

# Accurate analysis of neptunium 237 in a uranium matrix, using ICP-QQQ with MS/MS

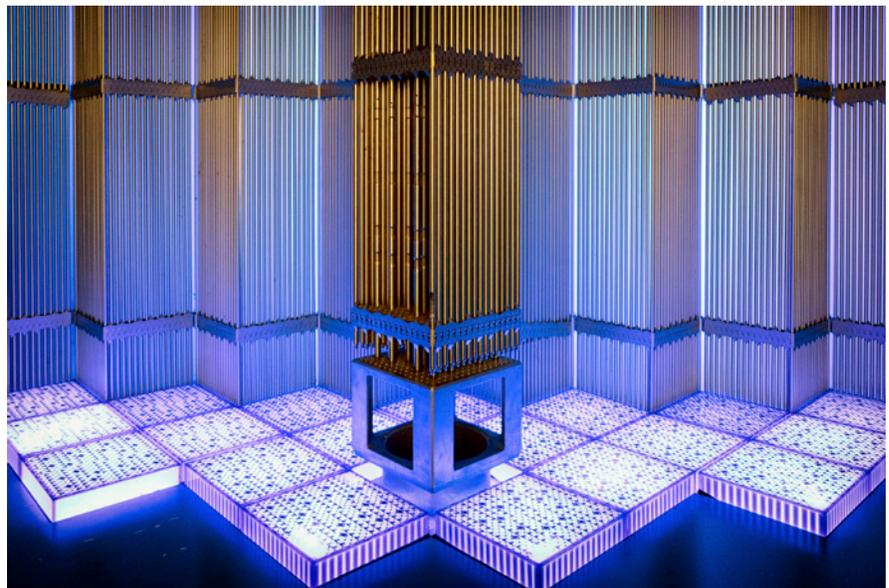
## Application note

Nuclear, environmental

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## Introduction

The radioactive actinide element neptunium (Np) is formed by neutron bombardment of uranium (U), with more than 50,000 kg of Np produced annually as a by-product of nuclear-power generation. Smaller quantities of Np can be found as a decay product of americium-241 ( $^{241}\text{Am}$ ) used in ionizing smoke detectors, with trace quantities being produced from nuclear bomb testing, and naturally (from natural neutron capture) in U ores.

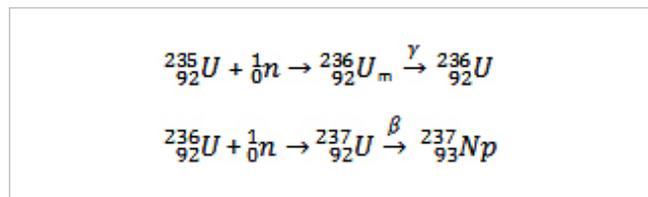


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**8900 ICP-QQQ**



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The predominant isotope  $^{237}\text{Np}$  is produced as follows:



$^{237}\text{Np}$  sits at the top of the “neptunium decay series” which in turn produces a series of other radioactive elements with medium to very short half-lives, eventually forming Bi and Tl (Figure 1).

$^{237}\text{Np}$  is extremely mobile in the environment, as it readily forms aqueous solutions (more so than any other actinide), attaches to particles and colloids, and does not readily become trapped in humic substrates such as soil.

Np also has a high affinity for calcium-rich materials including certain clays and concrete, so care is needed with its storage. Although Np is not readily absorbed in the human gut, once in the body, it will pre-concentrate in the bones.

The relatively long half-life of  $^{237}\text{Np}$  (~2.14 million years) means that it is persistent in the environment, so it requires suitable containment, and needs to be monitored at low levels.

#### Abundance sensitivity of ICP-QQQ with MS/MS

Samples that contain Np usually contain U at far higher concentrations. The determination of ultra-trace  $^{237}\text{Np}$  in environmental samples and nuclear materials (fuel or waste) is difficult by ICP-MS because of the overlap due to peak tailing from the large  $^{238}\text{U}$  peak.

