**HR ICP-MS Determination of Rare Earth Elements in the Open Ocean**

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There is a growing interest in determining the global distribution of dissolved rare earth elements (REEs) in the open ocean and understanding the processes that control their content in the water masses. REE patterns in seawater are a valuable tracer for anthropogenic pollution and the distinctions in the normalized REE patterns can be very useful in the ocean monitoring studies.

Despite important technological progresses over the past years, quantifying of REEs in sea waters remains a very difficult analytical challenge due to lack of sensitivity in the conventional methods, very high salt content in the sea water and low levels of REEs. To achieve accurate and reliable results efficient pre-concentration and matrix separation step before the instrumental measurement is usually required. Two analytical methods, based on the application of solid-phase extraction (SPE) for separation and pre-concentration of REEs are proposed in this study. The first one is based on the application of nano size TiO2 as solid phase extractant and the second one on the application of chelating resin integrated in SeaFast sample introduction system coupled to the HR ICP-MS.

The conditions for reproducible separation, elution and subsequent HR-ICP-MS determination were investigated. Optimum separation from typical seawater sample was studied by variation on sample size, loading pH, sample and elution rates. High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) was applied in the measurement step of the developed procedure and all interferences – isobaric and polyatomic carefully investigated.

The validation of the methodology was effectuated according to the ISO-17025 standard. Thereupon, blanks, selectivity, calibration curve, linearity, working range, recovery, precision, traceability and limits of detection and quantification were assessed. The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that the determination of REEs in marine waters could be achieved with demonstrated traceability to a stated system of reference. All major sources of uncertainty were identified and propagated together following the ISO/GUM guidelines. The obtained with proposed analytical procedures results were compared and the obtained correlation was very good.

The proposed analytical procedures were applied for the analysis of Mediterranean, Pacific, Antarctic and Irish seawater samples.