INL/CON-19-53664-Revision-0

Assessing the Impurities in Neptunium Metal

Luiza Gimenes Rodrigues Albuquerque,
Beau J Barker

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Assessing the Impurities in Neptunium Metal

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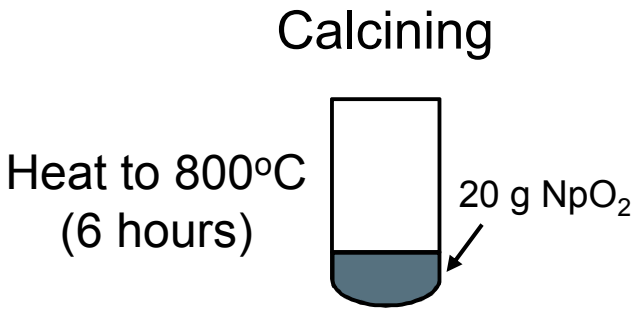
Introduction

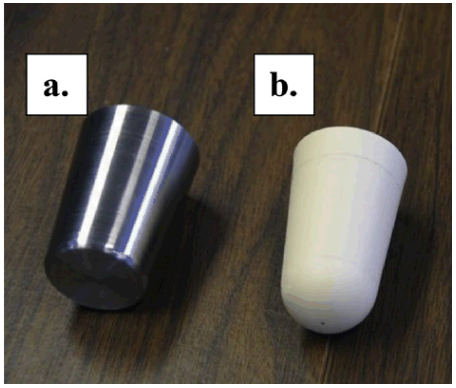
- Transmutation research was the motivation for isolating neptunium, as this element can be used as an additive to experimental fuels
- Ultra high-purity Np metal is required to accurately measure its fundamental physical properties
- A process of producing Np metal from NpO_2 was recently developed at MFC[1]
- A 99.999% pure Np metal is the goal of this research
- Very little Np is available in its metal form and the purity is unknown
- Purity of the Np metal produced by this process needs to be evaluated

[1] Squires, L.N. and Lessing, P., 2016. *Journal of Nuclear Materials*, *471*, pp. 65-68.

Casting process – direct oxide reduction

- Work is performed using the Hot Uniaxial Press (HUP) furnace in the Casting Laboratory Glovebox located in the Analytical Laboratory.
- Glovebox is maintained under argon atmosphere, with oxygen concentration <50 ppm.





a. Stainless steel crucible
b. MgO_2 crucible

HUP apparatus

Squires, L.N. and Lessing, P., 2016. *Journal of Nuclear Materials*, *471*, pp. 65-68.

Casting process – direct oxide reduction

Reduction

Heat to 850°C
and stir for 6 hours

20 g calcined NpO_2

100g $CaCl_2$

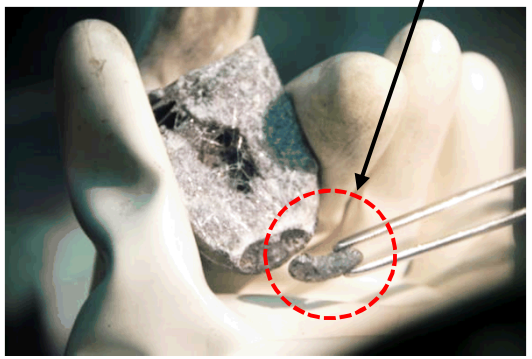
9g Ca metal

Np metal settles to the bottom, as it is more dense than the reactional mixture

Np metal button

$2Ca_{(metal)} + NpO_2 \rightarrow 2CaO + Np_{(metal)}$

In-house fabricated tantalum stirrer



Squires, L.N. and Lessing, P., 2016. *Journal of Nuclear Materials*, *471*, pp. 65-68.

Purity assessment

1st approach: measure the Np content in the sample

- 0.001% precision is required – in the AL, the lowest uncertainties can be obtained by ID-MC-ICP-MS, with uncertainty levels around ± 0.3%.
- Most accurate analytical techniques: controlled-potential coulometry[1,2] or high precision redox titration[3], with uncertainty levels around ± 0.2%.