Conventional quadrupole ICP-MS instruments (ICP-QMS) operate at unit mass resolution to separate adjacent masses, meaning a nominal resolution (expressed as  $M/\Delta M$ ) of 237 at  $m/z$  237. However, peak separation also depends on the abundance sensitivity (AS) of the spectrometer. AS is a measure of the peak tailing, calculated from the contribution that an intense peak makes to its neighbouring masses.

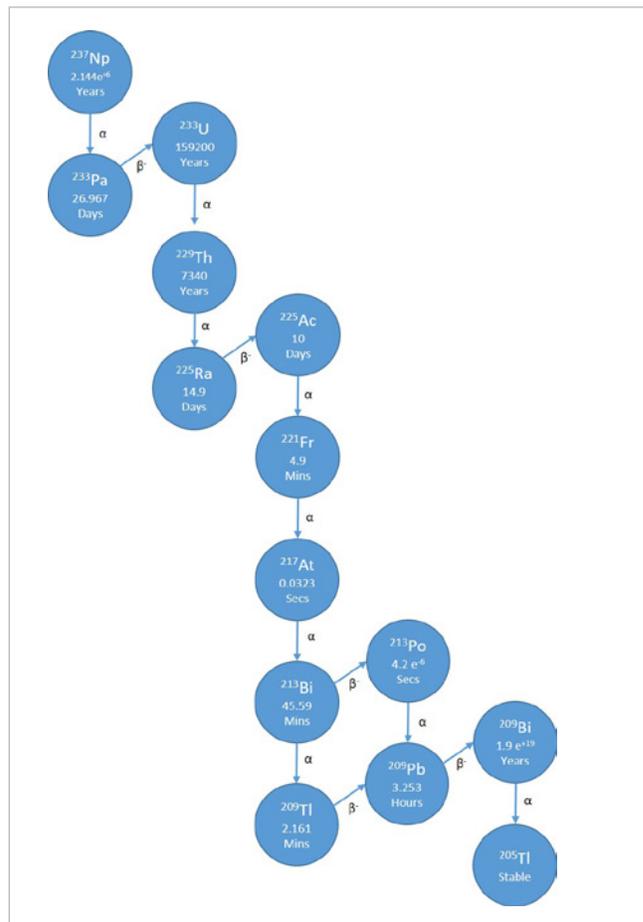
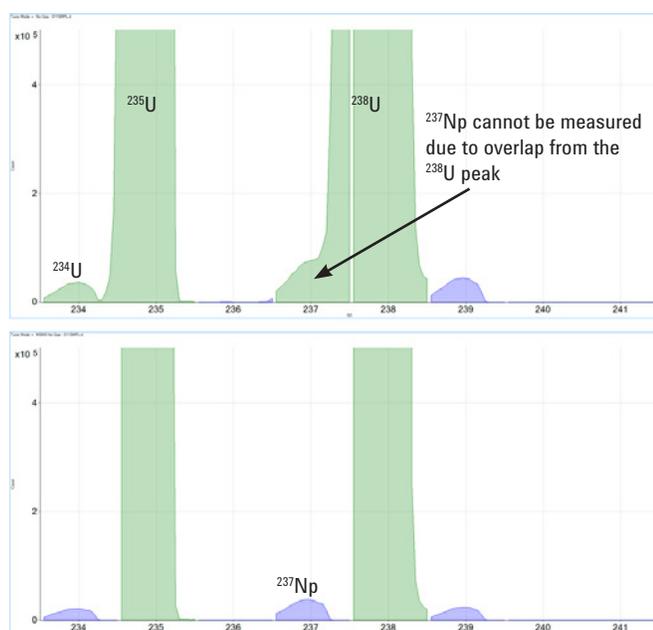


Figure 1. Np-237 decay series. Adapted from “The NUBASE Evaluation of Nuclear and Decay Properties”. Nuclear Physics A 729: 3–128. DOI: 10.1016/j.nuclphysa.2003.11.001

