Solution to isotope amount ratio measurement challenge

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Solution

The isotope ratio in mixture AB is the key to the answer posed in this Challenge [1]. Therefore, let us start with its isotope amount ratio which can be expressed as the sum of the amounts of ⁶⁵Cu and ⁶³Cu originating from bottles A and B, respectively:

$$R_{AB} = \frac{n_{AB}({}^{65}\text{Cu})}{n_{AB}({}^{63}\text{Cu})} = \frac{n_A({}^{65}\text{Cu}) + n_B({}^{65}\text{Cu})}{n_A({}^{63}\text{Cu}) + n_B({}^{63}\text{Cu})} \quad (1)$$

For example, the amount of ⁶⁵Cu in mixture AB originating from bottle A ($n_A({}^{65}\text{Cu})$) can be expressed with the amount fraction of ⁶⁵Cu in bottle A ($x_A({}^{65}\text{Cu})$) and the total amount of substance in mixture AB from bottle A (n_A):

$$n_A({}^{65}\text{Cu}) = x_A({}^{65}\text{Cu}) \times n_A \quad (2)$$

The total amount of copper in mixture AB from bottle A (n_A) can be rewritten using the molar mass of copper in bottle A (M_A) and the total mass of copper in mixture AB from bottle A ($m_A(\text{Cu})$):

$$n_A = \frac{m_A(\text{Cu})}{M_A} \quad (3)$$

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Combining Eqs. (1)–(3) yields

$$\begin{aligned} R_{AB} &= \frac{x_A({}^{65}\text{Cu}) \times n_A + x_B({}^{65}\text{Cu}) \times n_B}{x_A({}^{63}\text{Cu}) \times n_A + x_B({}^{63}\text{Cu}) \times n_B} \\ &= \frac{x_A({}^{65}\text{Cu}) \times \frac{m_A(\text{Cu})}{M_A} + x_B({}^{65}\text{Cu}) \times \frac{m_B(\text{Cu})}{M_B}}{x_A({}^{63}\text{Cu}) \times \frac{m_A(\text{Cu})}{M_A} + x_B({}^{63}\text{Cu}) \times \frac{m_B(\text{Cu})}{M_B}} \quad (4) \end{aligned}$$

The relation between the isotope ratios and the amount fractions

$$x_i({}^{63}\text{Cu}) = \frac{1}{1 + R_i} \quad x_i({}^{65}\text{Cu}) = \frac{R_i}{1 + R_i} \quad (5)$$

helps to eliminate the amount fractions from Eq. (4):

$$R_{AB} = \frac{\frac{R_A}{1 + R_A} \times \frac{m_A(\text{Cu})}{M_A} + \frac{R_B}{1 + R_B} \times \frac{m_B(\text{Cu})}{M_B}}{\frac{1}{1 + R_A} \times \frac{m_A(\text{Cu})}{M_A} + \frac{1}{1 + R_B} \times \frac{m_B(\text{Cu})}{M_B}} \quad (6)$$

But the molar masses of the copper in bottles A and B are still unknown. They can be rewritten using the amount fractions and the corresponding molar masses of the isotopes (e.g., bottle A):

$$M_A = x_A({}^{63}\text{Cu}) \times M({}^{63}\text{Cu}) + x_A({}^{65}\text{Cu}) \times M({}^{65}\text{Cu}) \quad (7)$$

Like before, we can eliminate the amount fractions using Eq. (5):

$$\begin{aligned} M_A &= \frac{1}{1 + R_A} \times M({}^{63}\text{Cu}) + \frac{R_A}{1 + R_A} \times M({}^{65}\text{Cu}) \\ &= \frac{M({}^{63}\text{Cu}) + R_A \times M({}^{65}\text{Cu})}{1 + R_A} \quad (8) \end{aligned}$$

