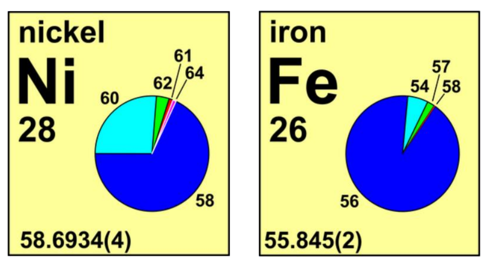
Development and validation of MC-ICP-MS based methods for Ni and Fe isotope analysis to study plant hyperaccumulation

Alexander V. Epov* [1], Stepan M. Chernonozhkin [1], Markus Puschenreiter [2], Alice Tognacchini [2], Thomas C. Meisel [1], Thomas Prohaska [1] and Johanna Irrgeher [1]

[1] Montanuniversität Leoben, Department General, Analytical and Physical Chemistry, Chair of General and Analytical Chemistry, 8700 Leoben, Austria
[2] University of Natural Resources and Life Sciences, Vienna, Department of Forest and Soil Sciences, Institute of Soil Research, 3430 Tulln an der Donau, Austria

INTRODUCTION

Nickel hyperaccumulating plants have Ni mass fraction levels in leaves exceeding 1000 µg g^{-1}. Whereas plant physiological mechanisms of Ni uptake and tolerance are already well investigated, processes in the root-soil interface (*i.e.* the rhizosphere) are still largely unknown. The focus of this FWF project (P 34719) is to investigate root-induced Ni solubilization processes in soil. Hyperaccumulation of Ni was observed to lead to isotope fractionation [1]. Thus, investigating Ni and Fe isotopic compositions in soil and plant materials may shed light onto the processes in the rhizosphere, and interactions in the plant soil microbe system.



Here we present our first results focusing on the measurement procedure development (Fig. 1) for Fe and Ni isotope ratio measurements with low uncertainty using the novel collision/reaction cell (CRC) MC-ICP-MS (Nu Sapphire).