2nd approach: Measure the impurities in the metal

- Assuming: Purity of the material (%) = 100% Np – Impurities (%) (most used around the globe, recent publications)[4,5]
- For a 99.999% purity level of Np metal, total mass of impurities in the solid should be less than 0.001%, or 10 µg g^{-1} of sample
- There are no "ZERO" values for any elemental impurity, the lowest achievable results are "less than the method limits of detection"

Analytical challenges:
Identify impurities and lower our current detection limits

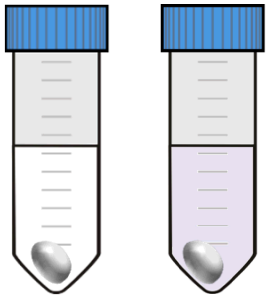
[1] Stromatt, R. W. and Scott, F. A., 1960. *Talanta, 6*, pp. 197.
[2] Xu, N. et al., 2013. *Journal of Radioanalytical and Nuclear Chemistry, 296*, 1, pp. 245.
[3] Godbole, A. G. and Patil, S. K. 1979. *Talanta, 26*, 4, pp. 330-332.
[4] Richter, S. *et al.,* 2013. *Journal of Analytical Atomic Spectrometry, 28*, 10, pp. 1540-1543.
[5] Becker, J. S. and Dietze, H. 2003. *International Journal of Mass Spectrometry, 228*, 2-3, pp. 127-150.

Purity assessment – sample preparation

Np metal button

Sequential etches

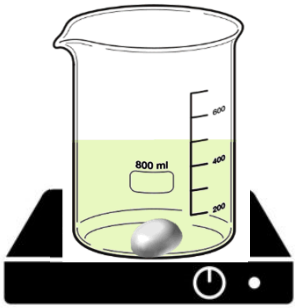
removal of surface contaminants



10 mL H_2O

10 mL 2M HCl

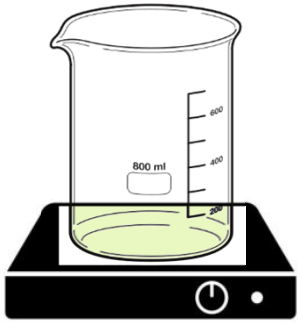
Dissolution



25 mL 6M HCl
+ 3 drops 24M HF

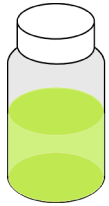
Elimination of HCl as Cl_2

Matrix conversion to HNO_3 media reduces the formation of Cl- interferences



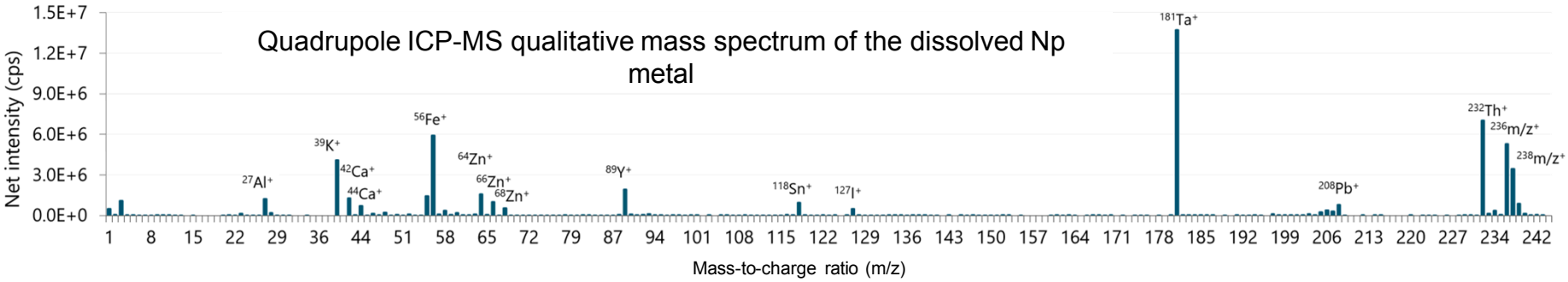
10 mL 16M HNO_3

Final solution



50 mL 8M HNO_3

Purity assessment – Qualitative mass spectrum



- Subtracted spectra from dissolution blank
- Analysis performed for samples diluted by 1:1000 factor

