Application Note 30187

NEPTUNE and NEPTUNE *Plus*: Breakthrough in Sensitivity using a Large Interface Pump and New Sample Cone

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Key Words
Neptune *Plus*, Multicollector ICP-MS, Sensitivity

Introduction

The Thermo Scientific™ NEPTUNE™ *Plus* is a major update of the proven NEPTUNE MC-ICPMS platform. Among the new features are an improved pumping capacity option at the interface and a new sample cone to significantly enhance sensitivity, in particular for dry plasmas. This option is also available as upgrade on existing NEPTUNE instruments.

The sensitivity improvement resulting from the use of the large dry interface pump (100 m^3/h pumping speed) is demonstrated using the standard sample cone and X-skimmer cone. Further enhancements to sensitivity arising from the Jet sample cone are reported.

This application note reports the sensitivity enhancements that can be achieved with these new features. It also reports Ar+ and oxide levels, demonstrates accuracy and precision data for Sr, Nd and Hf as well as a critical evaluation of mass bias for Nd and includes standard-sample bracketing analysis of U at the ppb level.

Instrumental Setup

All data presented in this study were obtained in low resolution mode using an Aridus II™ with a PFA concentric nebulizer having an uptake of 100 µL/min. Details are listed in the conditions below. The NEPTUNE Tune Solution (PN 1149340) was used for the tests. This is a dilute HNO_3 solution containing Li, Fe, Nd, Hf and Tl (all from Merck KGaA, Germany), Sr (NBS987), Pb (NBS981) and U (NIST3164).

Table 1. NEPTUNE and Aridus setting.

NEPTUNE	
Cool gas flow rate:	15 L/min
Auxiliary gas flow rate:	0.85-1.05 L/min
Sample gas flow rate:	0.85-0.95 L/min
Plasma power:	1200 W
Resolution:	low (450)
Sample uptake:	100 µL/min
Aridus	
Sweep gas (Ar) flow rate:	8 to 11 L/min
Nitrogen gas flow rate	3 to 6 mL/min
Spray chamber temperature:	110 °C
Membrane temperature:	160 °C

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Part 1: Large Interface Pump, Standard Sample Cone, X-Skimmer Cone

Sensitivity

First we accessed the improvement in sensitivity using the large interface pump in combination with the already characterized X-skimmer cone and Aridus II desolvating nebulizer. The sensitivity improvement factors using the large interface pump vs. the standard interface pump are shown in Figure 1a. Depending on mass range the sensitivity improvement factors range from a factor 50 for Li and 5 for U. The absolute sensitivity data achieved with the large interface pump are shown in Figure 1b and are presented in Table 2.

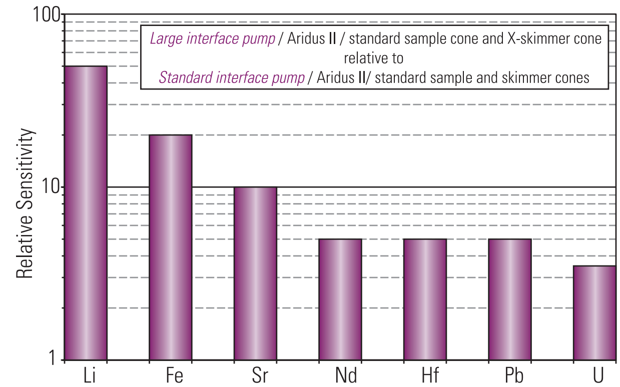

Figure 1a. Sensitivity improvement for the large interface pump (100 m^3/h) relative to the standard interface pump (30 m^3/h), using the same inlet system (Aridus II) and sample cones, but different skimmer cones. Please note: these sensitivity data are not specifications.

Table 2. Absolute sensitivity for the large interface pump in combination with the Aridus II, standard sample cone and X-skimmer cone. Please note: these sensitivity data are not specifications.

	V/ppm
Li	3200
Fe	1600
Sr	1200
Nd	900
Hf	900
Pb	1100
U	1100

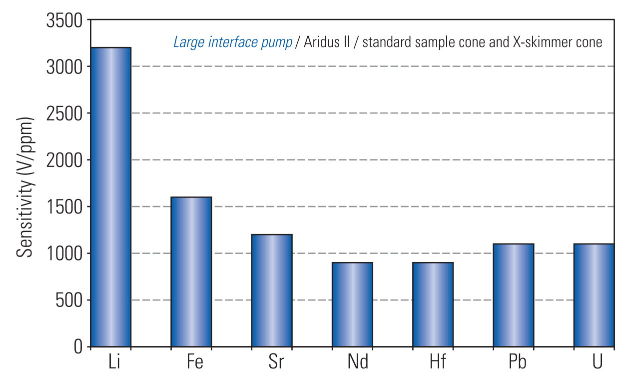

Figure 1b. Absolute sensitivity for the large interface pump with the Aridus II, standard sample cone and X-skimmer cone. Please note: these sensitivity data are not specifications.

