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ANALYTICAL CHALLENGE

Solution to best measurement challenge

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The winner of the best measurement challenge (published in volume 415 issue 16) is:

Cristhian Paredes, Instituto Nacional de Metrología de Colombia, Bogotá, D.C., Colombia.

The award entitles the winner to select a Springer book of their choice up to a value of €100.

Our Congratulations!

The best measurement challenge [1] is about the isotope pattern of bromine-containing molecules, which has been the topic of a previous Analytical Challenge [2, 3]. The mass spectrum of tribromobenzene features the familiar a:b:c:d = 1:3:3:1 pattern. Despite the fact that the two signal ratios b:a and c:a appear identical, turns out that they give different quality results for the isotopic abundance of bromine-81. To understand this observation, it is useful to establish data-generative measurement model.

The isotopic pattern of tribromobenzene can be modeled, as a first approximation, by taking into account only the bromine atoms. This can be accomplished using Pascal's triangle [4] and it involves a single variable—the isotopic abundance of bromine-81:

$$A_{312} : A_{314} : A_{316} : A_{318} \approx (1 - x_{81})^3 : 3x_{81}(1 - x_{81})^2 : 3{x_{81}}^2(1 - x_{81}) : {x_{81}}^3$$

From here, we can derive the model for the two isotope ratios, $R_{314/312}$ and $R_{316/312}$:

$$R_{314/312} = 3x_{81}/(1 - x_{81}) \quad (1)$$

$$R_{316/312} = 3x_{81}^2/(1 - x_{81})^2 \quad (2)$$

The inversion of these expressions provides us with the explicit measurement models for the quantity of interest, x_{81}:

$$x_{81} = \frac{R_{314/312}}{R_{314/312} + 3} \quad (3)$$

$$x_{81} = \frac{R_{316/312} - \sqrt{3R_{316/312}}}{R_{316/312} - 3} \quad (4)$$

Now, we can perform sensitivity analysis to determine how these two estimates of x_{81} are affected by measurement uncertainty associated with isotope ratios $R_{314/312}$ or $R_{316/312}$. This can be done by formal computation of the first-order derivatives, $\mathrm{d}x_{81}/\mathrm{d}R_{314/312}$ and $\mathrm{d}x_{81}/\mathrm{d}R_{316/312}$, or by simply calculating the values of x_{81} from several values of $R_{314/312}$ or $R_{316/312}$, as shown in Fig. 1.

Figure 1 shows that the estimates of bromine-81 abundance from the 316/312 ratio are twice less affected by the small variability (measurement uncertainty) of isotope ratios than those from the 314/312 ratio. This can be seen from the slopes of linear equations that approximate the relationships between x_{81} and $R_{316/213}$ or $R_{314/312}$ in the vicinity of $R = 2.90$. Put differently, ± 1% variations in $R_{314/312}$ will lead to ± 0.50% variations in x_{81} whereas ± 1% variations in $R_{316/312}$ will lead to twice smaller (± 0.25%) variations in x_{81}.

Thus, from statistical considerations, one should choose the 316/312 ratio. Of course, real-life measurements often involve more than just statistical considerations. For example, some ions may have spectral interferences. Nevertheless, this Analytical Challenge offers an example where statistical considerations can differentiate between two seemingly similar measurements.

This article is the solution to the Analytical Challenge to be found at http://dx.doi.org/10.1007/s00216-023-04732-5

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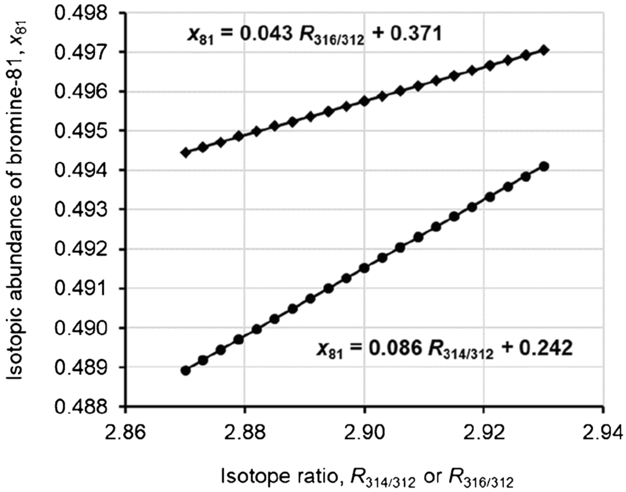

Fig. 1 Isotopic abundance estimates of bromine-81 (x_{81}) from isotope ratios $R_{314/312}$ and $R_{316/312}$ of tribromobenzene (ignoring the contributions of carbon and hydrogen isotopes)

Declarations

Conflict of interest The author declares no competing interests.

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