Potential contaminants

Fe, Ta (materials used in the casting process)
Actinides (NpO_2 feedstock)
Zn, Sn (environmental contamination)

Because of the potential for spectral interferences, HR-ICP-MS was used to obtain quantitative concentrations

Purity assessment – Interferences evaluation

Spectral interferences

- Overlap of the interferant m/z with analyte m/z;
- Isobaric: monoatomic species with the same m/z ($^{40}Ar^{+}$ and $^{40}Ca^{+}$);
- Double charged: monoatomic species with double charge, with the same m/z ($^{232}U^{++}$ and $^{116}Sn^{+}$);
- Polyatomic: molecular species with the same m/z as the analyte ($^{40}Ar^{16}O^{+}$ and $^{56}Fe^{+}$).

Plasma gas/air	**Sample prep.**	**Matrix components**
Ar-, O-, N-, C- species	O-, N-, Cl-, S- species	Np-, Ta-, Th- species
↑ *Background*	↑ *Blank*	
↑ *MQL*	↑ *MQL*	
Overestimated concentrations, false positives	*Overestimated concentrations, false positives*	*Overestimated concentrations, false positives*

Lum, T., and Leung, K., 2016. *Journal of Analytical Atomic Spectrometry,* 31, 5, pp. 1078-1088.

Purity assessment – HR-ICP-MS analysis

High Resolution ICP-MS (HR-ICP-MS)

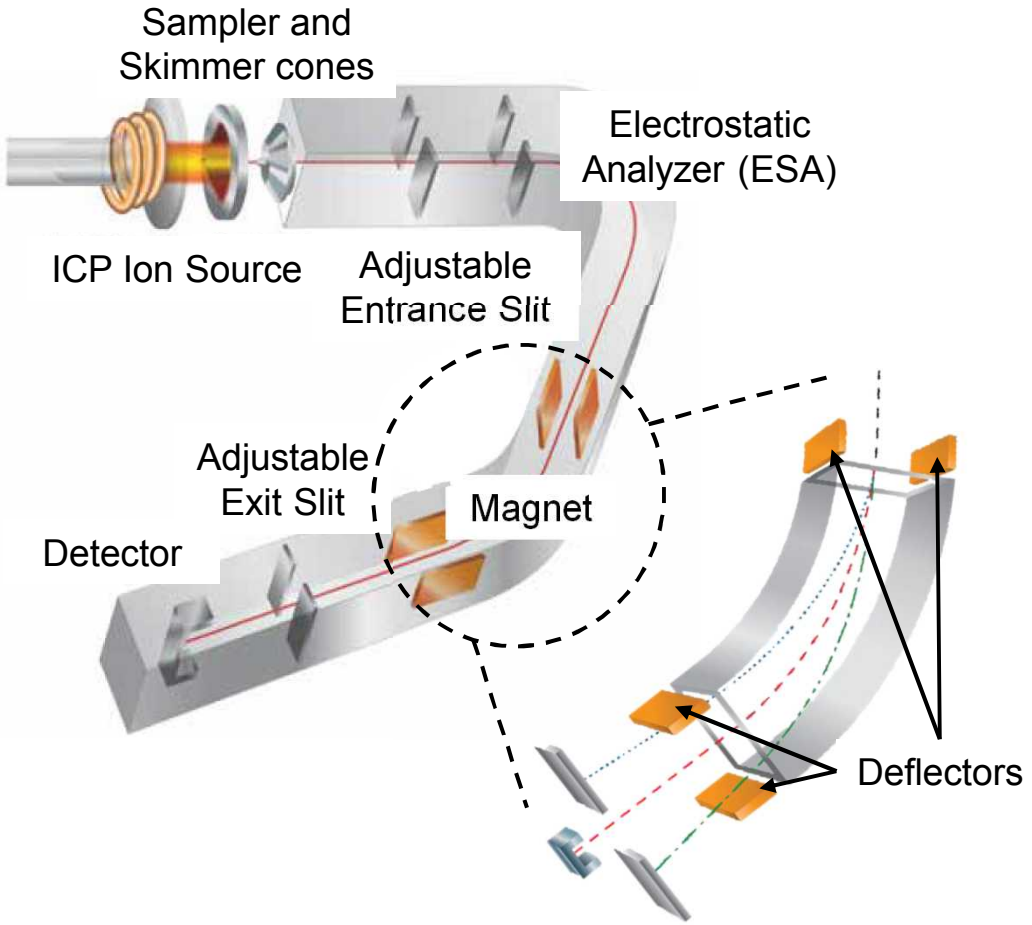
Nu Instruments Attom ES HR-ICP-MS – attached to a radiological hood