Argon and Oxide Formation

The use of the large interface pump does not increase the argon sensitivity and formation of oxides. Sensitivity for Ar is comparable to that with the standard interface pump (total Ar beam ~8000 V). The amount of oxide formation using the large interface pump was evaluated by measurement of $^{238}U^{16}O$ (mass 254). The uranium oxide formation was ~1 %, equivalent to the production rate with the standard interface pump.

Accuracy and Precision

It has been reported that the use of particular cones causes non-linear mass bias effects for particular elements.[1] In order to evaluate mass bias effects due to the use of the large interface pump in combination with the X-skimmer cone, we measured reproducibility and accuracy for Sr, Nd and Hf isotope ratios.

Figures 3–5 show reproducibility and accuracy for Sr, Nd and Hf isotope ratio measurements using the large interface pump with the Aridus II, standard sample cone and X-skimmer cone.

An extended electronic baseline of 3 minutes in defocused ion beam mode and a peak center were performed once at the beginning of each run. A cross calibration (gain calibration) for 1×10^{11} Ω and 1×10^{12} Ω amplifiers was carried out once a day. The isobaric interferences are corrected by measuring the intensities of ^{147}Sm, ^{85}Rb, ^{83}Kr, ^{173}Yb and ^{175}Lu (< 0.5 mV throughout this study) with low noise 1×10^{12} Ω amplifiers and the main isotopes with the standard 1×10^{11} Ω amplifiers. The measurement time for each run was approximately 20 minutes. A set of 10 runs completed the whole sequence.

The average of ten subsequent runs of 150 cycles of 8 seconds per run provides the basis for the calculation of the external reproducibility. A 2σ outlier test was performed at each run. Mass bias correction was done using the exponential law. We used the following normalizing ratios:

$^{88}Sr/^{86}Sr = 8.375209$
$^{146}Nd/^{144}Nd = 0.7219$
$^{179}Hf/^{177}Hf = 0.7325$

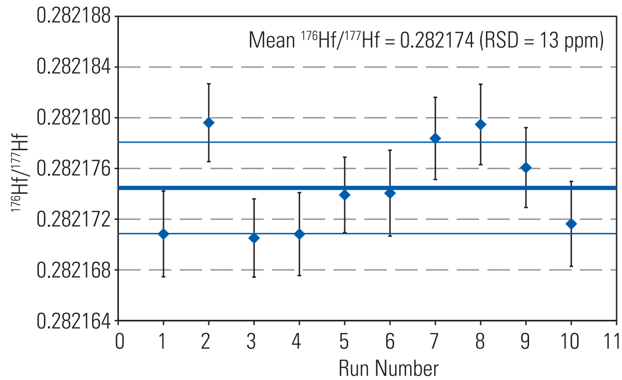

Figure 2. Reproducibility and accuracy for $^{87}Sr/^{86}Sr$ (SRM987, 10 ppb Sr) using the large interface pump, Aridus II, standard sample cone and X-skimmer cone.

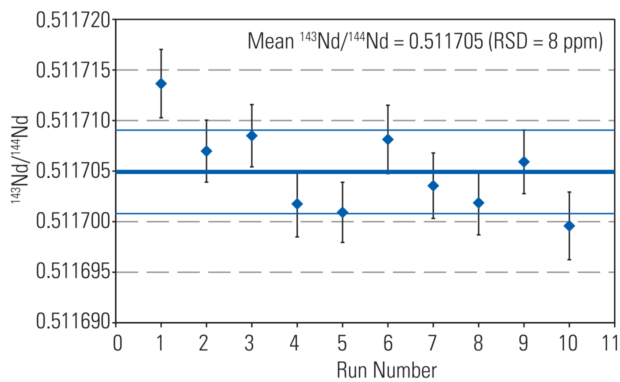

Figure 3. Reproducibility and accuracy for $^{143}Nd/^{144}Nd$ (Merck, 10 ppb Nd) using the large interface pump, Aridus II, standard sample cone and X-skimmer cone.

