Review of "On the potential use of materials with heterogeneously distributed parent and daughter isotopes ..." by D.V. Popov

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I enjoyed reading this paper, which formalises a method to calibrate ICP-MS data using primary standards that contain a variable mixture of known radiogenic and inherited endmember compositions. The manuscript is well written and the logic is easy to follow. Nevertheless, I believe that the paper could be further improved by using a different statistical approach.

The method is most easily understood in conventional isochron space, which sets out two ratios P/d and D/d, where P and D are the parent and daughter nuclides, and d is a non-radiogenic isotope of the daughter element. Elemental fractionation only affects P/d and not D/d. The correction algorithm assumes that the elemental fractionation can be captured by a single parameter, k which, when multiplied with the measured P/d-ratios, brings them into alignment with an isochron of known intercept $(D/d)_0$ and slope $(e^{\lambda t} - 1)$.

In its present form, the algorithm estimates k for each aliquot separately, and then averages these estimates into a single consensus value. Error propagation is done by conventional first order Taylor approximation. On lines 109–111 of the manuscript, the author gets stuck when trying to keep track of the systematic uncertainties ("I could not find an exact equation to calculate a", "a could *probably* be estimated as a simple average").

I think that these issues can be solved with a different approach, using the method of Maximum Likelihood. The same method has been successfully applied in Ludwig (1998)'s seminal paper on U–Pb concordance, and I frequently use it in my own work (e.g. Vermeesch, 2020, for a recent example). In the next paragraphs, I will follow Ludwig (1998) and use uppercase symbols for measured quantities and lower case symbols for true (but unknown) values. Note that this is the opposite convention of Dr. Popov's manuscript. Let x_i and y_i be the true P/d- and D/d-ratios of the i^{th} aliquot. Then x_i and y_i form an isochron:

$$y_i = y_0 + \left(e^{\lambda t} - 1\right) x_i \tag{1}$$

where y_0 is the non-radiogenic endmember composition of the primary standard, t is its age and λ is the decay constant. x_i and y_i are unknown, whereas y_0, λ and t are known within some uncertainty. x_i and y_i are related to the measurements X_i and Y_i as follows:

$$\begin{cases} X_i = k x_i + \epsilon(X_i) \\ Y_i = y_i + \epsilon(Y_i) \end{cases} \tag{2}$$

where k is the elemental fractionation factor and $\epsilon(X_i)$ and $\epsilon(Y_i)$ are bivariate normal residuals. We will assume that these are adequately captured by the measurement uncertainties propagated from the mass spectrometer data. I will now outline two algorithms to estimate k, first without and then with the systematic uncertainties of y_0, λ and t.

1. Without systematic uncertainties:

   Define the log-likelihood $\mathcal{LL}$ of the data given k and $x = \{x_1, \ldots, x_i, \ldots, x_n\}$:

$$\mathcal{LL} = \sum_{i=1}^{n} \Delta_i^T \Omega_i \Delta_i \tag{3}$$

   where n is the number of aliquots for the primary standard,

$$\Delta_i = \left[\begin{array}{c} kx_i - X_i \\ y_0 + (e^{\lambda t} - 1)x_i - Y_i \end{array} \right], \tag{4}$$

$$\Omega_i = \left[\begin{array}{cc} \sigma[X_i]^2 & \sigma[X_i, Y_i] \\ \sigma[X_i, Y_i] & \sigma[Y_i]^2 \end{array} \right]^{-1} \tag{5}$$

   and Δ^T is the transpose of Δ_i.

   Then k can be estimated by maximising $\mathcal{LL}$ with respect to k and $x_1 \ldots x_n$. I lack the time to work out the details, but it should be possible to do this by taking the first derivative w.r.t. the x_is and setting it to zero, followed by numerical optimisation for k. See Ludwig (1998) for an example.

2. With systematic uncertainties:

   Instead of the sum of n terms shown in Equation 3, the maximum likelihood estimation can also be captured in a single matrix expression. This has the benefit that it allows the uncertainties of y_0, λ and t to be captured in the estimation of k:

$$\mathcal{LL}' = \Delta'^T \left(J \Sigma_i J^T \right)^{-1} \Delta' \tag{6}$$

   where

$$\Delta' = \left[\begin{array}{c} kx_1 - X_1 \\ \vdots \\ kx_n - X_n \\ y_0 + \left(e^{\lambda t} - 1\right) x_1 - Y_1 \\ \vdots \\ y_0 + \left(e^{\lambda t} - 1\right) x_n - Y_n \end{array} \right], \tag{7}$$

$$\Sigma = \left[\begin{array}{ccccccccc} \sigma[X_1]^2 & \ldots & 0 & \sigma[X_1, Y_1] & \ldots & 0 & 0 & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & \ldots & \sigma[X_n]^2 & 0 & \ldots & \sigma[X_n, Y_n] & 0 & 0 & 0 \\ \sigma[X_1, Y_1] & \ldots & 0 & \sigma[Y_1]^2 & \ldots & 0 & 0 & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & \ldots & \sigma[X_n, Y_n] & 0 & \ldots & \sigma[Y_n]^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma[y_0]^2 & \sigma[y_0, t] & \sigma[y_0, \lambda] \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma[y_0, t] & \sigma[t]^2 & \sigma[t, \lambda] \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma[y_0, \lambda] & \sigma[t, \lambda] & \sigma[\lambda]^2 \end{array} \right] \tag{8}$$

   and

$$J = \left[\begin{array}{ccccc} -I_{n,n} & 0_{n,n} & 0_{n,1} & 0_{n,1} & 0_{n,1} \\ 0_{n,n} & -I_{n,n} & 1_{n,1} & \lambda e^{\lambda t} x & t e^{\lambda t} x \end{array} \right] \tag{9}$$

where $I_{a,b}$ is the $a \times b$ identity matrix, $0_{a,b}$ is an $a \times b$ matrix of zeros, and x is the n-element column vector of x_i-values. As before, the k and x_i-values are estimated by maximising $\mathcal{LL}'$, which can be done using numerical methods.

According to maximum likelihood theory, the covariance matrix of the estimated parameters can be obtained by inverting the matrix of second derivatives of the log-likelihood in the vicinity of the maximum. This is the approach used by Ludwig (1998) and it can also be applied to the present problem. If the author is not familiar with this method, then a simple proof is provided in Section 8.4 of these lecture notes: `https://github.com/pvermees/geostats/blob/main/latex/geostats.pdf`

I am happy to answer any questions arising from my review via the email address provided above.

References

Ludwig, K. R. On the treatment of concordant uranium-lead ages. *Geochimica et Cosmochimica Acta*, 62: 665–676, 1998.

Vermeesch, P. Unifying the U–Pb and Th–Pb methods: joint isochron regression and common Pb correction. *Geochronology*, 2(1):119–131, 2020.