

Equations used by UranOS for calculation of the presented values

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1) Signal intensity (cps) and analyte ratios presented on the main window and exported into output files

Blank cps of an analyte

$$BL = \frac{\sum cps}{n_{BL}}$$

where

BL: average blank cps of an analyte

cps: cps of the the analyte in the time slices selected for blank

n_{BL}: number of time slices in the selected blank

Standard deviation of blank cps

$$sdBL = \frac{\sum (cps - BL)^2}{n_{BL} - 1}$$

where

sdBL: standard deviation of blank cps of an analyte

cps: cps of the analyte in the time slices selected for blank

BL: average blank cps of an analyte

n_{BL}: number of time slices in the selected blank

Standard error of blank cps

$$seBL = \frac{sdBL}{\sqrt{n_{BL} - 1}}$$

where

seBL: standard error of blank cps of an analyte

sdBL: standard deviation of blank cps of an analyte

n_{BL}: number of time slices in the selected blank

Blank corrected average cps of an analyte

$$CPS = \frac{\sum (cps - BL)}{n_T}$$

where

CPS: blank corrected average cps of an analyte

cps: cps of the the analyte in the selected time slices

BL: average blank cps of an analyte

n_T: number of time slices in the selected sample interval (minus the

number of rejected time slices)

Standard deviation of average cps and the Standard error of average cps are calculated like in case of blank, but the average blank is extracted from the individual cps values.

abbreviations: sdCPS and seCPS, respectively

LoD# Factor of limit of detection

Expresses that how many times higher the signal than the

- (i) 'classical' LoD (i) or
- (ii) the scatter of the blank.

$$LoD\# = \frac{CPS}{BL + (3 * sdBL)}$$

- (i) This is the standard way, after the definition of LoD.

$$LoD\# = \frac{CPS}{3 * sdBL}$$

- (ii) The modified LoD# does not consider the level of blank. In the output of some instruments the blank voltage is rather high, thus the ratio of the signal to the absolute height of blank would result in a misleading value. Thus the modified LoD# relates the blank corrected signal simply to the 3 times s.d. of the blank.

where

CPS: blank corrected average cps of an analyte

xLoD: indicates that the average cps of an analyte is how many times more than the level of detection

BL: average blank cps of an analyte

sdBL: standard deviation of the blank

Hg --> 204Pb correction

$${}^{HgC}CPS_{204Pb} = \frac{\sum ({}^B cps_{204} - ({}^{Baver} cps_{Hg} / I_{Hg}))}{n_T}$$

where

${}^{HgC}CPS_{204Pb}$: Hg corrected average 204Pb cps

${}^B cps_{204}$: blank corrected cps of mass 204 in the time slices

${}^{Baver} cps_{Hg}$: blank corrected average cps of the measured Hg isotope

I_{Hg} : isotope ratio (measured Hg isotope / 204Hg)

(it can be a ratio from the literature or the user can measure the actual, fractionated ratio in the blank)

n_T : number of time slices in the selected sample interval (minus the number of rejected time slices)

Remark: In case of overcorrection (would result in negative 204Pb cps) UranOS indicates it by a red warning message and the corrected 204Pb value is considered to be zero. The common lead correction function is disabled.

204-based common lead correction

$${}^{PbC}CPS_{206} = CPS_{206} - \left(CPS_{204} * I_{206/204} / R_{HgBL_Sig} \right)$$

[same procedure also for 207Pb and 208Pb]

where

${}^{PbC}CPS_{206}$: common lead corrected average 206Pb cps

CPS_{206} : uncorrected average 206Pb cps

CPS_{204} : Hg corrected average 204Pb cps

$I_{206/204}$: ratio of lead isotopes, can be:

- present ratio,
- at the time of 206/238 age,
- at a user defined time

R_{HgBL_Sig} : ratio of the Hg blank and Hg signal at ablation of Hg-free material

Measured isotope ratio 1 --- RoMa: Ratio of Mean cps (all data)

$${}^{RoMa}MR_{6/8} = \frac{{}^B cps_{206Pb}}{{}^B cps_{206Pb}}$$

[same procedure also for the other isotope ratios]

[corrected cps data are used in case of Hg or Common Pb correction]

where

${}^{RoMa}MR_{6/8}$: ratio of mean cps values of the selected time slices (all data)