- Double focusing HR-ICP-MS
- Enhanced sensitivity interface optimized for dry sample introduction
- High performance ion optics
- Flexible resolutions from 300 to 10000 RP
- Combination of detectors gives a wide dynamic range

Purity assessment – HR-ICP-MS analysis

High Resolution ICP-MS (HR-ICP-MS)

- Double-focusing instrument – ESA focus the energy of the ions coming from the entrance slit, and magnet focus the ions related to their m/z onto the exit slit
- Mass resolution is adjusted by selecting different entrance and exit slits widths
- Deflectors voltage can be changed for each "parked mass" of the magnet – faster analysis over a wide mass range
- The higher the resolution, the narrower the slits used → sensitivity loss



Method development should aim not only on interferences separation, but also on achievable quantifications limits

Purity assessment – HR-ICP-MS analysis

- From the qualitative mass spectrum, Ti, Nb, I, Au, Tl, Na, Al, Sn, Ni, Zn, Y, Cr, Pb, K, Fe, Ca, Ta, Th, V, U and Pu were selected to be analyzed.
- Analysis performed for samples diluted by 1:1000 factor
- 6 different sets, accordingly to its expected concentration in the sample and/or possible isobaric interferences
- Internal standards used: Sc, In, Ho an Bi *(in order to account for sample introduction and instrumental drifts during the analysis)*
- Samples were run both on 300 RP and 4000 RP

Analytes	Calibration range (ng g^{-1})	Internal standard concentration (ng g^{-1})
Ti, Nb, I, Au, Tl	0.01 – 0.075	0.05
V	0.01 – 0.075	0.05
Na, Al, Cr, Ni, Zn, Y, Sn, Pb	0.1 – 0.7	0.5
Pu	0.15 – 0.75	0.5
U	0.5 - 5	1
K, Fe, Ca, Ta and Th	0.5 - 5	1

For each isotope, several items were evaluated:

- Raw signal for 5% HNO_3 (rinse) and sample preparation blanks
- Determination coefficient and sensitivity of calibration curves
- Possibility of interferences
- Comparison of results obtained using 300 RP and 4000 RP

Purity assessment – HR-ICP-MS analysis

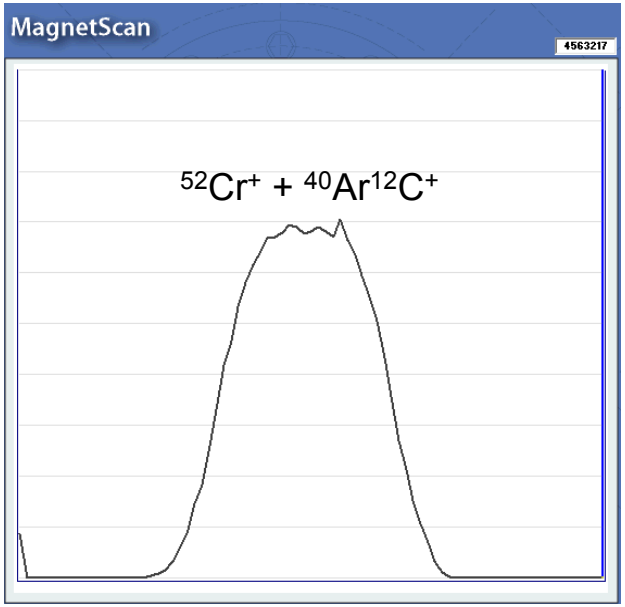
	300 RP	4000 RP
5% HNO_3 (blank) signal intensity	369118 cps	1820 cps

