

Reply to “Comment on ‘Existence of long-lived isomeric states in naturally-occurring neutron-deficient Th isotopes’”

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Barber and De Laeter state correctly in their Comment that “The mass spectrometric technique described in this article would be a novel procedure for investigating such isomeric states.” It is routinely used for trace element analysis with detection limit down to the ppq (10^{-15}) level [1].

The first argument of the Comment is that “the claim that four isomeric states of Th have been discovered, using an inductively coupled plasma-sector field mass spectrometer (ICP-SFMS), with abundances from $(1-10) \times 10^{-11}$ relative to ^{232}Th , cannot be accepted, given the known abundance sensitivities of other sector field mass spectrometers.” This argument is based on the statement that “The abundance sensitivity of a mass spectrometer is defined as ‘the ratio of the maximum ion current recorded at a mass m to the ion current arising from the same species recorded at an adjacent mass ($m \pm 1$). . .’” It is claimed that this value for the Neptune multicollector ICP-SFMS is about 5 ppm. In addition it is mentioned that with a retarding lens in front of the axial secondary electron multiplier, an abundance sensitivity of 24 ppb has been demonstrated for a two mass unit separation comparing ^{232}Th with $m/z = 230$.

In our case, as can be deduced from the background seen in Fig. 1(b) of the article, the abundance sensitivity for the same two mass unit separation comparing ^{232}Th and $m/z = 230$ is 70 ppb, which is in accord with the figure mentioned in the Comment. However, in our article the abundance sensitivity that concerned us was the abundances given by the intensities, relative to ^{232}Th , of the observed peaks at masses 211, 213, 217, and 218. In these cases the spectra are clean and no tails are seen from the far away peak of ^{232}Th ($\Delta m = 14$ to 21 u). There is no reason to assume that abundance sensitivities which are correct for a one or two mass unit separation are the same for a separation of 14 to 21 mass units. Under the conditions of our experiments, where the studied masses are far away from the major peak, and where no stable or long-lived radioactive isobar exists, the abundance sensitivity depends, among other

factors, on the concentration of the solution studied and the length of the measurement. The fact that the sensitivity in our experiment was suitable for measuring abundances in the region of 10^{-11} – 10^{-12} can be seen from Fig. 1(a) of our article. A peak due to $2 \mu\text{g l}^{-1}$ of ^{209}Bi with a total intensity of about 2.2×10^7 counts is seen in this figure. Normalization to 20 or 50 mg l^{-1} (concentrations that were used in the Th isotope measurements) gives the abundance limit relative to Bi of 5×10^{-12} and 2×10^{-12} , respectively. (The somewhat longer measuring periods for the Th isotopes of 24 to 30 s compared 18 s for Bi reduces these values even further.) Such a procedure, where one estimates the intensity of the major peak at high concentration by normalization to data at low concentration, is standard in ICP-SFMS measurements. The response of the ICP-SFMS is linear up to 9–10 orders of magnitude. In the counting mode the maximum measurable counting rate is 5×10^6 counts/s. After that, the current is measured with the same detector up to an equivalent of 6×10^9 counts/s. The error in the cross-calibration between the counting and the analog mode is usually <2%, so one can calculate expected sensitivity for 1 or 20 ppm solutions using data for a 1 ppb solution. We verified that the intensity, at the maximum of the peak, for 1 mg l^{-1} ^{232}Th solution is about 2×10^8 counts/(ch 1s), as stated in our article. This figure is about a factor of two lower than the value given in Ref. [1] for ^{232}Th . The intensities of the low abundance peaks and the backgrounds in their respective regions are of course measured in the presence of the concentrated major isotope.

Let us refer now to the argument made in the Comment that “The reliable measurement of isotope ratios must include a consideration of potential interferences, particularly isobaric interferences. . .”

The question of isobaric interferences is dealt with in the article: “These measurements are necessarily limited to radioactive nuclei, where no stable or long-lived isobars exist,” as seen in the nuclear chart for all 211, 213, 217, and 218 isobars. Regarding other interferences, it is mentioned in the article that “the masses of the isotopes of Th and U are higher than, and resolvable from, the masses of all molecules of the same mass number, except for multihydrogen-containing molecules.” Multihydrogen molecules and particularly

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hydrocarbons are also considered in the article and it is mentioned that “Their typical masses are higher than and well separated from the masses of the new peaks seen here.” Hydrocarbon molecules were given special attention because they could in principle come from the pump oil. Because we used pure Th solutions the chance of having other organic compounds or multi-Li, -Be, or -B based molecules is extremely small, especially in an ICP source with a plasma temperature of 6000–8000 K. In addition, such peaks were not seen in the background measurements and it is difficult to see how such molecules would form peaks just at the correct masses of $^{211,213,217,218}\text{Th}$ and how this would repeat itself 19 times for four different isotopes.

On the basis of known results about ^{14}C it is claimed in the Comment that “Accelerator mass spectrometry is the only mass spectrometric methodology capable of measuring relative abundances of the magnitude claimed by Marinov *et al.*”

The system used by us is not suitable for measuring ^{14}C because of the existence of the isobar ^{14}N . However, the fact that it is impossible to measure ^{14}C with the ICP-SFMS does not mean that the system is unable to measure masses with low abundances under entirely different and specific conditions. In our experiment these special conditions were the following: pure solutions were used, the mass region studied was far

away from the major mass in the solution, and no isobars were present.

The Comment specifies four factors that limit the abundance sensitivity: (1) the dark current of the detector, (2) ions from the (nearby) peak that have collided with the residual gas in the instrument and have undergone small angle scattering, (3) ions that have scattered off the walls or slits of the analyzer, and (4) unidentified trace peaks, e.g., singly or multiply charged molecular ions.

- (i) It is difficult to see how the dark current would form peaks at just the correct masses of $^{211,213,217,218}\text{Th}$ and how this would repeat itself 19 times for four different isotopes.
- (ii) In our cases the nearest large peak is 14 to 21 mass units away from the measured masses and no tails are seen from this peak in the measured spectra.
- (iii) Argument (i) above applies also here.
- (iv) The question of molecular ions was considered in the article and mentioned above. As concerns multiply charged molecular ions, let us mention that if, for instance, $m/z = 218$, then for $z = 1$, $m = 218$, and for $z = 2$, $m = 436$, which is unreasonable.

In summary we have refuted all the arguments raised in the Comment against our paper.

[1] J. S. Becker and H.-J. Dietze, *J. Anal. At. Spectrom.* (JAAS) **14**, 1493 (1999).