MEASUREMENT PROCEDURE

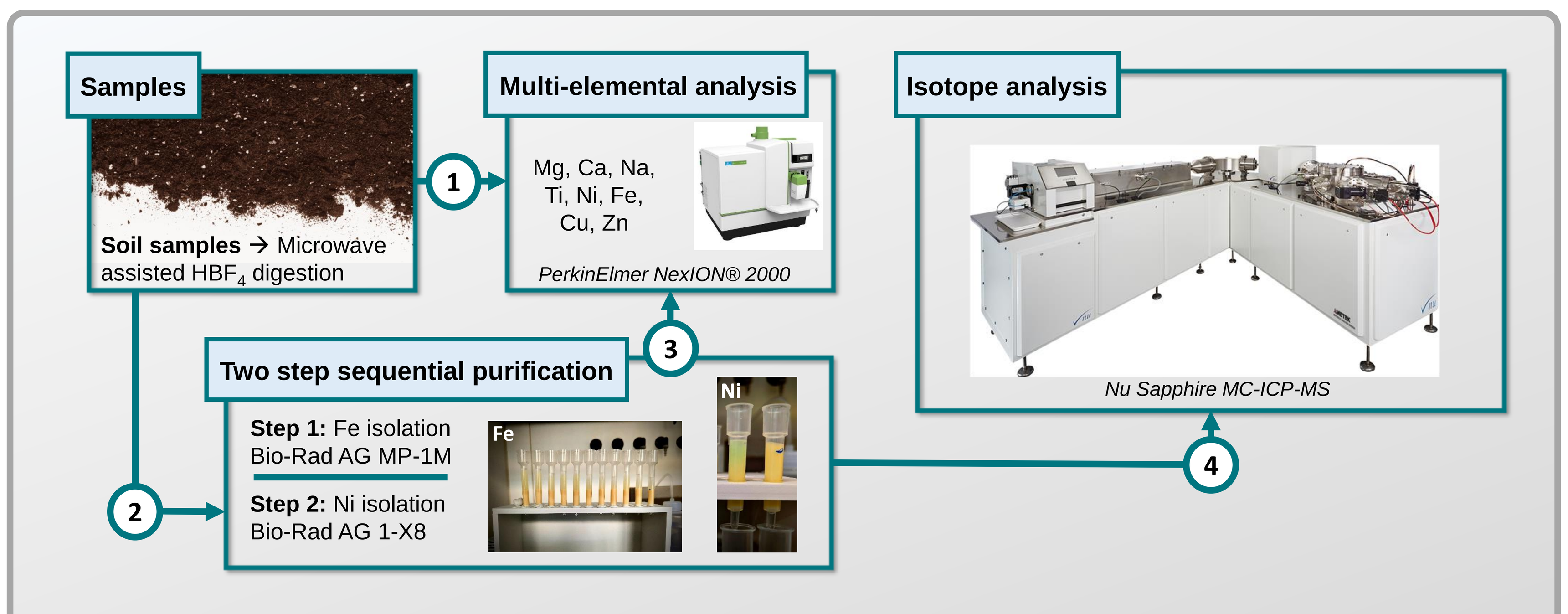


Fig.1: Measurement procedure, from the sample to the isotope ratio measurement by CRC MC-ICP-MS

NU SAPPHIRE: COLLISION REACTION CELL MC-ICP-MS

The Nu Sapphire is a CRC MC-ICP-MS offering two ion paths: "**high energy**" for traditional MC-ICP-MS measurements and "**low energy**" for using a hexapole CRC (Fig. 2).

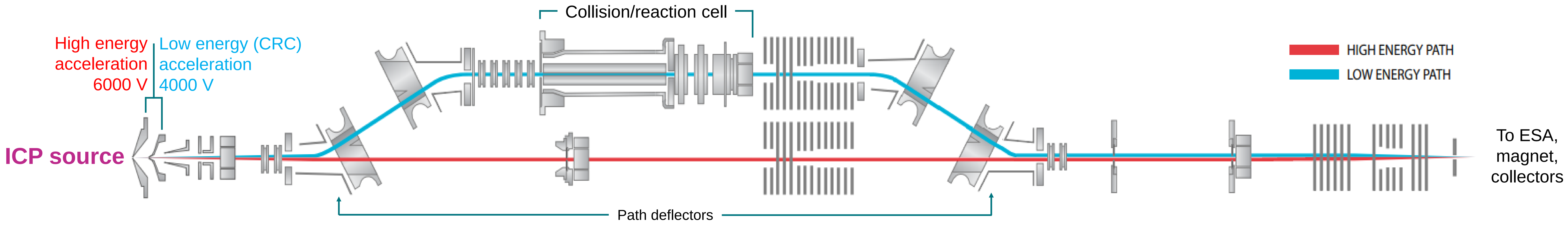


Fig.2: High and Low energy paths in the Nu Sapphire, *adapted from www.nu-ins.com*