${}^B cps_{206Pb}$: blank corrected average cps of 206Pb

${}^B cps_{238U}$: blank corrected average cps of 238U

The error of the mean isotope ratio calculated by RoMa:

$$erMR_{6/8} = \sqrt{\left(\frac{rse206Pb}{100}\right)^2 + \left(\frac{rse238U}{100}\right)^2 - 2 * r * \left(\frac{rse206Pb}{100}\right) * \left(\frac{rse238U}{100}\right)}$$

where

$erMR_{6/8}$: error of the measured isotope ratio (RoMa)

$rse206Pb$, $rse238U$: relative standard error of the average cps

r : correlation coefficient of the two analytes

Measured isotope ratio 2 --- AMoR: Arithmetic Mean of Ratios (with rejection)

$${}^{AMoR}MR_{6/8} = \frac{\sum ({}^B cps_{206Pb} / {}^B cps_{238U})}{n_T}$$

[same procedure also for the other isotope ratios]

[corrected cps data are used in case of Hg or Common Pb correction]

where

$^{AMoR}MR_{6/8}$: mean of the isotope ratios of the selected time slices

$^{B}cps_{206Pb}$: blank corrected cps of ^{206}Pb in the time slices

$^{B}cps_{238U}$: blank corrected cps of ^{238}U in the time slices

n_T : number of time slices in the selected sample interval (minus the number of rejected time slices)

The error of the mean isotope ratio calculated by AMoR:

Calculated as relative standard error.

$$rseMR = 100 * \left(\frac{sdMR}{\sqrt{n_{SIG} - 1}} \right) / ^{AMoR}MR$$

where

rseMR: error of the measured isotope ratio (AMoR)

sdMR: standard deviation of blank corrected isotope ratio

n_{SIG} : number of time slices in the selected signal interval

$^{AMoR}MR_{6/8}$: mean of the isotope ratios of the selected time slices

Measured isotope ratio 3 --- MEDoR: Median of Ratios (all data)

The median is calculated from the individual isotope ratios by the usual way.

The confidence interval of median is calculated according to Rink Hoekstra & Henk Kiers (University of Groningen) using the procedure of Bonett & Price (2002).

Measured isotope ratio 4 --- Tzero (intercept of linear regression)

$$^{Tz}IR_{6/8} = a * x + b$$

[same procedure also for the other isotope ratios]

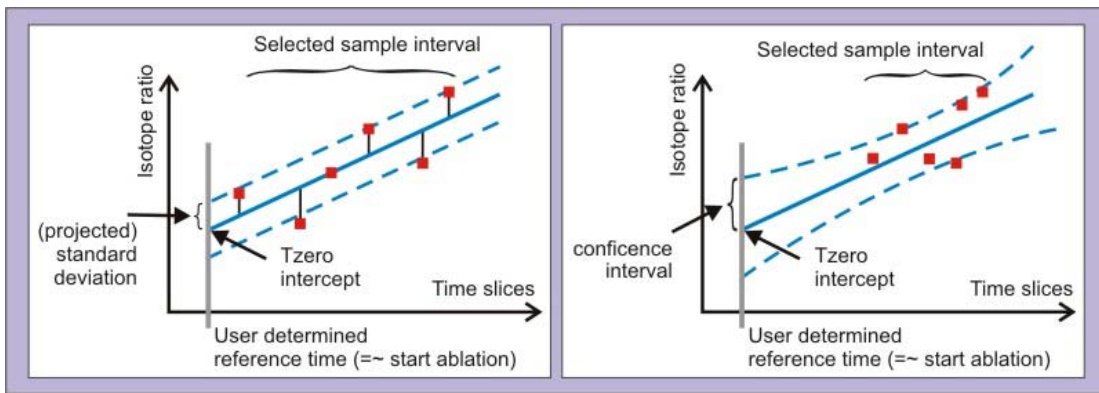
where

$^{Tz}IR_{6/8}$: Tzero intercept calculated from the isotope ratios

a and b: parameters of linear regression

x: position of Tzero at the beginning of ablation (user defined)

Error of Tzero isotope ratio (intercept of linear regression)



The s.e. of Tzero can be calculated by two ways (user's decision). One 'optimistic estimation' calculates from the residuals of the individual isotope ratios relative to the linear interpolation (see figure, left panel). A more realistic way is considering the confidence interval (right panel).

M/Tz - ratio of mean and Tzero intercept

It is the ratio of two isotope ratios calculated by different way. It aims to help at the judgement of the usage of mean or Tzero. If it is strongly differs from 1, then the usage of Tzero is recommended due to strong down-hole fractionation.

