

Rare earth elements detection in dredging sediments:

ICP-MS versus pXRF

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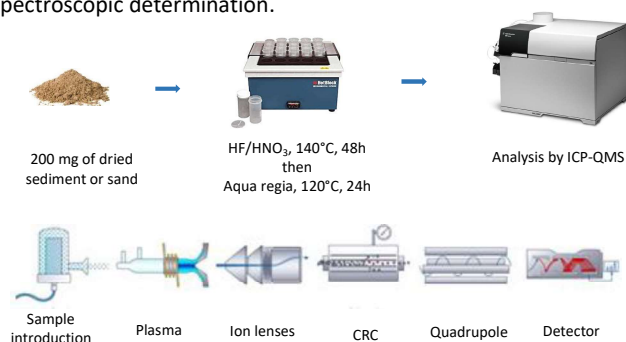
Introduction

Technology Critical Elements are increasingly used in advanced industries with often scarce primary resources. Among them, rare earth elements (REE) are a group that is both valuable and a potential source of pollution. Most come from the extraction stages in producing countries, mainly China. However, their increasing use in Europe and other consumer countries may also lead to an accumulation of rare earths in sediments. 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 FWVI Valse project. The sediment samples came from a disposal site belonging to "Voies Navigables de France" at Saint Omer (northern France).

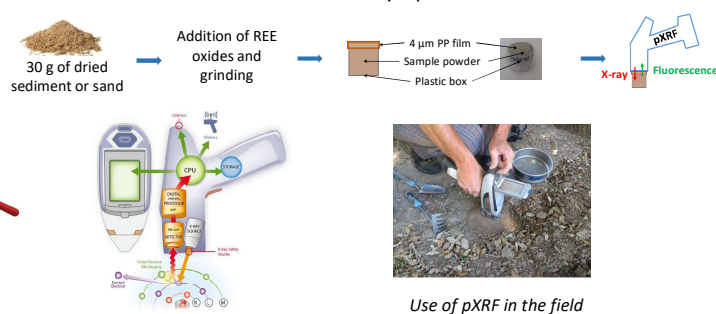
Material and methods

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.



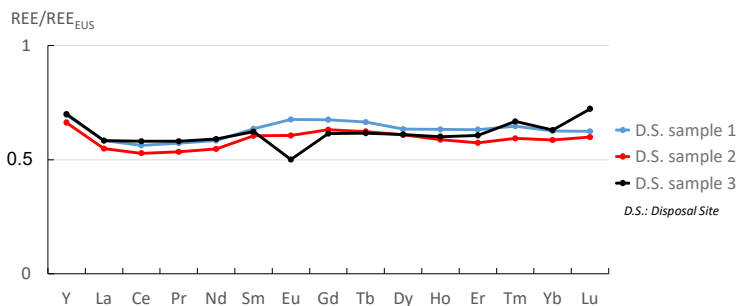
The second one is portable X-ray fluorescence (pXRF), that would allow measuring REE directly on the field, in the case of high enough sensitivity. Interferences management is of paramount importance to determine accurately concentrations. Two models of pXRF have been tested: a Niton XL3t980 and a Olympus Delta.



Results and discussion

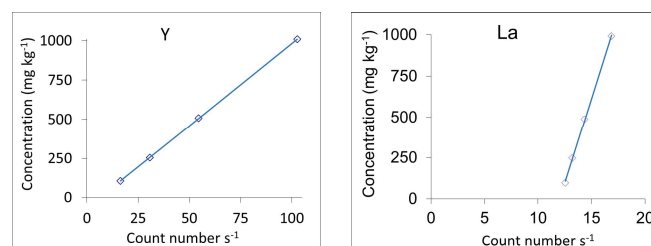
By using ICP-QMS, all REE can be determined with a collision reaction cell flushed with He to break the interferences. However, interferences remain for Sc (Ca and Zr) and Eu (Ba).

Isotope studied	Main spectral interferences	LOQ sediment (mg kg ⁻¹)	Disposal site, sample 1 (mg kg ⁻¹)
⁴⁵ Sc	CaH ⁺ , SiO ⁺ , SiOH ⁺ , Zr ²⁺	1.05	11.7
⁸⁹ Y	SrH ⁺ , CrCl ⁺ , FeCl ⁺ , GeO ⁺ , GeOH ⁺	0.027	6.94
¹³⁹ La	BaH ⁺ , SbO ⁺ , TeO ⁺ , TeOH ⁺	0.013	25.8
¹⁴⁰ Ce	LaH ⁺ , MoAr ⁺ , SbOH ⁺ , TeO ⁺ , TeOH ⁺	0.009	49.8
¹⁴¹ Pr	CdCl ⁺ , CeH ⁺ , TeO ⁺ , TeOH ⁺	0.005	6.07
¹⁴⁶ Nd	BaO ⁺ , CdAr ⁺ , CdCl ⁺ , TeO ⁺	0.013	23.1
^{147,149} Sm	BaOH ⁺ , CdCl ⁺ , CsO ⁺ , TeOH ⁺	0.014	4.64
¹⁵¹ Eu	BaO ⁺ , BaOH ⁺ , CdCl ⁺ , CdAr ⁺ , SnCl ⁺	0.013	1.00
¹⁵⁷ Gd	BaOH ⁺ , CeCl ⁺ , CeOH ⁺ , PrO ⁺	0.017	4.28
¹⁵⁹ Tb	CeOH ⁺ , CdH ⁺ , NdOH ⁺ , NdO ⁺	0.007	0.63
¹⁶³ Dy	NdOH ⁺ , SbAr ⁺ , SmOH ⁺	0.021	3.72
¹⁶⁵ Ho	BaCl ⁺ , NdOH ⁺ , SmO ⁺ , SmOH ⁺	0.002	0.74
^{166,167} Er	BaCl ⁺ , NdO ⁺ , NdOH ⁺ , SmO ⁺ , SmOH ⁺	0.015	2.17
¹⁶⁹ Tm	BaCl ⁺ , EuO ⁺ , NdOH ⁺ , IAr ⁺ , SmOH ⁺	0.002	0.32
¹⁷² Yb	BaCl ⁺ , BaAr ⁺ , GdO ⁺ , GdOH ⁺	0.018	2.04
¹⁷⁵ Lu	BaCl ⁺ , BaAr ⁺ , GdOH ⁺ , TbO ⁺ , YbH ⁺	0.007	0.30



Normalized REE patterns of 3 surface sediment samples from the disposal site, according to the European Shale (Bau et al., 2018)

REE considered in this study for pXRF analysis: La, Ce, Nd, Pr, Y and Sc are also included. These 6 elements are assumed to be the most concentrated naturally in the sediments. This hypothesis has been checked by ICP-MS measurements (see table).



Calibration curves of Y and La by using pXRF

According to the calibration results :

- Y can be determined at environmental level without interferences
- Sc may also be measured but a strong interference with Ca occurs
- For La (see the figure), Ce, Nd and Pr, the detection limits are in the range of 250-500 mg kg⁻¹

Conclusions

To conclude, pXRF could provide a diagnosis of the rare earth contamination of sediments provided that this contamination is very significant.

ICP-MS is much more sensitive and allows the reliable quantification of all REE in sediments (excepted Eu and Sc subject to residual interferences).

It would now be interesting to see if sediments potentially contaminated with rare earths can be used to validate our protocols under different conditions.