CHROMATOGRAPHIC SEPARATION AND ISOTOPE ANALYSIS USING CRC MC-ICP-MS

THE POTENTIAL OF CRC FOR IRON ISOTOPE MEASUREMENT

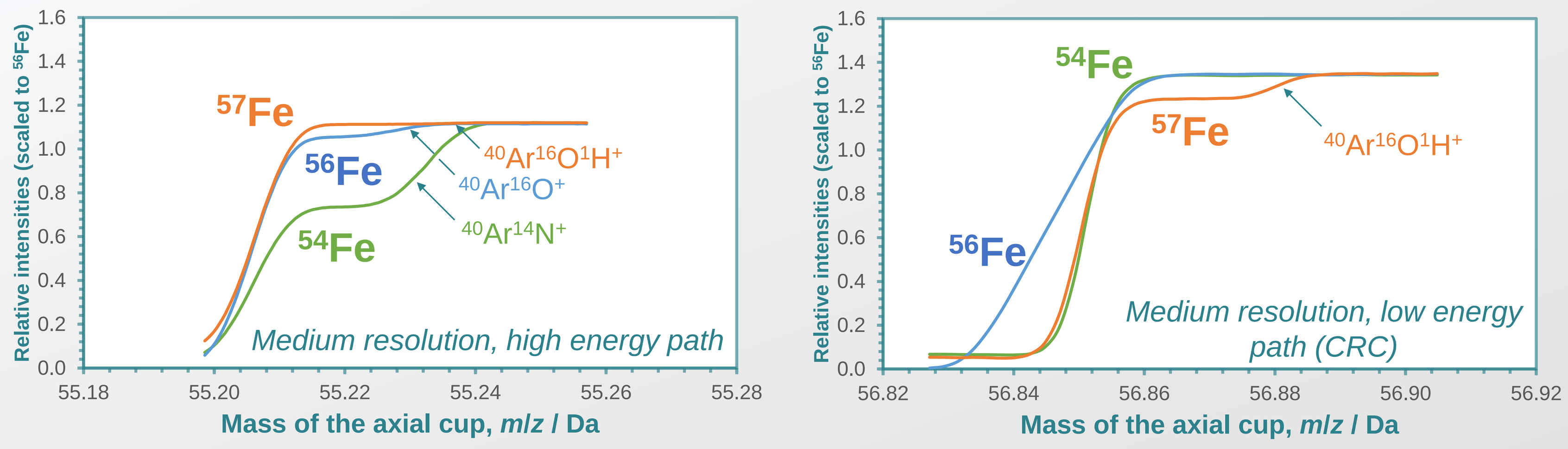


Fig.3: Magnet scans observed for Fe isotopes (w = 100 ng·g^{-1}) and their interferences in medium resolution with and without CRC

- Using the cell set to 4 mL/min of H_2 and 5 mL/min of He removed $^{40}Ar^{14}N^+$, $^{40}Ar^{16}O^+$ and $^{40}Ar^{18}O^+$ interferences from $^{54}Fe^+$, $^{56}Fe^+$ and $^{58}Fe^+/^{58}Ni^+$ respectively (Fig. 3).
- $^{40}Ar^{16}O^1H^+$ could not fully be removed from $^{57}Fe^+$ using the cell, thus medium resolution was used to resolve the interference [2].

MATRIX EFFECTS ON IRON AND NICKEL SEPARATIONS

A two-step protocol for Fe and Ni isolation was used [3]. Three elution profiles were realised in order to test the effect of residual matrix from soil extracts:

