How accurate are precise data?

A) Observations

I have analyzed the raw data of three TRITON generated data files of approx. the same lenght (~ 11.5 h) of an Ames Nd standard sample. Data acquisition parameters are said to be identical.
Files : F4 and F12 obtained from J. Schwieters,
        P12 obtained from G. Caro.

Using the La Jolla standard value ($R_N = R^{144/146}$ = 1.3852), one observes a remarkable static offset of the observed raw ratio $r^{144/146}$:

        F4:   3.917 ‰   }
        F12: 3.852 ‰   }   per mass unit
        P12: 2.477 ‰   }

This static offset ε is defined as

$$\varepsilon = \frac{\beta_N \cdot \frac{R_N}{r_{N(0)}} - 1}{\Delta m} \qquad (\beta_N = \sqrt{\frac{146}{144}} = 1.00692)$$

$r_N(0)$ is the raw ratio of the i_{144} and i_{146} ion currents at the very beginning of the data acquisition. The question is:
Has this offset any influence on the fractionation corrected 'true' ratio ?

B) Theory

The computation of this 'offset' is based on the assumption that (according to the Langmuir evaporation law) the observed ratio r_{obs} of an evaporated sample should always be larger (by the factor of 'β') as the ratio R_S in the bulk of the sample at a given time.

$$r_{obs} = \beta \cdot R_S \qquad\qquad (1)$$

In particular :The ratio in the bulk *at the beginning of the evaporation* is the 'true' ratio $R_T = R_{S(t=0)}$.
If this is not the case, one may explain this discrepancy by the existance of cut-off effects for the ion beam in its way through the ion optical system.
In fact, the data of files F4 and F12 were (probably) taken with a small magnet in the ion source (to deflect electrons which may destroy the entrance slit in negative ion operation), but which is not needed for positive ions. Data of file P12 are definitely taken after the removal of such a deflection magnet. In fact,the observed 'offset' of P12 data is significantly smaller.
One may try to correct the observed ratios for such an offset by a recalculation of these ratios, using the offset as measured at the beginning of the data acquisition. Such a re-calculation would lead to ratios (r_{corr}) as they would be observed in the vapor phase just on top of the evaporation filament :

$$r_{corr} = (1 + \varepsilon \cdot \Delta m) \cdot r_{obs} \qquad\qquad (2)$$

These 'corrected' ,static offset free ratios may then be used to be further corrected for evaporation induced fractionation , using, for instance, the common 'Exponential Law' ('Expo law') .

The *Exponential Law* makes a simple basic assumption: The differences between the true (R_T) and the observed (r_{obs}) isotope ratios depend
- on the ratio of the masses (m_1, m_2) of the two isotopic species of the ion current ratio, and
- on a time dependent parameter P, which describes the time dependence of the fractionation, and which is identical for all ratios of the given isotopic system at a given time . It must **not depend on mass**.

$$\frac{r_{obs}}{R_T} = \left(\frac{m_1}{m_2}\right)^P \qquad (3)$$

No further assumptions are made, especially nothing on the numeric value of parameter P. The simple physical message of the Expo law is, thus, the assuption of the ruling role of the **mass ratio**.

For fractionation processes which are only determined by a thermal evaporation process, one may assume P = ½ for the beginning of the evaporation. E.g.:

$$P(t) = \tfrac{1}{2}(1 - q(t)) \qquad (4)$$

$q(t)$ describes the (oftenly complicated) time dependence of the raw fractionation profile. One would, e.g., expect: $q(t{=}0) = 0$ and $q(t{=}tend) \to \infty$).

Other, not time dependent (i.e. 'static') mass discriminations may be described by an additional parameter s. If one may assume, that also such discriminations are physically determined by the mass ratio only (e.g., magnetic deflections), one would, e.g., write :

$$P(t) = \tfrac{1}{2}(s - q(t)) \qquad (5)$$

Parameter s must, as well, *not be time dependent*, to reflect the intentions of the Expo Law. Please note: Cup offsets are not covered with this equation.