signal reduction of more than 2 orders of magnitude

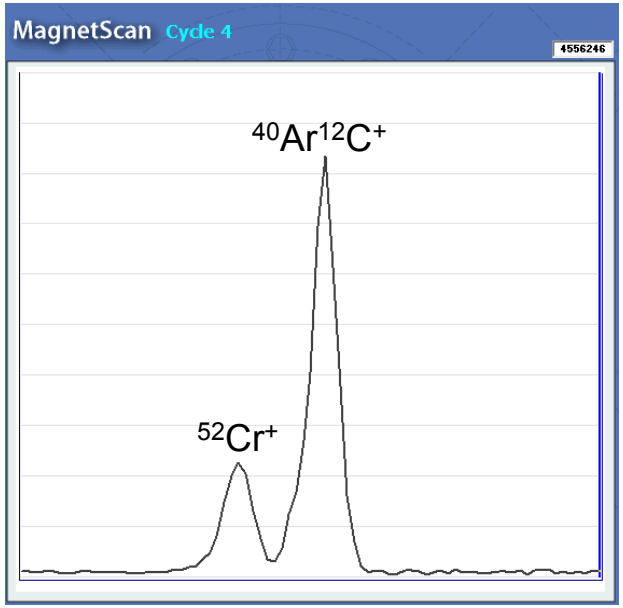
interference from the plasma gas resolved

Mass spectrum of a 0.2 ng g^{-1} Cr solution

300 RP



4000 RP



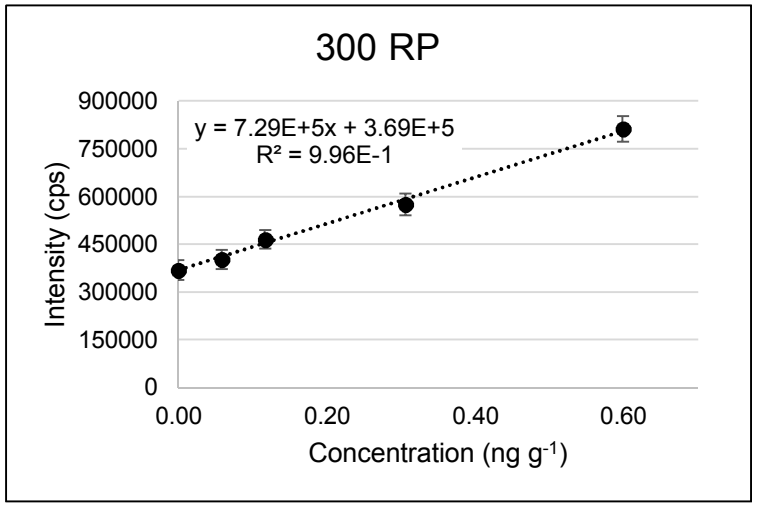
Purity assessment – HR-ICP-MS analysis

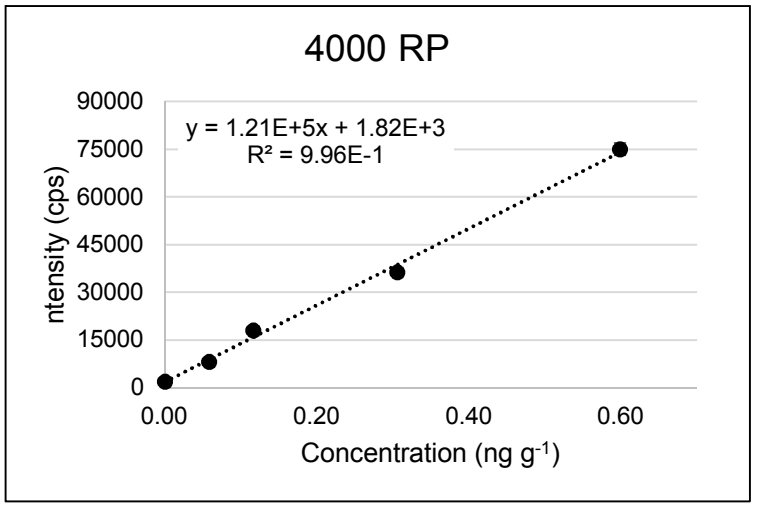
	300 RP	4000 RP
5% HNO_3 (blank) signal intensity	369118 cps	1820 cps
Calibration slope	728542 cps g µg^{-1}	120756 cps g µg^{-1}
Calibration r^2	0.9957	0.9964
Quantification limit	40 µg g^{-1}	0.3 µg g^{-1}