Thus, Eq. (6) becomes

$$R_{AB} = \frac{\frac{R_A}{1+R_A} \times \frac{m_A(\text{Cu})}{M(^{63}\text{Cu}) + R_A \times M(^{65}\text{Cu})} + \frac{R_B}{1+R_B} \times \frac{m_B(\text{Cu})}{M(^{63}\text{Cu}) + R_B \times M(^{65}\text{Cu})}}{\frac{1}{1+R_A} \times \frac{m_A(\text{Cu})}{M(^{63}\text{Cu}) + R_A \times M(^{65}\text{Cu})} + \frac{1}{1+R_B} \times \frac{m_B(\text{Cu})}{M(^{63}\text{Cu}) + R_B \times M(^{65}\text{Cu})}} \quad (9)$$

The terms $(1+R_A)$ and $(1+R_B)$ can be canceled and Eq. (9) yields

$$R_{AB} = \frac{\frac{R_A \times m_A(\text{Cu})}{M(^{63}\text{Cu}) + R_A \times M(^{65}\text{Cu})} + \frac{R_B \times m_B(\text{Cu})}{M(^{63}\text{Cu}) + R_B \times M(^{65}\text{Cu})}}{\frac{m_A(\text{Cu})}{M(^{63}\text{Cu}) + R_A \times M(^{65}\text{Cu})} + \frac{m_B(\text{Cu})}{M(^{63}\text{Cu}) + R_B \times M(^{65}\text{Cu})}} \quad (10)$$

An expression that merely contains known and measured quantities except for the desired calibration factor (K) is obtained after replacing the isotope amount ratios (R_i) with the signal intensity ratios (r_i) and the calibration factor (K):

$$K \times r_{AB} = \frac{\frac{K \times r_A \times m_A(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_A \times M(^{65}\text{Cu})} + \frac{K \times r_B \times m_B(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_B \times M(^{65}\text{Cu})}}{\frac{m_A(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_A \times M(^{65}\text{Cu})} + \frac{m_B(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_B \times M(^{65}\text{Cu})}} \quad (11)$$

Dividing Eq. (11) by K and multiplying with the denominator yields

$$\begin{aligned} & \frac{r_{AB} \times m_A(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_A \times M(^{65}\text{Cu})} + \frac{r_{AB} \times m_B(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_B \times M(^{65}\text{Cu})} \\ &= \frac{r_A \times m_A(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_A \times M(^{65}\text{Cu})} + \frac{r_B \times m_B(\text{Cu})}{M(^{63}\text{Cu}) + K \times r_B \times M(^{65}\text{Cu})} \end{aligned} \quad (12)$$

This equation can now be rearranged to solve for the calibration factor (K):

$$\begin{aligned} & \frac{[M(^{63}\text{Cu}) + Kr_B M(^{65}\text{Cu})] r_{AB} m_A(\text{Cu}) + [M(^{63}\text{Cu}) + Kr_A M(^{65}\text{Cu})] r_{AB} m_B(\text{Cu})}{[M(^{63}\text{Cu}) + Kr_A M(^{65}\text{Cu})] [M(^{63}\text{Cu}) + Kr_B M(^{65}\text{Cu})]} \\ &= \frac{[M(^{63}\text{Cu}) + Kr_B M(^{65}\text{Cu})] r_A m_A(\text{Cu}) + [M(^{63}\text{Cu}) + Kr_A M(^{65}\text{Cu})] r_B m_B(\text{Cu})}{[M(^{63}\text{Cu}) + Kr_A M(^{65}\text{Cu})] [M(^{63}\text{Cu}) + Kr_B M(^{65}\text{Cu})]} \end{aligned} \quad (13)$$

After eliminating the common denominator, we obtain

$$\begin{aligned} & r_{AB} m_A(\text{Cu}) M(^{63}\text{Cu}) + Kr_B r_{AB} m_A(\text{Cu}) M(^{65}\text{Cu}) + r_{AB} m_B(\text{Cu}) M(^{63}\text{Cu}) + Kr_A r_{AB} m_B(\text{Cu}) M(^{65}\text{Cu}) \\ &= r_A m_A(\text{Cu}) M(^{63}\text{Cu}) + Kr_A r_B m_A(\text{Cu}) M(^{65}\text{Cu}) + r_B m_B(\text{Cu}) M(^{63}\text{Cu}) + Kr_A r_B m_B(\text{Cu}) M(^{65}\text{Cu}) \end{aligned} \quad (14)$$