If we have an isotopic system with at least 3 isotopic species, we can calculate two non trivial isotope ratios (r_{obs1} and r_{obs2}), and, for both ratios the above equ. (5) is valid.

If, additionally, the 'true' ratio (R_{T2}) of one of these ratios is known, we can compute the 'true' ratio (R_{T1}) of the other ratio just by eliminating parameter $P(t)$, which is identical for all simultaniously evaporating isotopic species of the same isotopic system. The normalizing formula would thus be as follows:

$$\frac{r_{obs1}}{R_{T1}} = \left(\frac{r_{obs2}}{R_{T2}}\right)^{\frac{\ln(\beta 1)}{\ln(\beta 2)}} \qquad (6)$$
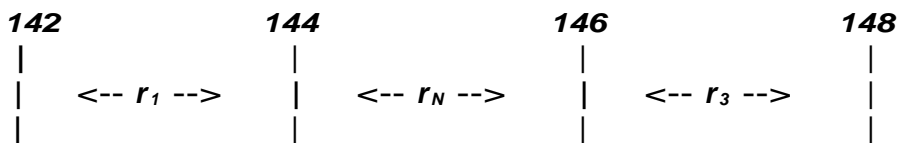
In summary: As long as static and dynamic mass discriminations only depend on the mass ratio of the isotopic species, then the Expo law makes no difference,

i.e., *static and dynamic discriminations are both eliminated in the same way by the normalization formula.*
Especially, we may thus expect that uncorrected raw ratios on the one side, and corrected ratios (equ. 2) on the other side, *may lead to the very same result.*

C) Evaluation

Three raw data files (F4, F12, P12) have been used to test the above statements. A special, symetric evaluation scheme is choosen, in order to exclude other possibly mass-dependent effects, for instance, to exclude influences from a mass dependent parameter *s* :

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    142              144              146              148
     |                |                |                |
     |   <-- r₁ -->    |   <-- rₙ -->    |   <-- r₃ -->    |
     |                |                |                |
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r_1(142/144) and r_3(146/148) are calculated, using r_N(144/146) as the 'normalizing' ratio.
All ratios are defined (unidirectionally) as 'light over heavy'. This kind of definition is arbitrary, but it enables us to also evaluate the data using the so called 'explicite' Rayleigh law, if needed.

The 'true' value for $^{144/146}$Nd was assumed to be R_N = 1.38523 ("La Jolla").

The evaluation of all 3 files show excellent internal precision (σ_{n-1} < 40 ppm for F4 resp. F12, and <15 ppm for P12). The calculated residual fractionation after the correction (Expo law) is practically negligible. It is in the order of 2 ppm/h, i.e., it is far within measuring precision.

However : *The fractionation corrected run means (R_1 resp. R_3) are by no means identical for static discrimination corrected or straight raw data, respectively.*

We obtain, using the *LaJolla standard value*:

		R_1	R_3
Not corrected data:	F4	1.1418 44	2.9882 57
	F12	1.1418 40	2.9882 21
	P12	1.1418 44	2.9882 57
	Average:	1.1418 43	2.9882 45
Corrected data:	F4	1.1417 20	2.988 539
	F12	1.1417 28	2.988 506
	P12	1.1417 65	2.988 458
	Average:	1.1417 37	2.988 501

The normalized, i.e. the so called 'true' values are significantly different (~ 100 ppm) for corrected (R_{corr}) and not corrected (R_o) raw data.
Moreover, we find : $R_{o1} > R_{corr1}$ whereas $R_{o3} < R_{corr3}$,
i.e.: The values are, so to speak, "mirrored" at the normalizing ratio.