Sensitivity reduced by a factor of 5

Quantification limit increased by 2 orders of magnitude

$$Limit\ of\ detection = 3x\ \frac{Standard\ deviation\ of\ 10\ measurements\ of\ the\ blank}{Slope}$$



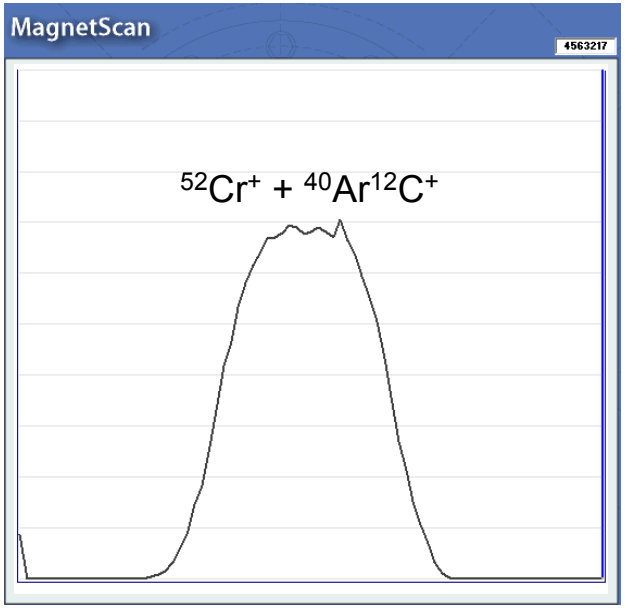


Purity assessment – HR-ICP-MS analysis

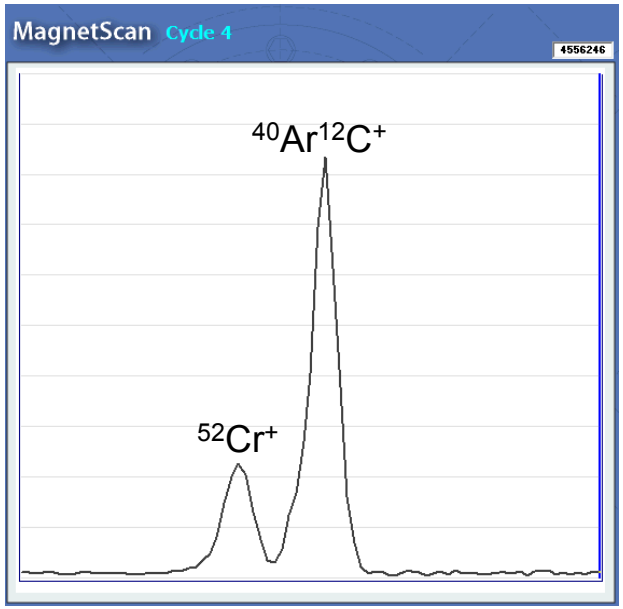
	300 RP	4000 RP
5% HNO_3 (blank) signal intensity	369118 cps	1820 cps
Calibration slope	728542	120756
Calibration r^2	0.9957	0.9964
Quantification limit	40 µg/g	0.3 µg/g
Measurement RSD	5 – 20%	1 – 15%
$^{52}Cr^+$ concentration in samples	<40 µg g^{-1}	34.3 ± 1% µg g^{-1}