From here,

$$\begin{aligned} & K \times M(^{65}\text{Cu}) [r_A r_{AB} m_B(\text{Cu}) + r_B r_{AB} m_A(\text{Cu}) - r_A r_B m_A(\text{Cu}) - r_A r_B m_B(\text{Cu})] \\ &= M(^{63}\text{Cu}) [r_A m_A(\text{Cu}) + r_B m_B(\text{Cu}) - r_{AB} m_A(\text{Cu}) - r_{AB} m_B(\text{Cu})] \end{aligned} \quad (15)$$

and

$$\begin{aligned} K &= \frac{M(^{63}\text{Cu})}{M(^{65}\text{Cu})} \\ &\times \frac{m_A(\text{Cu}) \times (r_A - r_{AB}) + m_B(\text{Cu}) \times (r_B - r_{AB})}{r_B m_A(\text{Cu}) \times (r_{AB} - r_A) + r_A m_B(\text{Cu}) \times (r_{AB} - r_B)} \end{aligned} \quad (16)$$

Since you did not mix solid pieces of copper but rather aqueous solutions with copper mass fractions w_A and w_B , the masses of solid copper ($m_A(\text{Cu})$ and $m_B(\text{Cu})$) have to be replaced with masses of these solutions (m_A and m_B):

$$K = \frac{M(^{63}\text{Cu})}{M(^{65}\text{Cu})} \times \frac{m_A w_A \times (r_A - r_{AB}) + m_B w_B \times (r_B - r_{AB})}{m_A w_A r_B \times (r_{AB} - r_A) + m_B w_B r_A \times (r_{AB} - r_B)} \quad (17)$$

This is the required analytical solution for the calibration factor K . Now let us put the given numerical values into Eqs. (17):

$$K = \frac{62.929598}{64.927790} \times \frac{2.2561 \times 851.63 \times (0.00370125 - 0.985414) + 2.6432 \times 725.47 \times (48.6537 - 0.985414)}{2.2561 \times 851.63 \times 48.6537 \times (0.985414 - 0.00370125) + 2.6432 \times 725.47 \times 0.00370125 \times (0.985414 - 48.6537)}$$

$$K = 0.94895 \left(\text{mol/mol} \right) / \left(\text{V/V} \right) \quad (18)$$

With this calibration factor, the isotope ratios can be calculated from the signal intensity ratios

$$R_i = \frac{n_i(^{65}\text{Cu})}{n_i(^{63}\text{Cu})} = K \times r_i \quad (19)$$

$$R_A = K \times r_A = 0.94895 \times 0.00370125 \text{ mol/mol} = 0.0035123 \text{ mol/mol} \quad (20)$$

$$R_B = K \times r_B = 0.94895 \times 48.6537 \text{ mol/mol} = 46.170 \text{ mol/mol} \quad (21)$$

$$R_{AB} = K \times r_{AB} = 0.94895 \times 0.985414 \text{ mol/mol} = 0.93511 \text{ mol/mol} \quad (22)$$

The isotopic abundances are obtained from these isotope amount ratios using Eq. (5):

	Bottle A	Bottle B
$x(^{63}\text{Cu})$ in mol/mol	0.9965	0.0212
$x(^{65}\text{Cu})$ in mol/mol	0.0035	0.9788

Therefore, you were able to verify that the solutions in bottles A and B are spike solutions enriched in copper-63 and copper-65, respectively. The isotopic enrichment is even larger than what was written on the bottles. Your boss should be happy!

References

1. Rienitz O, Pramann A. Isotope amount ratio measurement challenge. *Anal Bioanal Chem*. 2016;408:5953–5.