ATTOM® ES

HR-ICP-MS

APPLICATION NOTE **AN47**

QUANTITATIVE ANALYSIS OF NEPTUNIUM-237 IN URANIUM MATRIX

- **Medium resolution and retardation filter to improve abundance sensitivity**
- **Use of software baseline correction capability for most accurate results without the need for matrix-matched blank measurements**
- **Excellent calibration linearity and spike recoveries in increasing U matrix concentrations**

Introduction

Currently, quantitative analysis of ^{237}Np in U matrices is achieved with laborious and time-consuming sample preparation to separate the Np from the U. The analysis has traditionally required a high decontamination factor using a co-precipitation method with a processing time of 1-1.5 days, resulting in a relatively poor sample throughput and customer response times. High levels of decontamination from the uranium matrix are required as the tail of a strong ^{238}U signal affects neighbouring masses, for example ^{237}Np, increasing the baseline and showing an exponential-type curve when monitored at low resolution (300) as shown in the example in Figure 1.

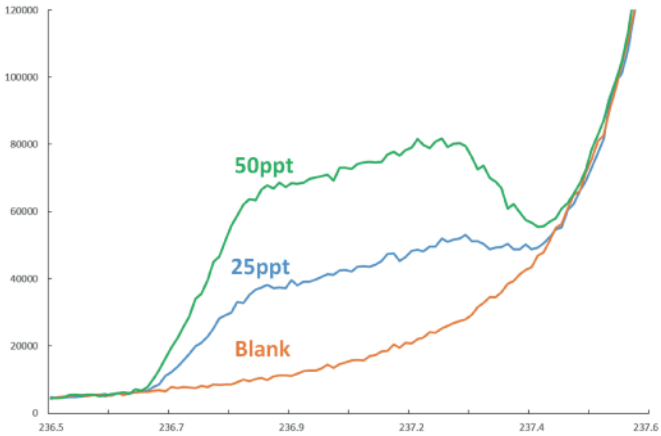

Figure 1: Example of ^{238}U tail effect on the measurement of ^{237}Np (blank, 25 and 50ppt standards in 1ppm U matrix) at low resolution. Here the flat top feature of a low resolution peak is lost and quantification becomes difficult.

This makes quantitative analysis very difficult, involving substantial matrix matching and background corrections for best accuracy. This application showcases the versatility of the Nu Quant quantification software and its ability to deal with such analyses.

Baseline correction management

The first aspect of the baseline correction at m/z 237 is to minimise as much as possible the curved feature at low resolution. This is achieved by selecting a medium resolution setting (~4000), which focuses on a smaller mass range and therefore increases the linearity of the baseline.

Subsequently, the Nu Quant software has the ability to perform a "valley with baseline" correction of the integrated counts. Where the integration valleys are defined automatically, a straight line is calculated and all data below that line is rejected from the integration. This allows for the peak signal only to be integrated and used in subsequent quantification steps. The features described are highlighted in Figure 2.

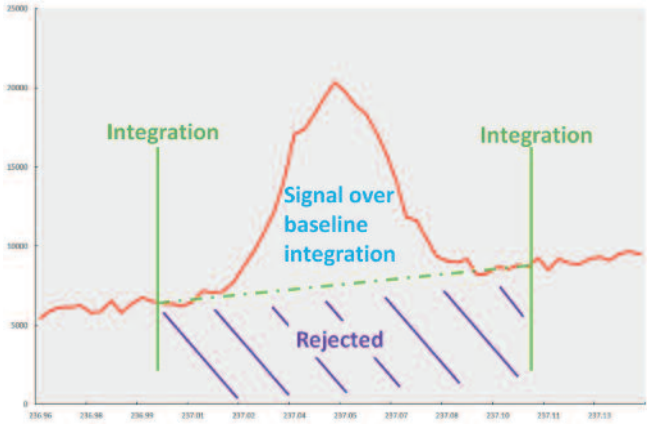

Figure 2: Example of a 100ppt ^{237}Np signal in 100ppm U matrix. The integration bars are manually adjustable, and allow for a linear baseline correction at the point of intercept with the signal, after which only the true analyte signal is integrated for further data manipulation.

Linearity of calibration

A calibration line is drawn from a blank and six standards (25, 50, 100, 250, 500 and 1000ppt ^{237}Np) all in 100ppm U matrix. Spectra overlay, calibration line and figures of merit are given in Figure 3, Figure 4 and Table 1 respectively.

