

## Using DMT and AF4-HR-ICP-MS to characterize trace metal speciation in soil water extracts

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Diffuse contamination of soils with trace metals like Cu and Zn is an ubiquitous problem all over the world. Trace metals in 0.45  $\mu\text{m}$ -filtered soil solution samples can be present in the free form or they can be associated with inorganic ligands, DOM, and inorganic colloids. Inorganic colloids like clay and Fe-(hydr)oxide nanoparticles can pass the 0.45  $\mu\text{m}$ -filter, but their concentration, composition, and effect on trace metal speciation is largely unknown. For ecological risk assessment of contaminated soils, total trace metal concentrations in soil solution are often measured. However, uptake of trace metals by plants and soil organisms is not necessarily related to their total dissolved concentrations, but generally correlates best with their free concentrations. Hence, the speciation of trace metals in soil solution needs to be known to understand their bioavailability in soils. During the presentation, we will focus on the Donnan Membrane Technique (DMT) and Asymmetric Flow Field-Flow Fractionation (AF4), which can be used to measure the trace metal speciation in soil solution. The DMT allows for the measurement of free trace metal concentrations in solution [1]. Using a chemical equilibrium model in combination with the NICA-Donnan model, the complexation of trace metals with inorganic ligands and DOM can be predicted [2]. However, the role of inorganic colloids in soil solution in the binding of trace metals remains poorly understood when using this approach. An emerging analytical technique with a high potential to analyse the colloidal trace metal fraction in 0.45 soil  $\mu\text{m}$ -filtered solution samples is AF4. AF4 is a chromatographic-like technique for size fractionation of colloids, and allows for online multi-element detection in combination with HR-ICP-MS. We will briefly describe the analytical developments in the DMT and present examples of the application of both DMT and AF4-HR-ICP-MS to measure specific trace metal forms in soil solution extracts to demonstrate (i) the complementary character of both analytical techniques and (ii) their potential to obtain a full speciation of total dissolved trace metals.

[1] Temminghoff *et al.* (2000) *Anal. Chim. Acta* **417**, 149-157.

[2] Weng *et al.* (2002) *Environ. Sci. Technol.* **36**, 4804-4810.

## Use of $10^{12}$ and $10^{13}$ Ohm resistors in TIMS analysis of Sr and Nd isotopes in sub-nanogram geological and environmental samples

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Analysis of isotope ratios in small geological and environmental samples such as inclusions in diamonds or individual human hairs is ultimately limited by the detection system of the mass spectrometer. We report a technique using a TRITON Thermal Ionisation Mass-Spectrometer (TIMS) to measure sample sizes up to 10 times smaller than currently feasible. Use of current amplifiers with  $10^{12}$  Ohm and  $10^{13}$  Ohm resistors instead of the standard  $10^{11}$  Ohm resistors promises a 2-3 fold and 4-5 fold improvement in signal to noise ratios, respectively. This improvement results in higher precision on analyses of small ion beams.

Internal precision and external reproducibility are both better for Sr and Nd isotope ratios collected on small samples using  $10^{12}$  Ohm and  $10^{13}$  compared to the standard  $10^{11}$  Ohm resistors. At a  $^{87}\text{Sr}$  intensity of 3 mV the internal precision (2SE) of  $^{87}\text{Sr}/^{86}\text{Sr}$  is twice better for  $10^{12}$  Ohm and 5 times better for  $10^{13}$  Ohm resistors compared to  $10^{11}$  Ohm resistors. The external reproducibilities (2SD) at this beam intensity are 4 and 9 times better, respectively.

We additionally tested the precision of  $^{143}\text{Nd}/^{144}\text{Nd}$  measured by  $10^{13}$  Ohm resistors in the beam intensity range usually covered by ion counting ( $< 3$  mV or  $2 \times 10^5$  cps). For a  $^{143}\text{Nd}$  intensity of  $6.25 \times 10^4$  cps (1 mV) the precision is 480 ppm (2SE) and at  $2 \times 10^3$  cps (32  $\mu\text{V}$ ) it is 1%. At intensities higher than  $2 \times 10^4$  cps the precision using the  $10^{13}$  Ohm resistors is better than 0.2%, which is the lower limit for ion counting owing to the instability and non-linearity of ion counters. This observation indicates that the high gain amplifiers can be used instead of multi ion counting or Faraday cups equipped with the standard  $10^{11}$  Ohm resistors in the range between  $2 \times 10^4$  cps and 20 mV.

The reproducibility of  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for 100 pg standards using  $10^{12}$  Ohm resistors is 176 ppm for Nd (2RSD,  $n=28$ ) and 92 ppm for Sr (2RSD,  $n=20$ ). Using  $10^{13}$  Ohm resistors the reproducibility is twice better. Thus, variability in Nd and Sr isotope ratios in the 4th decimal place, e.g.  $^{143}\text{Nd}/^{144}\text{Nd}$  0.5110 – 0.5119 or  $^{87}\text{Sr}/^{86}\text{Sr}$  0.7100-0.7109, can be resolved in such small samples provided that the procedural blanks and chemical separation are optimal.