If the also supposedly 'known' CalTech standard ratio (R_N = 1.38103) is used instead, then the observed static discriminations, consequently, are smaller:

F4:   2.386 ‰   }
F12: 1.985 ‰   }   per mass unit
P12: 0.951 ‰   }

And, correspondingly, we obtain, using the *CalTech standard value*:

		R_1	R_3
Not corrected data:	F4	1.138 327	2.979 266
	F12	1.138 322	2.979 266
	P12	1.138 226	2.979 301
	Average:	1.138 292	2.979 278
Corrected data:	F4	1.138 251	2.979 459
	F12	1.138 259	2.979 426
	P12	1.138 296	2.979 378
	Average:	1.138 269	2.979 421

The normalized, i.e. the 'true' values are still different for corrected and not corrected raw data, but much less (~ 20 ppm resp. ~50 ppm).
And still, we find : $R_{o1} > R_{corr1}$ whereas $R_{o3} < R_{corr3}$,
This finding suggests to search for an R_N value, for which the corrected and not corrected normalized R_1- or R_3-ratios possibly become equal, respectively.
Hence, R_N has been systematically varried in the range [1.366< R_N <1.382], and plotted against the differences of the means of the corrected and not corrected normalized data.
In fact, R_1 gets continuously smaller with growing R_N , whereas R_3 continuously grows, and the differences get *zero* at values R_N - values, which are very near to each other, but they slightly depend on the raw data itself. One gets:

From F4: R_N = 1.3745
From F12: R_N = 1.3755
From P12: R_N = 1.3785
Average: R_N = 1.3762

$R_N(F4)$ and $R_N(F12)$, which originate from runs, taken with similar instrumental conditions (additional magnet), are equal within measuring precision. These values are relatively near to the *"CalTech"* value, but significantly away from *"La Jolla"*.
The normalized, i.e. the 'true' ratios using the 'New Standard' (the average of all three files) are, thus,

		R_1	R_3
Not corrected data:	F4	1.134 294	2.969 000
	F12	1.134 290	2.968 899
	P12	1.134 294	2.969 034
	Average:	1.134 293	2.969 011
Corrected data:	F4	1.134 274	2.969 050
	F12	1.134 282	2.969 018
	P12	1.134 319	2.968 897
	Average:	1.134 292	2.969 013

And the (much smaller) static offsets, assuming this 'New Standard' would be :

> F4: 0.012 ‰   }
> F12: -0.023 ‰   }   per mass unit
> P12: 0.035 ‰   }

D) Discussion

If fractionation biases are produced by prefered evaporation of the lighter species of an isotope ratio, then the observed isotope ratio (light/heavy) is at any time larger than the isotope ratio in the bulk of the sample by a factor of $\sqrt{m_1/m_2}$ ($m_1 > m_2$). If this is not the case, static offsets, caused, e.g., by cutoff effects, may be the explanation.
If the size of such static offsets can be measured, one is able to 'reconstruct' the non biased, plain evaporation induced ratio, which may then be used for calculating the fractionation corrected, i.e., the 'true' isotope ratio by applying, for instance, the *'Exponential Law'* (Internal normalization).

In normal practice, static offsets are not seperately handled, before internal normalization is performed. In other words, one silently assumes that there are no static offsets or one hopes, that any possibly existing static offsets are 'automatically' handled by the Expo Law, as if they were a kind of evaporation induced fractionation offsets.
If such an assumption would be correct, one would,thus, expect that reconstructed data (freed from static offsets) or plain raw data, respectively, would result in the same normalized, 'true' isotope ratio.
Or, still another approach: One would apply 'second order corrections'.

Using data which are known to be statically biased one can show that the above assumption is wrong. In other words:
There are founded reasons that the result of an internal normalization not only depends on the knowledge of the 'true' (or agreed upon) value of the normalizing ratio, but also on certain instrumental conditions like static biases. Hence, such normalized results are not comparable from instrument to instrument (laboratory to laboratory), as long as there is any uncertainty on the existance of static biases.

The weak point of this argumentation is the difficulty to measure the static offset with sufficient accuracy. This has several reasons, for instance:
(a) All available raw data are already fractionated by evaporation (because data are not acquired from the very beginning of the heating of the sample), or data may be 'falsified' by other effects, like the evaporation of molecular species with higher masses and, consequently, less fractionation bias.
(b) The assumed standard ratio does not reflect the true ratio of the normalizing ratio of the sample.

In any case, we have learnt: Internal normalization of high precision data does not automatically mean accurate results. They, possibly, cannot be reproduced by another laboratory with a differently configured mass spectrometer.

<div align="right">(Karleugen Habfast)</div>