall sediment contamination by most metals is no longer an analytical problem in the laboratory. Plasma spectroscopy techniques allow reliable measurements by dissolving the sediment using concentrated acids or alkaline fusion. On-site, pXRF gives good results if the equipment is calibrated for the matrix under investigation and the samples are slightly pre-treated before analysis [1-2]. This technique allows quick mapping, quick detection of hotspots, etc.

In this study, we have developed an electrochemical protocol for the measurement of labile Cu and Pb, applicable in the field (particularly on sediment deposition sites) at a scale of one hour. This protocol can also be used for the measurement of these two metals in pore water, leakage water from dredged sediment... Indeed, pollution is not limited to the determination of total concentrations but must take into account the lability of the elements [3].

## Methods:

The device used is an Autolab type II potentiostat connected to the VA 663 stand and controlled by the GPES software. The IME 663 is used to manage the agitation and degassing of the solution present in the cell. Three different electrodes are used: a 3M Ag/AgCl/KCl reference electrode, a working electrode with a micro gold wire and a platinum counter electrode.

The sediment is partially mineralised for 1 hour with a 1M hydrochloric acid solution. This solution is then diluted 100 times before a voltammetric analysis by anodic redissolution. The quality of the protocol is evaluated according to the criteria of standard NF 17075.

## Results:

The analysis at pH 2 allows the measurement of Pb and Cu with a limit detection of 0.3 and 0.1  $\mu\text{g L}^{-1}$ , respectively. In sediments, the analyzable concentration ranges are 1.5 - 190  $\text{mg kg}^{-1}$  for Pb and 0.5 - 190  $\text{mg kg}^{-1}$  for Cu.

The methods bias, repeatability, linearity, and limit of quantification for Pb and Cu are also measured. The impact of Zn interference on the measurements of these two metals is evaluated as well. All these parameters together make it possible to calculate an overall measurement uncertainty of 22% for Cu and 49% for Pb. Although high, particularly for Pb, these uncertainties are considered sufficient to determine

the order of magnitude of the contamination for a rapid characterization tool in the field.

Furthermore, the results indicate that the linearity range of these methods is relatively low and therefore, the dilution of acid digestates in sediments prior to analysis must be chosen carefully.

## Discussion:

Given the results, voltammetric techniques are likely to obtain information on the mobility of metallic elements in sediments. However, pre-treatments are unavoidable, and the number of metals analyzed is very limited. Application in the field can be done using a miniaturized system but requires numerous manipulations (sampling, weighing, mineralization, filtration and dilution). This voltammetric approach could be more operational for aqueous matrices which are more diluted and do not require mineralisation.

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## References:

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