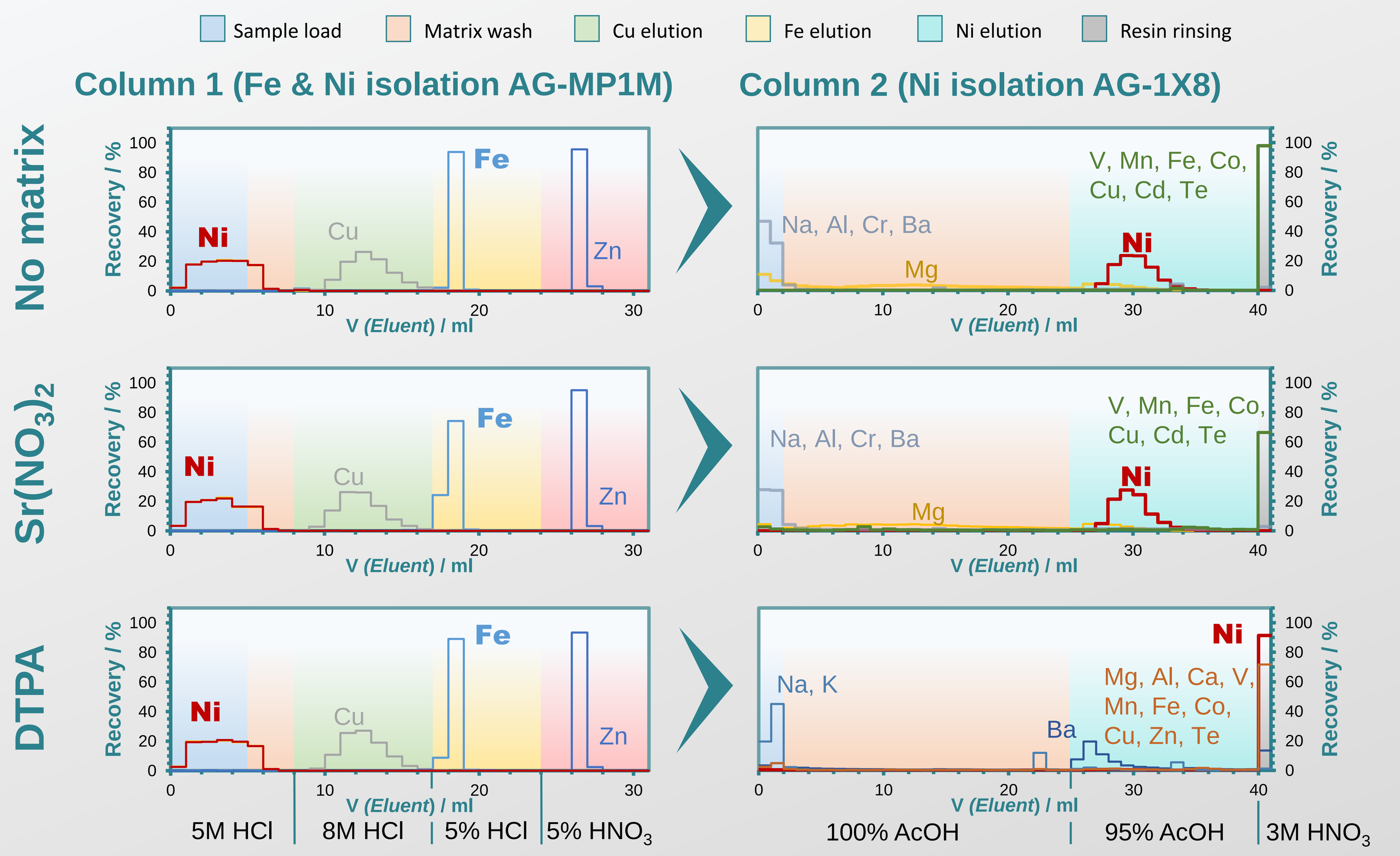
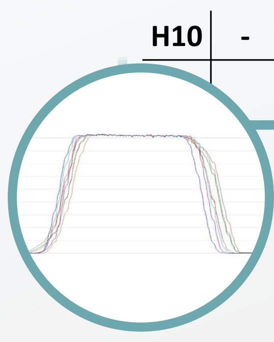


Fig.4: Elution profiles for Fe and Ni separation using AG-MP1M and AG-1X8 resins for different matrices typical for soil extracts

COLLECTOR CONFIGURATION AND IIF CORRECTION

Collector configuration:

H10	-	H9	-	H8	-	H7	-	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	-	L5
		^{66}Zn		^{65}Cu		^{64}Ni		^{63}Cu		^{62}Ni		^{61}Ni		^{60}Ni				^{58}Ni		^{57}Fe



Procedure:

- All isotopes of Ni, Cu, ^{57}Fe, and ^{66}Zn
- Low resolution
- Low energy path (CRC)

Instrumental Isotope Fractionation (IIF):

- Linear behaviour of Ni vs Cu isotope ratio in logarithmic scale in CRC mode
- The slopes correspond to kinetic equation
- Internal – external IIF correction using Cu and NIST986 Ni (Baxter's model)
- Sample standard bracketing (SSB) using NIST986

