Rare earth elements detection in dredging sediments: ICP-MS *versus* pXRF

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Introduction: TCEs (Technology Critical Elements) are increasingly used in advanced industries (aeronautics, microelectronics...) with often scarce primary resources [1]. Among them, rare earths are a group of elements (REE) that is both valuable and a potential source of pollution. Most comes from the extraction stages in producing countries, mainly China. However, their increasing use in Europe and other consumer countries can also lead to an accumulation of rare earths in sediments [2]. In view of REE price, highly contaminated sediments could even then be considered as a secondary resource. As there is no information on the contents of these elements in most European sediments, a preliminary analytical study on these elements has started in the framework of the Interreg V FWVl Valse project.

Methods: Two analytical tools have been used and their performance have been tested and compared. The first one is a conventional quadrupole ICP-MS (model 7900, Agilent Technologies). It necessitates a sampling step and in the laboratory, digestion with aqua regia, if needed coupled with HF, before spectroscopic determination. The second one is portable X-ray fluorescence (pXRF) that would allow measuring REE directly on the field, in the case of high enough sensitivity. Two pXRFs were used in this study: a Niton XL3t980 and an Olympus Delta. In all cases, interferences management is of paramount importance to determine accurately concentrations.

Results: The development of a robust method for the analysis of rare earths by ICP-Q-MS has been undertaken using a collision reaction cell, without any mathematical corrections and preconcentration steps. The exhaustive list of interferences (argides, chlorides, oxides, hydroxides, hydrides and doubly charged) have been investigated for the first time at different concentration levels, relevant with those found in environmental matrices based on the FOREGS database [3,4]. Although the impact of barium interferences onto europium and the impossibility to measure Sc have been pointed out, this method has been validated for all the other REEs in standard reference sediments [5]. In parallel, the performance of pXRF for field measurements on some of these elements has been tested. Selected rare earths are those occurring at levels above 10 mg/kg and likely to be detected with pXRF such as La, Ce, Nd, Pr. Y and Sc were also investigated, as they have a rare earth-like behaviour. Results obtained with spiked sand and spiked sediments showed that pXRF could provide a rapid diagnosis of rare earth high concentrations, except for Sc for which the interference with Ca cannot be resolved.

Discussion: The developed method was applied to sediments from a disposal site [TD 26 in Saint Omer (France) belonging to VNF, the French Waterways]. It allowed the determination of all rare earths by ICP-Q-MS (and ICP-OES for Sc). The normalization with reference shales (PAAS, NASC and EUS) did not show any particular contamination. The pXRF devices are not sensitive enough for sediments not enriched in rare earths and finally only yttrium was detected at concentrations very comparable to those of ICP-MS (about 20 mg kg^{-1}).

To conclude, pXRF could provide a diagnosis of the rare earth contamination of sediments provided that this contamination is very significant. It would now be interesting to see if sediments potentially contaminated with rare earths can be used to validate our protocols under different conditions.

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