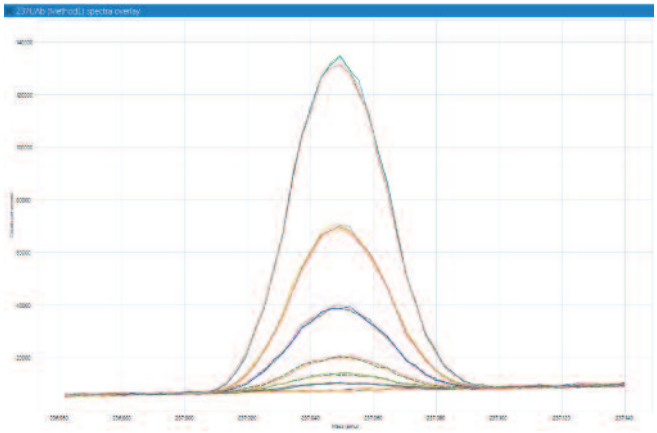

Figure 3: Spectra overlay showing 100ppm U blank and six calibration standards at ~4000 resolution.

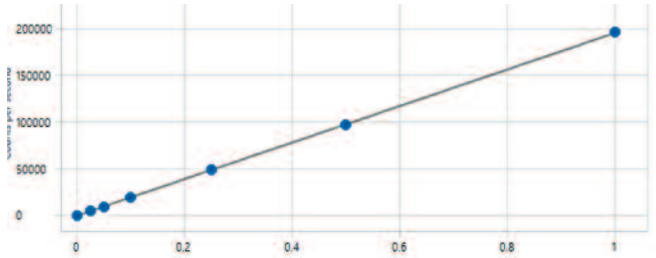

Figure 4: Calibration line obtained after baseline correction for a blank and six ^{237}Np standards in 100ppm U matrix.

Table 1: Figures of merit for ^{237}Np calibration in 100ppm U matrix. (a) Detection limit based on 3SDs of the blank measurements.

Criteria	Value
Sensitivity slope	195 kcps/ppb
Background equivalent concentration	1.27 ppt
Correlation factor (R^2)	0.99997
Detection Limit[a]	2.56 ppt
Direct detection limit in U	0.66 Bq/gU

Table 2: Concentrations of spikes in various U matrices. Results feature the Nu Quant baseline correction tool, without the tool using conventional whole signal integration and with matrix matched blank correction. All data in ppt unless stated otherwise.

Matrix (ppm U)	Nu Quant baseline correction conc.	No baseline correction conc.	With matrix blank correction
10	50.4	66.0	50.6
50	50.9	129	50.8
100	49.9	205	50.8
200	48.8	356	53.0

Spike recoveries

A range of U concentrations, namely 10/50/100/200ppm, were measured unspiked and spiked with 50ppt of ^{237}Np. Figure 5 shows the different U concentration matrices and their respective spikes in Nu Quant's spectra overlay tool.

For spike recovery results, a set of unspiked and spiked samples with no U present (in 2% HNO_3 v/v) was used to establish a one point calibration and apply it to the remaining spiked samples. For each matrix concentration, the spiked sample data was integrated with and without the baseline subtraction tool (excluding or including the background). Both sets of results are given in Table 2.

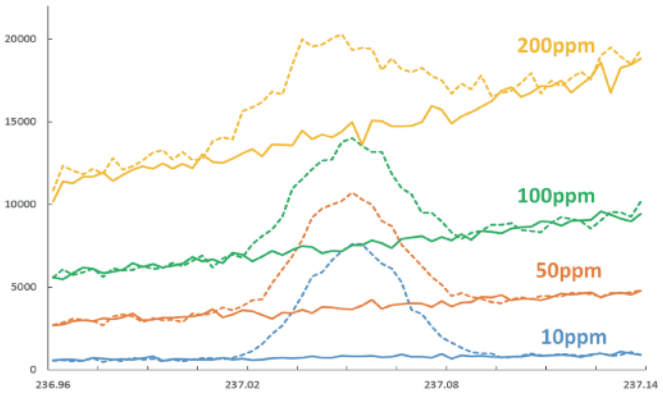

Figure 5: Spectra overlay of the increasing U concentrations and their respective ^{237}Np spikes of 50ppt.

Conclusions

Without the appropriate purification steps, the quantitative measurement of ^{237}Np in U matrix is difficult to achieve. Conventional integration methods require a matrix-matched blank to be analysed and a blank subtraction to be performed to obtain accurate data. The baseline correction tool available in Nu Quant allows for the appropriate correction independent of the concentration of the U matrix and without the necessity to measure a matrix-matched blank. With fully adjustable integration bars, it also allows for individual modifications to track any moving peak whereas fixed integrations will generate biased data in that instance. Both calibration and spike recoveries give excellent data with maximum sample throughput achievable.