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Publisher's version / Version de l'éditeur:
https://doi.org/10.1007/s00216-014-8279-5
Analytical and Bioanalytical Chemistry, 407, 1, pp. 1-3, 2015-01

Solution to isotope dilution challenge

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Over the years, isotope dilution mass spectrometry (IDMS) witnessed many reformulations. One of the earliest expressions for this quantitation model was given by the single isotope dilution (ID^{1}MS). In ID^{1}MS the mass fraction of an analyte A is calculated upon mass spectrometric analysis of a mixture (blend) of sample and an isotopically enriched form of the analyte (B) which acts as an ideal internal standard:

$$w_A = w_B \cdot \frac{m_{B(AB)}}{m_{A(AB)}} \cdot \frac{R_B - R_{AB}}{R_{AB} - R_A} \cdot \frac{\sum R_A}{\sum R_B} \cdot \frac{M_A}{M_B} \quad (1)$$

This model requires that the mass fraction of the isotopic standard (w_B), the isotopic composition of natural (R_A) and enriched (R_B) material, and their respective molar masses (M_A and M_B) are known beforehand. It is possible to design an experiment in order to bypass the prior knowledge of these quantities. For example, in addition to the blend of sample and isotopic standard (AB) one can prepare and measure additional three blends of a primary standard (with natural isotopic composition) and isotopic standard. These blends are denoted A*B-1, A*B-2, A*B-3, and the following system of four equations now describes the experiment:

$$\begin{cases} w_A = w_B \cdot \frac{m_{B(AB)}}{m_{A(AB)}} \cdot \frac{R_B - R_{AB}}{R_{AB} - R_A} \cdot \frac{\sum R_A}{\sum R_B} \cdot \frac{M_A}{M_B} \\ w_{A^*} = w_B \cdot \frac{m_{B(A^*B\text{-}1)}}{m_{A(A^*B\text{-}1)}} \cdot \frac{R_B - R_{A^*B\text{-}1}}{R_{A^*B\text{-}1} - R_A} \cdot \frac{\sum R_A}{\sum R_B} \cdot \frac{M_A}{M_B} \\ w_{A^*} = w_B \cdot \frac{m_{B(A^*B\text{-}2)}}{m_{A(A^*B\text{-}2)}} \cdot \frac{R_B - R_{A^*B\text{-}2}}{R_{A^*B\text{-}2} - R_A} \cdot \frac{\sum R_A}{\sum R_B} \cdot \frac{M_A}{M_B} \\ w_{A^*} = w_B \cdot \frac{m_{B(A^*B\text{-}3)}}{m_{A(A^*B\text{-}3)}} \cdot \frac{R_B - R_{A^*B\text{-}3}}{R_{A^*B\text{-}3} - R_A} \cdot \frac{\sum R_A}{\sum R_B} \cdot \frac{M_A}{M_B} \end{cases} \quad (2)$$

Eq. 2 can be solved for w_A to yield:

$$w_{\mathrm{A}} = -w_{\mathrm{A^*}} \cdot \frac{m_2 \cdot m_3 \cdot R_4 + m_1 \cdot m_3 \cdot R_5 + m_1 \cdot m_2 \cdot R_6}{m_1 \cdot R_4 + m_2 \cdot R_5 + m_3 \cdot R_6} \cdot \frac{m_{\mathrm{B}}}{m_{\mathrm{A}}}$$

$$\begin{cases} m_i = \dfrac{m_{\mathrm{A^*}\text{-}i}}{m_{\mathrm{B}\text{-}i}} \\ R_4 = (R_{\mathrm{AB}} - R_{\mathrm{A^*B\text{-}1}}) \cdot (R_{\mathrm{A^*B\text{-}2}} - R_{\mathrm{A^*B\text{-}3}}) \\ R_5 = (R_{\mathrm{AB}} - R_{\mathrm{A^*B\text{-}2}}) \cdot (R_{\mathrm{A^*B\text{-}3}} - R_{\mathrm{A^*B\text{-}1}}) \\ R_6 = (R_{\mathrm{AB}} - R_{\mathrm{A^*B\text{-}3}}) \cdot (R_{\mathrm{A^*B\text{-}1}} - R_{\mathrm{A^*B\text{-}2}}) \end{cases} \tag{3}$$

Eq. 3 is known as quadruple isotope dilution (ID^4MS) [1-3] and it involves only the gravimetric data regarding the four blends along with their isotopic composition. Note that the variables w_{B}, R_{B}, and R_{A} have been eliminated in Eq. 3.

The possibility of choosing the isotopic composition of the three calibration blends offers the options of more sophisticated experimental designs when high-precision is needed. In this vein, for best results the analyst might choose one of the A*B blends to match the isotopic composition the sample blend (AB) while the other two blends A*B bracketing the isotopic composition of AB (Fig. 1). The data reported in Table 2 reflect the experimental design of Fig. 1 and can be used to calculate the mass fraction of bromide in the sample of groundwater by using Eq. 3:

$$w_{\mathrm{A}} = -97.44 \cdot \frac{\left(\dfrac{2.00312}{0.06013} \cdot \dfrac{4.10538}{0.05989}\right) \cdot R_4 + \left(\dfrac{1.02652}{0.05992} \cdot \dfrac{4.10538}{0.05989}\right) \cdot R_5 + \left(\dfrac{1.02652}{0.05992} \cdot \dfrac{2.00312}{0.06013}\right) \cdot R_6}{\dfrac{1.02652}{0.05992} \cdot R_4 + \dfrac{2.00312}{0.06013} \cdot R_5 + \dfrac{4.10538}{0.05989} \cdot R_6} \cdot \frac{0.06002}{2.00811}$$