Quadrupole ICP-MS instruments can achieve AS of up to  $1 \times 10^{-7}$  (a peak of  $1 \times 10^7$  cps contributes 1 cps to the adjacent masses), so a peak with an intensity much higher than  $10^7$  cps will make a significant contribution to the peaks either side. High Resolution-Sector Field (HR-SF)-ICP-MS has better resolution than ICP-QMS ( $M/\Delta M$  of up to 10,000), but poorer AS. So adjacent peaks may appear to be separated on the mass scale, but the peak tail of an intense peak may still contribute to the masses above and below. The Agilent 8800 or 8900 Triple Quadrupole ICP-MS (ICP-QQQ) use a unique configuration with two quadrupole mass analyzers (Q1 and Q2) either side of the collision reaction cell. When both quadrupoles are operated as unit mass filters (MS/MS mode), this configuration delivers unmatched peak separation because the abundance sensitivity performance is the product of two mass separations – Q1 AS x Q2 AS – giving an overall AS of  $\ll 10^{-10}$ .

ICP-QQQ is therefore able to successfully separate  $^{237}\text{Np}$  from the  $^{238}\text{U}$  overlap, even when the U is present at many orders of magnitude higher concentration. This is demonstrated in Figure 2, which shows the spectra of 100 ppt Np in a 10 ppm U matrix measured in Single Quad (SQ) mode (top) and MS/MS mode below. The ICP-QQQ spectrum shows the superior peak separation provided by MS/MS mode, and the clear elimination of the contribution on mass 237 from the adjacent 238 U peak.



**Figure 2.** Spectra of 100 ppt Np in a 10 ppm U matrix sample solution obtained using ICP-QQQ in Single Quad mode (top) and MS/MS mode (bottom). MS/MS mode eliminates the peak tail on the low mass side of the intense  $^{238}\text{U}$  peak.

## Experimental

### Instrumentation

The Agilent 8800\* ICP-QQQ was configured with an SPS 4 autosampler, and the standard sample introduction system consisting of a Micromist nebulizer, quartz spray chamber, quartz torch and Ni interface cones. Instrument operating parameters are given in Table 1.

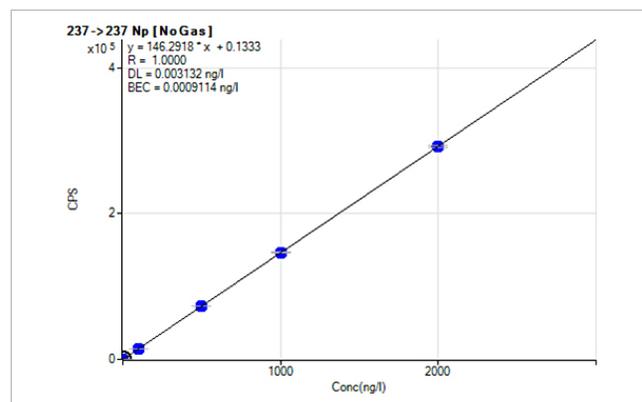
\* The Agilent 8800 ICP-QQQ has been superseded by the 8900 ICP-QQQ

**Table 1.** ICP-QQQ operating parameters.

Parameter	Value
RF power	1550 W
Sampling depth	8.0 mm
Nebulizer gas flow rate	1.15 L/min
Spray chamber temp	2 °C
Cell gas	None

### Calibration

A blank and four neptunium calibration standards from 100 to 2000 ng/L (ppt) were prepared in nitric acid (2% v/v, Ultrapur, Merck, Germany). The calibration curve obtained by ICP-QQQ showed excellent linearity over the calibrated range with a calibration coefficient of 1.0000 (Figure 3). As Np is essentially absent from the environment and does not occur as a typical reagent contaminant, the Background Equivalent Concentration (BEC) obtained was  $\sim 0.0009$  ng/L (0.9 pg/L, ppq) and the Detection Limit (DL) was  $\sim 0.0031$  ng/L (3.1 ppq). This illustrates the exceptionally low background and high ion transmission (sensitivity) of the ICP-QQQ when operating in MS/MS mode.