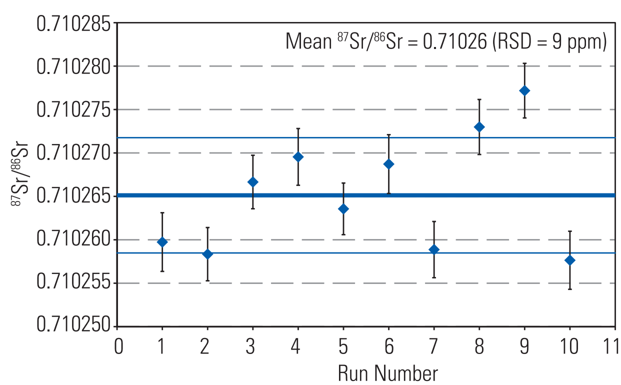

Figure 4. Reproducibility and accuracy for $^{176}Hf/^{177}Hf$ (Merck, 10 ppb Hf) using the large interface pump, Aridus II, standard sample cone and X-skimmer cone.

To access whether the large interface pump together with the X-skimmer cone creates additional mass bias effects, all measured Nd isotopes ratios were compared to TIMS measurements. The deviation from TIMS values are plotted in Figure 5a. Comparison of these data with those obtained using the standard interface pump and standard cones (Figure 5b) clearly indicates that no additional mass bias effects are created using the large interface pump and X-skimmer cone.

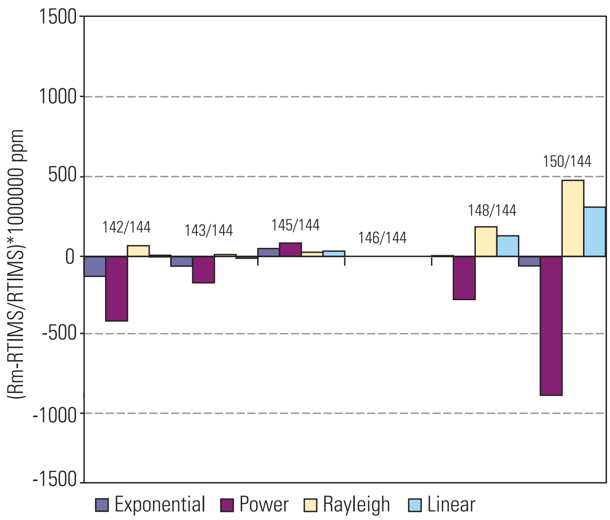

Figure 5a. Deviation of Nd isotope ratios from TIMS using different normalization laws. The data are obtained using the large interface pump, Aridus II, standard sample cone and X-skimmer cone.

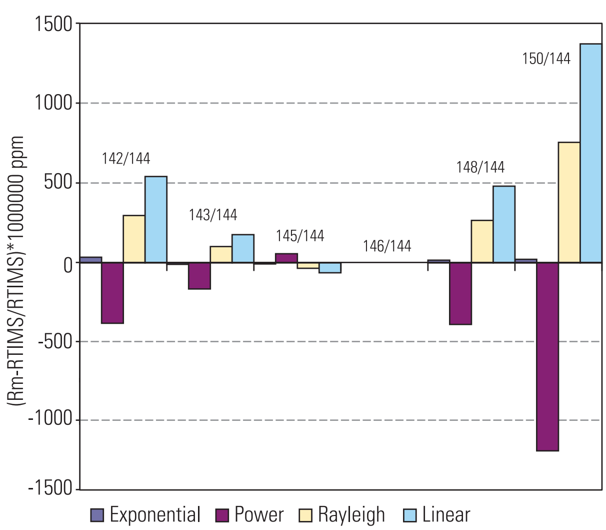

Figure 5b. Deviation of Nd isotope ratios from TIMS using different normalization laws. The data are obtained using the standard interface pump, Aridus II, standard sample and skimmer cone.

Part 2: The Jet Sample Cone

In order to further improve sensitivity we tested a specially designed sample cone, the "Jet sample cone". Figure 6a shows the sensitivity improvement factors for the Jet sample and X skimmer cone and large interface pump vs. the standard sample and skimmer cones and standard interface pump, using the Aridus II. Absolute sensitivity for the Jet sample cone, large interface pump, Aridus II and X-skimmer cone are plotted in Figure 6b.

