

Introduction

Abundance sensitivity is a measure of the contribution of the peak 'tail' of a major isotope on an adjacent minor isotope. The tailing is due to the collision of ions with residual gas molecules in the mass spectrometer causing a loss of ion energy. This is manifest on a mass spectrum as a loss in mass giving rise to a 'tail' on the low mass side of a peak. Hence there is a direct correlation between abundance sensitivity and the quality of the analyser vacuum.

Additionally, since any peak tail contribution from a major isotope will be proportional to its beam size, the associated errors will produce an apparent non-linearity in the measured ratio. Hence it is crucial that an MS system has low inherent abundance sensitivity and that an effective correction can be made for any small contribution that remains.

By convention, abundance sensitivity is referred as the contribution of the ^{238}U peak on mass 237 where there are no U isotopes, e.g. $237/^{238}\text{U} = 5e^{-6}$ or 5ppm. In U analysis the abundance sensitivity is of particular importance since the ^{236}U isotope of natural samples is less than 1ppm of the ^{238}U peak so that even a small amount of ^{238}U peak tailing down to m/z 236 is significant.

Experimental

We have used the standard U030a to illustrate the effect of abundance sensitivity on the Phoenix Thermal Ionization Mass Spectrometer. The certified isotopic composition of U030a is shown in Table 1.

NBL U030a	
	Atom%
^{234}U	0.027778
^{235}U	3.0404
^{236}U	0.0006
^{238}U	96.9312
$^{234}\text{U}/^{238}\text{U}$	0.000287
$^{235}\text{U}/^{238}\text{U}$	0.031367
$^{236}\text{U}/^{238}\text{U}$	0.000006

Table 1. Composition of NBS U030a

Figure 1 shows a mass scan on the axial ion counting Daly detector from m/z 233.5 to mass 237.5. The peak on the left is the ^{234}U isotope which has an isotopic abundance of 287ppm of the ^{238}U which is off scale to the right of this figure. The ^{235}U peak is off scale on this scan, whilst the ^{236}U peak with an abundance of 5.86ppm relative to the ^{238}U is very small. The flat top of the ^{236}U is clearly apparent, and the peak itself is readily resolvable from the baseline.

To the right of the ^{236}U peak there is a clear uplift in baseline due to the peak tail from the ^{238}U . This is shown in more detail in Figure 2 (over).