**Figure 3.** Calibration curve for  $^{237}\text{Np}$  obtained by ICP-QQQ.

## Results and discussion

**Table 2.** Measurement of  $^{237}\text{Np}$  in a series of U matrix samples using ICP-QQQ and ICP-QMS.

Sample Name	8800 ICP-QQQ		7900 ICP-QMS	
	Reported $^{237}\text{Np}$ conc., $\mu\text{g/L}$	CPS	Reported $^{237}\text{Np}$ conc., $\mu\text{g/L}$	CPS
1 ppm U - unspiked	<b>0.0000</b>	<b>1.10</b>	<b>0.0016</b>	<b>570.48</b>
1 ppm U, 0.1 ppb Np	0.1021	14942.85	0.1018	36525.19
1 ppm U, 1.0 ppb Np	1.0445	152806.38	1.0100	362304.66
10 ppm U - unspiked	<b>0.0000</b>	<b>0.83</b>	<b>0.0154</b>	<b>5519.75</b>
10 ppm U, 0.1 ppb Np	0.1029	15052.99	0.1152	41339.80
10 ppm U, 1.0 ppb Np	1.0486	153402.27	1.0196	365764.86
100 ppm U - unspiked	<b>0.0000</b>	<b>3.97</b>	<b>0.1581</b>	<b>56728.76</b>
100 ppm U, 0.1 ppb Np	0.0997	14586.02	0.2494	89482.09
100 ppm U, 1.0 ppb Np	0.9859	144228.95	1.0597	380137.27

The Abundance Sensitivity performance of the ICP-QQQ in MS/MS mode was tested using a series of spiked and unspiked uranium solutions. Three sets of uranium solutions were prepared, at concentrations of 1, 10 and 100 mg/L (ppm). For each concentration level, the U matrix solutions were measured unspiked, and with Np spikes at 0.1 and 1.0  $\mu\text{g/L}$  (ppb). For comparison purposes, the samples were analyzed using an Agilent 8800 ICP-QQQ and an Agilent 7900 ICP-QMS, to assess the impact of the improved AS performance of the QQQ configuration.

The results in Table 2 show that accurate recoveries were achieved for both Np spike levels in all of the U matrix samples analyzed by ICP-QQQ—even with U:Np concentrations at a ratio of 1,000,000:1. In contrast, the Np results measured on the 7900 quadrupole ICP-MS show a small contribution from the U matrix. This U signal contributes to a false-positive result for Np in the higher U matrix samples, including the unspiked U matrices. While the U signal only increased the apparent Np concentration by a small amount (sub- $\mu\text{g/L}$ ), the low level at which Np must be monitored means that this false signal is significant. The ICP-QMS results show that the interference effect is more pronounced with increasing U matrix concentration, due to the relatively poor AS of ICP-QMS compared to ICP-QQQ.

## Conclusions

ICP-MS is used successfully for the analysis of trace elements in a wide range of complex sample matrices. However, several challenging interferences remain, including the measurement of trace analytes that occur close to major or matrix element peaks. This study has shown that the superior abundance sensitivity provided by the ICP-QQQ's tandem quadrupole mass analyzer configuration (MS/MS) has practical benefits for the analysis of trace concentrations of Np at  $m/z$  237 in the presence of high concentrations of the adjacent major isotope of U at  $m/z$  238.

Conventional quadrupole-ICP-MS cannot resolve the overlap/peak tailing from the  $^{238}\text{U}$  isotope sufficiently to allow ultra-trace level analysis of  $^{237}\text{Np}$ ; SF-ICP-MS also has insufficient abundance sensitivity to resolve the adjacent masses well enough to perform this analysis.

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Results presented in this document were obtained using the 8800 instrument, but performance is also verified for the 8900 ICP-QQQ

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