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# Comment on “Existence of long-lived isomeric states in naturally-occurring neutron-deficient Th isotopes”

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In their article “Existence of Long-Lived Isomeric States in Naturally-Occuring Neutron-Deficient Th Isotopes” [Phys. Rev. C **76**, 021303 (2007)], Marinov *et al.* fail to demonstrate that basic mass spectrometric protocols, such as abundance sensitivity, linearity, and freedom from possible interferences, have been met. In particular, 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) × $10^{-11}$ relative to $^{232}$Th, cannot be accepted, given the known abundance sensitivities of other sector field mass spectrometers. Accelerator mass spectrometry is the only mass spectrometric methodology capable of measuring relative abundances of the magnitude claimed by Marinov *et al.*

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In a recent article [1], Marinov *et al.* claim to have found evidence for four long-lived, neutron-deficient Th isotopes with atomic mass numbers 211, 213, 217, and 218. The abundances of these four isomeric states are given as (1–10) × $10^{-11}$ relative to $^{232}$Th. A mass spectrometric methodology was used, in which samples of Th were introduced into the ion source of an Element 2 inductively coupled plasma-sector field mass spectrometer (ICP-SFMS). The resolving power of an instrument, $M/\Delta M_0$, is a characteristic of the instrument (given a standard setup of slits, etc.). For standard deflection instruments this does not depend on mass. It gives the width of a peak, $\Delta M_0$, normally at the level of ∼10% of the peak height. The resolution of the ICP-SFMS was approximately 4000, which was considered sufficient to separate atomic ions from interfering molecular ions with the same mass number. The Th source material was evaluated for impurity concentration levels [1].

The mass spectrometric technique described in this article would be a novel procedure for investigating such isomeric states. As such, the validity of the methodology must be considered in the light of well-established mass spectrometric properties and protocols. A properly calibrated isotope ratio measurement must include a check of the abundance sensitivity and the linearity of the entire ion conversion/measurement system. The linearity depends on the type of detector in use, and the accuracy of the measurement system is closely associated with baseline effects. This implies the necessity of checking the baseline on a routine basis. The reliable measurement of isotope ratios must include a consideration of potential interferences, particularly isobaric interferences as well as instrumental fractionation effects.

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 ($m \pm 1$)” [2]. In practice, the abundance sensitivity is often described in terms of its reciprocal. The abundance sensitivity gives information about the extreme tails of the peak, inasmuch as it gives the intensity of the peak at the next mass number higher or lower. Although the definition given above is the commonly accepted definition, it would probably be better to state it for a standard change in mass, say, for $\Delta M/M$ of 1%.

*Factors that limit abundance sensitivity.* Away from a peak of interest, the count rate is made up of (1) the dark current in 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.

The contribution to the count rate from (1) gives a constant contribution to the spectrum and is independent of the mass.

The contribution from (2) decreases as one moves away from a given peak. It depends on the pressure in the instrument and the length of the ion path. In mass spectrometers the ion energy is typically in the 8 to 10 keV range. It should be noted that for Accelerator Mass Spectrometry (AMS) in which a tandem van de Graaff accelerator is used, the ion energy is in the tens of MeV, a range in which the small angle scattering cross section drops by many orders of magnitude. It is this property that makes AMS the appropriate technique for studies of extremely low abundance, such as $^{14}$C dating [3]. In present day C, the abundance of $^{14}$C is at the level of ∼$10^{-10}$ of $^{13}$C from which it must be reliably distinguished. In ancient samples, the $^{14}$C abundance is correspondingly lower. The abundance sensitivity of conventional deflection mass spectrometers is insufficient to meet this requirement.

The contribution from (3) is difficult to predict. For example, it may arise from a very intense beam that is striking, say, the wall of the analyzer and being deflected through the collector slit. Such scattering may be localized in one region, but may also form a broad band. In many instruments the beam may spread axially and be scattered from the surfaces of the tube in the magnetic analyzer.