$$\begin{aligned} R_4 &= (4.226 - 6.143) \cdot (4.215 - 2.764) \\ R_5 &= (4.226 - 4.215) \cdot (2.764 - 6.143) \\ R_6 &= (4.226 - 2.764) \cdot (6.143 - 4.215) \end{aligned}$$

whose solution is w_{A} = 96.59 ng/g of bromide. Alternatively, one can construct a graph in order to derive the value of w_{A}. For this, one plots the ratios $w_{\mathrm{A^*}} m_{\mathrm{A^*}} / m_{\mathrm{B}}$ on the abscissa for the three blends A*B-1, A*B-2 and A*B-3, and the corresponding isotope ratios (r_{AB} or $1/r_{\mathrm{AB}}$) on the ordinate (Fig. 2). Then, the data points are fitted with a suitable function, and the value corresponding to the ratio r_{AB} is calculated. This corresponds to $w_{\mathrm{A}} m_{\mathrm{A}} / m_{\mathrm{B}}$ which then yields w_{A}.

Table 1. Symbols and quantities

Symbol	Description
A	Analyte in the sample (natural isotopic composition)
A*	Analyte in the primary standard (natural isotopic composition)
B	Analyte in the isotopic standard (isotopically enriched composition)
AB	Blend of sample (A) and isotopic standard (B)
A*B	Blend of primary standard (A*) and isotopic standard (B)
n_X	Amount of X (X = A, A*, or B)
M_X	Molar mass of X (X = A, A*, or B)
w_X	Mass fraction of X in the aqueous solution (X = A, A*, or B)
$m_{X(XY)}$	Mass of the aqueous solution of X used to prepare the blend of X and Y (X,Y = A, A*, or B)
R_X	Isotope amount ratio corresponding to material X
ΣR_X	Sum of all isotope amount ratios of the same denominator

Table 2. Experimental data

Sample, X	m_A/g	w_{A^*}/(ng/g)	m_{A^*}/g	m_B/g	R_X/(V/V)
A (and A*)	n/a	n/a	n/a	n/a	1.018
B	n/a	n/a	n/a	n/a	15.81
AB	2.00811	n/a	n/a	0.06002	4.226
A*B-1	n/a	97.44	1.02652	0.05992	6.143
A*B-2	n/a	97.44	2.00312	0.06013	4.215
A*B-3	n/a	97.44	4.10538	0.05989	2.764

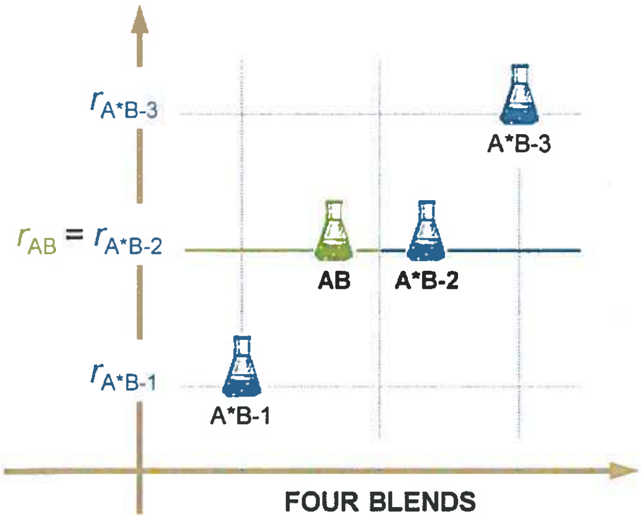

Fig. 1. Exact-matching quadruple isotope dilution. The isotopic ratio of the sample blend (AB) is matched to one of the standard blends (A*B-2), while the remaining two standard blends (A*B-1 and A*B-3) are chosen to bracket this isotope ratio.

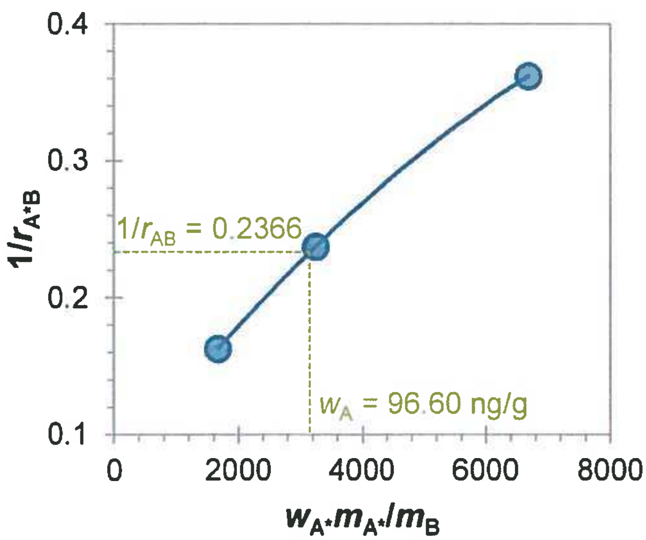

Fig. 2. Graphical solution of the isotope dilution challenge based on a nonlinear least square fit.

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