Results could be quantified after the separation of the interference

300 RP



4000 RP



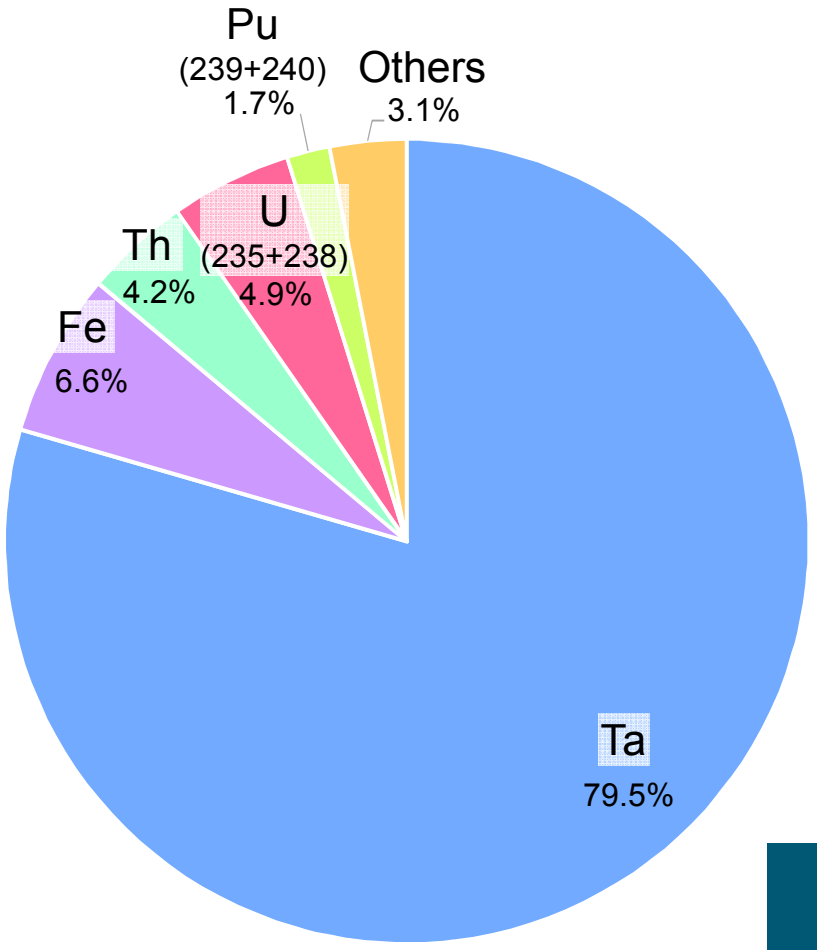
Purity assessment – HR-ICP-MS analysis

		300RP			4000 RP		
Analyte	Interferences	Concentration (µg g^{-1})	RSD (%)	MQL* (µg g^{-1})	Concentration (µg g^{-1})	RSD (%)	MQL* (µg g^{-1})
$^{50}Cr^{+}$	$^{50}Ti^{+}$, $^{50}V^{+}$, $^{36}Ar^{14}N^{+}$, $^{38}Ar^{12}C^{+}$	1.81	±4%	0.09	1.99	±5%	0.6
$^{51}V^{+}$	$^{14}N^{37}Cl^{+}$	1.81	±4%	0.06	**1.67**	**±6%**	**0.02**
$^{52}Cr^{+}$	$^{36}Ar^{16}O^{+}$, $^{38}Ar^{14}N^{+}$, $^{40}Ar^{12}C^{+}$	<40	N/A	40	**34.3**	**±1%**	**0.3**
$^{57}Fe^{+}$	-	<7	N/A	7	**3.38**	**±9%**	**2**
$^{58}Ni^{+}$	$^{40}Ar^{18}O^{+}$	16.8	±10%	3	**13.4**	**±2%**	**2**
$^{60}Ni^{+}$	$^{44}Ca^{16}O^{+}$	**5.14**	**±7%**	**0.2**	4.98	±9%	2
$^{89}Y^{+}$	-	**10.8**	**±1%**	**0.005**	10.8	±0.4%	0.05
$^{93}Nb^{+}$	-	**1.55**	**±4%**	**0.003**	-	-	-
$^{116}Sn^{+}$	$^{232}Th^{++}$	4.02	±2%	0.1	**<0.3**	**N/A**	**0.3**
$^{118}Sn^{+}$	-	**<0.2**	**N/A**	**0.2**	<0.3	N/A	0.3
$^{120}Sn^{+}$	-	**<0.3**	**N/A**	**0.3**	<0.7	N/A	0.7
$^{181}Ta^{+}$	-	**1920**	**±2%**	**0.1**	1990	±2%	2
$^{203}Tl^{+}$	-	**<0.001**	**N/A**	**0.001**	-	-	-
$^{205}Tl^{+}$	-	**<0.003**	**N/A**	**0.003**	-	-	-
$^{206}Pb^{+}$	-	**<0.05**	**N/A**	**0.05**	<0.4	N/A	0.4
$^{208}Pb^{+}$	-	**<0.1**	**N/A**	**0.1**	<0.7	N/A	0.7
$^{232}Th^{+}$	-	**103.0**	**±0.1%**	**0.006**	111.0	±0.8%	0.06
$^{235}U^{+}$	-	**2.74**	**±1%**	**0.001**	-	-	-
$^{238}U^{+}$	-	**115**	**±1%**	**0.01**	-	-	-
$^{239}Pu^{+}$	-	**35.6**	**±1%**	**0.002**	-	-	-
$^{240}Pu^{+}$	-	**6.05**	**±1%**	**0.002**	-	-	-

