Elemental Scientific Inc
Technical Note-12

## Online matrix removal and preconcentration.
REE in Seawater

Determination of REE's in seawater is complicated by matrix suppression, oxide interferences and naturally occurring sub ppt concentrations. The Apex-*FAST* system is connected to the ELEMENT-XR (HR-ICP-MS) and adapted for online matrix removal and preconcentration (20 fold) of low volume (1.5mL) samples. An ACM membrane is used to eliminate oxide interference and capitalize on high sensitivity in low resolution.

Instrumentation & Sample Intro.
- Thermo ELEMENT-XR
- ESI SC-E2
- ESI PFA-ST Nebulizer
- ESI Apex-FAST
- ESI ACM Membrane
- IDA Global FIA Microcolumn

SC-FAST for preconcentration
The Apex is combined with a 6 port valve, controlled via SC-E2 auto sampler software and easily integrated with any ICP. Substitution of the sample loop for a column containing the IDA functional group combined with programmed autosampler movement and valve position allows the system to be used for online matrix removal and preconcentration. The ELEMENT-XR and Apex-FAST are tuned for maximum sensitivity (~4 fold increase at 100µL min^{-1}) and desolvation (>50 fold reduction in oxides) relative to standard sample introduction.
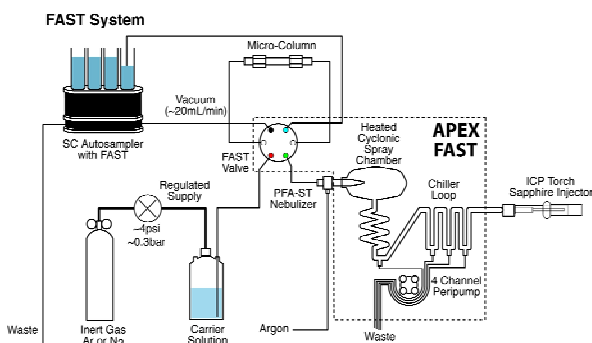
Interferences
The middle REE's are interfered upon by Ba and light REE oxides and hydroxides. In seawater much higher Ba (~5ppb) concentrations result in significant interferences on very low Eu (~ 300 ppq) signals. Although light REEs are only 100 time greater than middle REE's they readily form oxides (CeO% typically 7% on ELEMENT-XR) producing significant interferences. The combination of removing nearly all the Ba (eluent contains ~20 ppt) with the column and reducing oxides (<0.1% CeO) with the Apex-FAST result in interference free determination of REE's in seawater.

Operating parameters
Samples are vacuum loaded and mixed with buffer before the column (0.5mL min^{-1}), washed with Milli-Q water/Buffer solution then pressure eluted (0.1mL min^{-1}) into the Apex via a PFA-ST nebulizer (see Table). The ELEMENT-XR is operated in low resolution mode to maximize sensitivity. A sample uptake time of 220s is used and corresponds with column loading and washing. This is followed by 240s of rapid scanning. The first 120 to captures the eluted signal then the valve is switch and the column conditioned for 120s while carrier is injected to the Apex-FAST.

Operation	Time (s)	Valve	Flow Rate
Load column	180	Load	500 uL/min
Wash column	40	Load	500 uL/min
Elute column	120	Inject	100 uL/min
Condition column	120	Load	500 uL/min

Elution profiles
The low dead volume column, tubing, valve and PFA-ST MicroFlow nebulizer result in the rapid elution of peaks (60s) at 100µL/min flow rates. The exclusion of a peristaltic pump combined with a PFA flow path provides low blanks and eliminates pump noise. Smooth elution profiles (3 point moving average) illustrate the high signal to blank ratio and standard additions to NASS-5
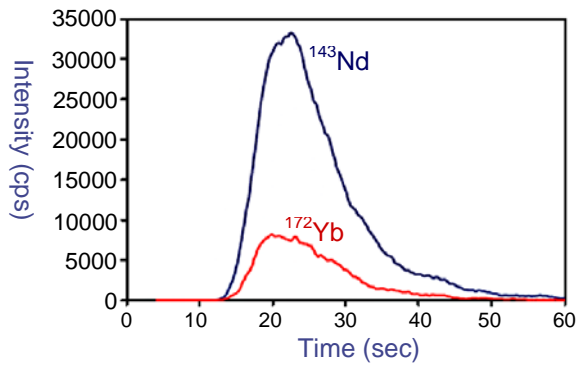
Calibration

Summed data are used to calculate concentrations by both isotope dilution and a calibration curve. The calibration curve is made by standard addition to a seawater sample and the slope is used in combination with an internal standard (Hafnium) to calculate REEs in unknown samples. Alternatively enriched isotope spikes (Nd and Yb) are added to every sample and the full suite of REE's are calculated based on a scheme developed by Field and Sherrell (1999).

Precision and Accuracy

Although no REE certified reference material exists for seawater, the REE values for NASS-5 have been determined in a number of studies (ref). To illustrate precision and accuracy, Nd and Yb data (as examples) are presented for 10 replicate analysis of NASS-5. Both methods of standardization fall within the range of literature values and exhibit excellent precision (Isotope Dilution $<\pm4\%$, Standard additions calibration curve $<\pm7\%$).