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All of this does not raise the further issue of unknown ion species (4), including those from trace elements, being formed in a plasma discharge. The Element 2 manufacturer's brochure specifically warns that "Even in a sample matrix as simple as ultra pure water (UPW), interferences do exist, especially at low analyte concentration levels." Marinov *et al.* [1] have, in fact, listed the trace elements in their Th samples. They have identified some unusual ion species, viz., PbHe, AuO, and DyArO, although the basis of this identification is not stated, nor is it confirmed by the necessary related peaks in the same spectrum. They appear to have underestimated the possibilities for molecular ions that can be formed in (not after) a plasma source, including those from organic impurities that do not originate in the sample, particularly when they occur in the spectrum at the level of a few counts.

*Performance of actual instruments.* A standard mass spectrometer that has only one magnetic analyzer, with a radius of curvature of 20–30 cm, typically has an abundance sensitivity in the $10^4$ to $10^5$ range [4]. Two such magnetic analyzers operated in tandem have an abundance sensitivity typically in the $10^8$ range. Instruments that use three analyzers (one or more of which may be an electrostatic analyzer) have been used to reach a somewhat higher level, approaching $10^9$ [4,5]. Additional sectors have not produced significant further improvements. An alternate approach has been to introduce a retarding grid [6] in front of the final detector that is used to discriminate against ions that have suffered inelastic scattering. In tandem mass spectrometers, which also incorporate retarding grid collectors, abundance sensitivities approaching $10^9$ have been achieved [7].

In using the Thermo Electron Finnigan Neptune multicollector ICP-SFMS, Wieser [8] has observed an abundance sensitivity of $\sim 2 \times 10^5$ (or expressed as <5 ppm), measured at $m/z = 237$ in the presence of a large $^{238}$U beam. This instrument is similar in scale, geometry (reverse Nier-Johnson), and performance characteristics to the Element 2 instrument. With a retarding lens in front of the axial secondary electron multiplier, the abundance sensitivity improved to better than $2 \times 10^6$ (or expressed as $\sim$0.5 ppm). Under the same instrumental arrangement, for the two mass unit separation comparing $^{232}$Th with $m/z = 230$, an abundance sensitivity of $4 \times 10^7$ (24 ppb) has been demonstrated.

It is difficult to accept the validity of the evidence for the four Th isomers reported in Ref. [1], because essential mass spectrometric protocols [9] appear not to have been met. Of obvious concern is the claim that the abundances of the isomeric states are $(1\text{–}10) \times 10^{-11}$ relative to $^{232}$Th, a claim not supported by the evidence presented. The use of ICP-MS carries with it the probability that characteristic unknown interferences are present. This casts doubt on the reality of the existence of the reported Th isomers.

In summary, the abundance sensitivity claimed here [1] exceeds that of any known deflection mass spectrometer by at least two orders of magnitude and is not believable. In this work the ions are sought where the mass separation, $\Delta M/M$, is in the range of 0.06 to 0.09. For comparison, $\Delta M/M$ for the separation of $^{13}$C from $^{14}$C in AMS is 0.077. The claimed performance would then be competitive with AMS systems—a proposition that has not been demonstrated. Further, the statistical analysis would not be applicable to counts arising at least from factors (3) and (4), outlined above, which produce ions concentrated at certain (unpredictable) locations in the mass spectrum. The analysis is based on the assumption that a peak exists at a calculated location and it does not take into account the probability distribution defined by the peak shape. It does not first distinguish a peak from the background and subsequently derive its location.

This paper does not demonstrate the existence of rare Th isomers.

*Note added in proof.* Since the original submission of this Comment, two recent AMS searches [10,11] for these alleged Th isotopes have been reported. Lachner *et al.* [10] have set upper limits for these isotopes at least one order of magnitude lower than the Marinov values. Dellinger *et al.* [11] have reported upper limits for the abundances of these isotopes of below $10^{-14}$.

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