*MQL: Method Quantification Limit

Bold: values used for total concentration calculation

Purity assessment – HR-ICP-MS analysis



Element	Conc. (µg g^{-1})	MQL* (µg g^{-1})	RP
Cr	41.0 ± 1%	0.4	4000
V	1.68 ± 6%	0.02	4000
Fe	160 ± 9%	94	4000
Ni	19.6 ± 7%	0.8	300
Y	10.8 ± 1%	0.01	300
Nb	1.55 ± 4%	0.003	300
Sn	<MQL	0.8	4000
Ta	1920 ± 2%	0.1	300
Tl	<MQL	0.003	300
Pb	<MQL	0.2	300
Th	102.5 ± 0.2%	0.01	300
^{235}U	2.74 ± 1%	0.001	300
^{238}U	115 ± 1%	0.01	300
^{239}Pu	35.6 ± 1%	0.002	300
^{240}Pu	6.05 ± 1%	0.002	300

Total Np purity: 99.758%
Maximum achievable purity (Σ MQL): 99.990%

Purity assessment – Conclusions and next steps

- Np metal that was produced did not achieve the desired purity: 99.999%
  - It was possible to identify the main sources of impurities, with great precision and accuracy
  - *The casting process will be modified accordingly to the results obtained for the main contaminants*
- Using the current detection limits, we could determine up to 99.990% of purity
  - *Detection limits should be improved – using of lower RP (2500) and separating the Np from the solution (so a lower dilution factor can be used)*
- Other analytes still need to be determined for a complete characterization of the Np metal
  - *K, Na, Al, Ca and Zn will be determined by ICP OES*
  - *C, N and O will be determined by Light Elements Analysis*

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HR-ICP-MS Instrument Scientist

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Q-ICP-MS Instrument Scientist

Scott R. Wilde
Np Metal Reduction

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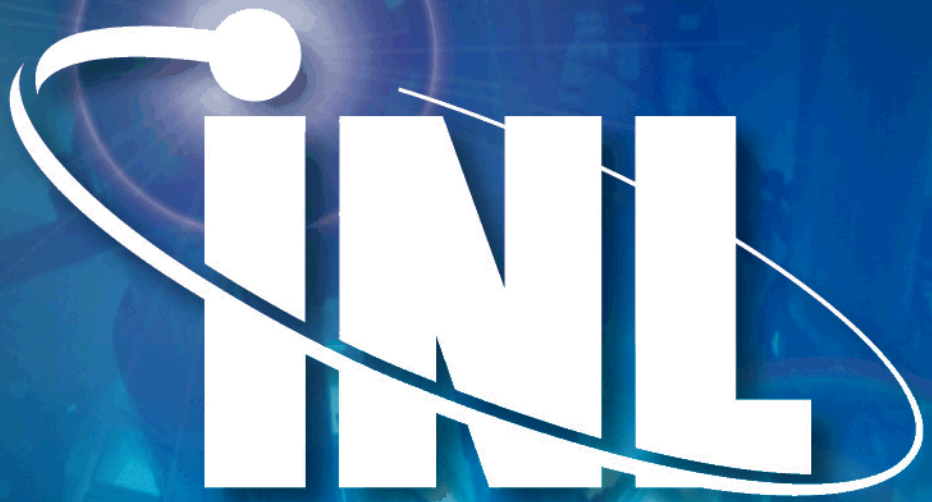

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