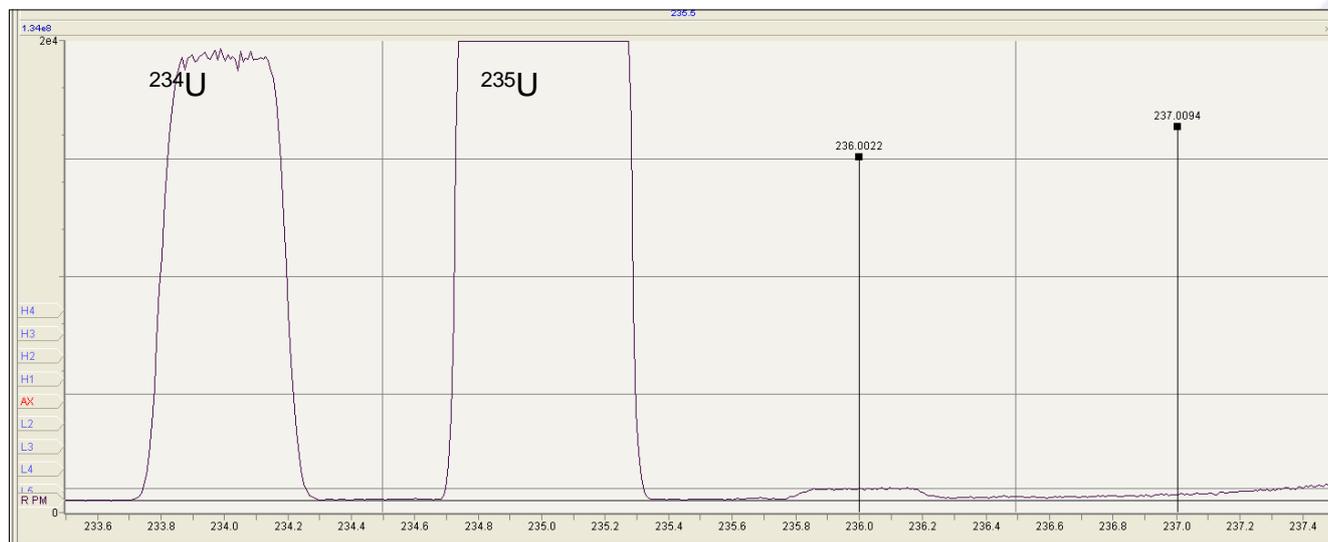


Figure 1. Mass scan (Daly) from m/z 233.5 to m/z 237.5

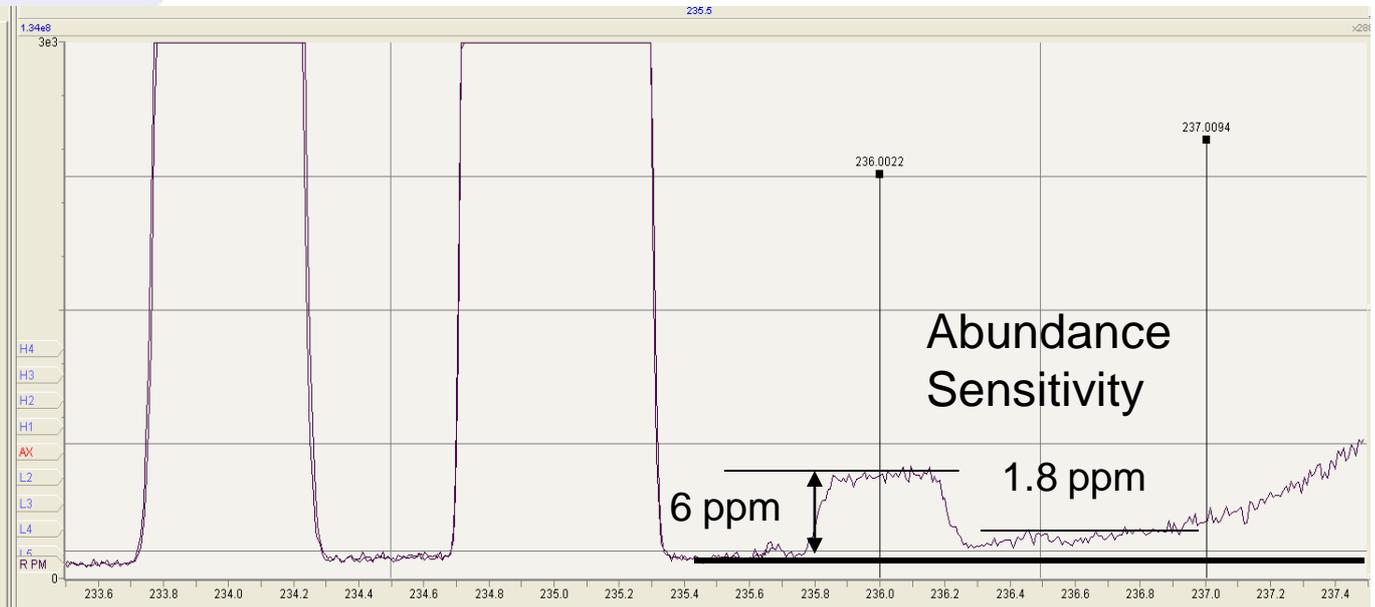


Figure 2. Mass scan (Daly) from m/z 233.5 to m/z 237.5 with magnified ion intensity scale.

Figure 2. shows that the ^{238}U peak tail extends very slightly beneath the ^{236}U peak. At mass 237 the tail is less than 1/3 that of the ^{236}U peak, and the abundance sensitivity is 1.8ppm. The analyser vacuum was $<2\text{e}^{-9}$ mbar.

Summary - The abundance sensitivity of the Phoenix TIMS is $<2\text{ppm}$ at mass 237 with respect to ^{238}U