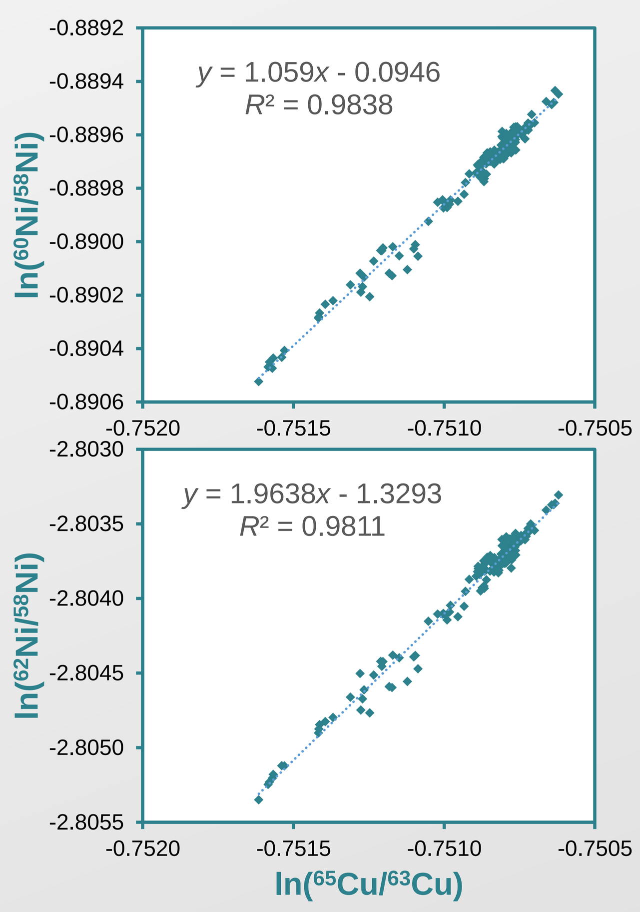


Fig.5: Ni-Cu isotope plots in LN scale

VALIDATION USING AN IN-HOUSE NICKEL SOLUTION

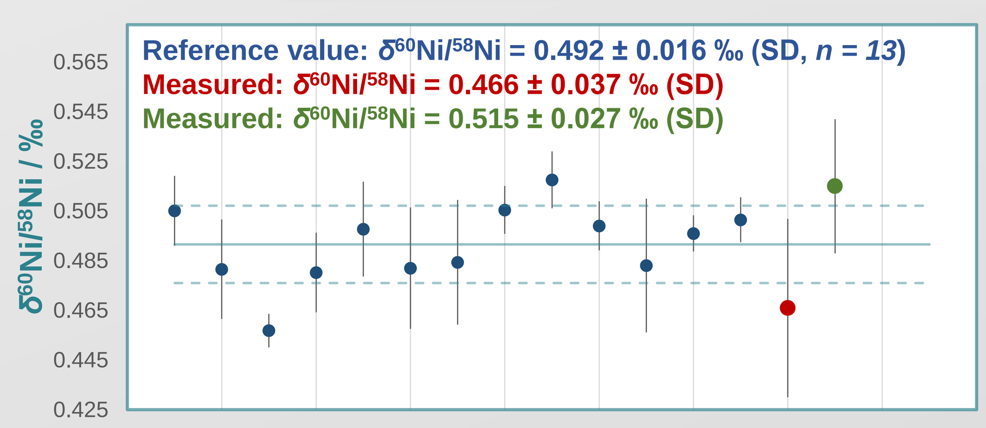


Fig.6: Measured δ^{60}Ni/^{58}Ni (‰) on Nu Sapphire (red, green) compared to earlier measurements on Thermo Neptune (blue).

- The measurements done on the Nu Sapphire have no systematic bias
- Repeatability of δ^{60}Ni/^{58}Ni when using Cu as a calibrator is **0.020 ‰ (SD)**
- Intermediate precision of δ^{60}Ni/^{58}Ni when using Cu as a calibrator is **0.027 ‰ (SD)**

WORK IN PROGRESS

- Final optimisation of measurement parameters to further improve the uncertainty
- Evaluation of the effect of interfering elements on Ni and Fe measurements

NEXT STEPS

- Method validation using reference materials, characterising plant and rock RMs
- Investigation of the potential effect of digestion/extraction on isotopic composition

[1] Zelano et al., Plant Soil, 2020, 454, p. 225-243
[2] Beunon et al., J Anal At Spectrom, 2020, 35, 2213-2223
[3] Arnold et al., Spectrochim Acta Part B At Spectrosc, 2008, 63, 666-672

Chair of General and Analytical Chemistry | Franz Josef-Straße 18, 8700 Leoben, Austria
alexander.epov@unileoben.ac.at