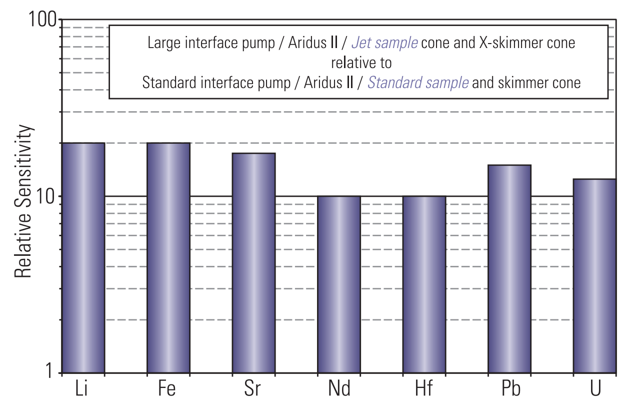

Figure 6a. Sensitivity improvement for the large interface pump (100 m^3/h) relative to the standard interface pump (30 m^3/h), using the same inlet system (Aridus II), but different sample and skimmer cones. Please note: these sensitivity data are not specifications.

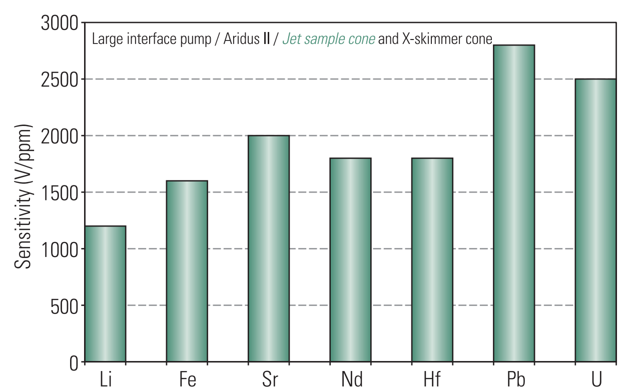

Figure 6b. Absolute sensitivity for the Jet sample cone with the large interface pump, Aridus II and the X-skimmer cone. Please note: these sensitivity data are not specifications.

The combination of the Jet sample cone with the large interface pump, the desolvating nebulizer and the X-skimmer cone seems especially suited for measurements of the very heavy elements, like Pb and U, because of the significant sensitivity enhancement for these elements. The absolute sensitivity using the Jet sample cone are reported in Table 3.

Table 3. Absolute sensitivity of the large interface pump in combination with the Aridus II, Jet sample cone and X-skimmer cone. Please note: these sensitivity data are not specifications.

	V/ppm
Li	1200
Fe	1600
Sr	2000
Nd	1800
Hf	1800
Pb	2800
U	2500

The Jet sample cone was used to analyze natural uranium. The higher sensitivity resulting from the combination of the Jet sample cone with the large interface pump enables measurement of U samples with much lower concentrations compared to the standard interface (standard interface pump and standard sample and skimmer cones), without sacrificing accuracy and precision.

Table 4. Reproducibility and accuracy of U isotope ratios in natural U using the Jet sample cone and the large interface pump (1 ppb sample concentration).

	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{234}U/^{238}U$
Sample 1	0.00005466	0.00725037	0.0075411
Sample 2	0.00005465	0.00725105	0.0075372
Sample 3	0.00005467	0.00725160	0.0075388
Sample 4	0.00005467	0.00725009	0.0075371
Sample 5	0.00005475	0.00724848	0.0075530
Average	0.00005468	0.00725032	0.0075415
stdev ‰	0.73	0.16	0.88
Deviation TRUE ‰	–0.7	–0.3	–0.4
TRUE	0.00005472	0.0072527	0.0075448

Conclusions

The use of the large interface pump on the NEPTUNE *Plus* significantly increases sensitivity across the entire mass range (an improvement of between 4 and 50 compared to the standard interface pump) and provides accurate and precise Sr, Nd and Hf isotope ratio data. External precisions for $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ are 9, 8 and 13 ppm, respectively for 10 ppb solutions.

The Jet sample cone in combination with the large interface pump is especially useful for the analysis of U and presumably other heavy elements. Sensitivity of >2500 V/ppm U was achieved, enabling high precise U isotope measurements at concentrations down to 1 ppb (i.e. <1 ng total sample consumption). External precision for $^{234}U/^{238}U$ and $^{235}U/^{238}U$ were <0.8 ‰ and <0.2 ‰, respectively.

Please note: the sensitivity, accuracy and precision data shown here are not specifications. Please refer to our specification sheet for details.

Reference

1. Newman, K., Freedman, P.A., Williams, J., Belshaw, N.S. and Halliday, A.N. (**2009**) High sensitivity skimmers and non-linear mass dependent fractionation in ICP-MS. *Journal of Analytical Atomic Spectrometry*, Vol 24, p742–751.