EPE - Extra-Poisson Error

Expresses the ratio of the empirical scatter of the individual isotope ratios of the selected interval relative to the Poisson distribution estimated from the counts.

$$EPE = \frac{\sqrt{\left(\frac{sdCPS_{206Pb}}{CPS_{206Pb}}\right)^2 + \left(\frac{sdCPS_{238U}}{CPS_{238U}}\right)^2}}{\sqrt{\left(\frac{1}{CPS_{206Pb} * DWE_{206Pb}}\right) + \left(\frac{1}{CPS_{238U} * DWE_{238U}}\right)}}$$

where

- EPE: extra-Poissonal error
- sdCPS: standard deviation of mean cps of the analyte
- CPS: average cps of the analyte
- DWE: dwell time of the analyte (in seconds)

Skewness

Indicates the shewness of the distribution of the individual isotope ratios relative to their mean.

$$skew = \frac{n_T * \sum (r_{6/8} - mMR_{6/8})^3}{(n_T - 1) * (n_T - 2) * (sdMR_{6/8})^3}$$

[same procedure also for other ratios]

where

skew: skewness of the distribution of individual isotope ratios

n_T : number of time slices in the selected sample interval (minus the number of rejected time slices)

$r_{6/8}$: isotope ratio in the time slices

${}^mMR_{6/8}$: mean of the isotope ratios of the selected time slices

$sdMR_{6/8}$: standard deviation of the individual isotope ratios

Discordance

Available only in sequential mode, at the processing of sample files. Indicates the ratio of corrected 206/238 and 207/235 ages (Disc. I) and 206/238 and 207/206 ages (Disc. II) in percent.

$$DiscI = \left(1 - \left({}^{206}Pb / {}^{238}U \right)_{age} / \left({}^{207}Pb / {}^{235}U \right)_{age} \right) * 100$$

$$DiscII = \left(1 - \left({}^{206}Pb / {}^{238}U \right)_{age} / \left({}^{207}Pb / {}^{206}Pb \right)_{age} \right) * 100$$

As a visual aid reverse discordance is marked by red color on the main screen and the intensity of the color indicates the degree.

Selection refinement

Modifies slightly the boundaries of the user selected interval and investigates the improvement of residual error.

Option 1: testing the improvement of the selection by using the skewness as a measure of normality. Skewness determined as described above.

Option 2: testing the improvement of the selection by the residuals to normal distribution calculated from the individual isotope ratios.

$$x1 = \frac{1}{1 + 0.33267 * \left| \left(r_{6/8} - {}^mIR_{6/8} \right) / sdIR_{6/8} \right|}$$

$$x2 = \frac{\exp\left(-\left(r_{6/8}\right)^2 / 2\right)}{\sqrt{2 * \pi}} * \left(0.4361836 * x1 - 0.1201676 * x1^2 + 0.937298 * x1^3\right)$$

$$rms_{6/8} = \sum_{i=1}^{n_T} \left(\left(i / n_T \right) - x_2 \right)^2$$

where

$rms_{6/8}$: residual of individual 206/238 ratios relative to the normal distribution having parameters calculated from the individual datapoints

$r_{6/8}$: isotope ratio in the time slices

${}^mMR_{6/8}$: mean of the measured isotope ratios of the selected time slices

sdIR_{6/8}: standard deviation of the individual isotope ratios
 n_T: number of time slices in the selected sample interval (minus the number of rejected time slices)

"...% reduction of residual error" indicates the difference between the residual error calculated by the variable boundaries of time slice selections (withing the user defined range) relative to the residual error calculated from the user selected time slices.

$$REDU \% = 100 * (((_U rms_{6/8} - _B rms_{6/8}) / _U rms_{6/8}) + ((_U rms_{7/5} - _B rms_{7/5}) / _U rms_{7/5})) / 2$$

[same procedure also for Tera-Wasserburg isotope ratios]

where

REDU%: reduction of residual error
_Urms: residual of user selected interval
_Brms: residual of the best selected interval

Outlier test and rejection

The tested isotope ratios can be determined by the user, but the usage of the 206/238 & 207/235 ratios or the 206/238 & 207/206 ratios is recommended. Spikes in other isotope ratios maybe not relevant for geochronological purpose. UranOS version 2.0 rejects the complete suspicious time slice and none of the isotope ratios will be considered at averaging.

Two versions of the outlier tests are available.

(a) The n x s.d. criterion can be used for the outlier test. The n can be determined by the user. This is a rather coarse procedure that can not be used in case of assymetric distributions (e.g. in case of spikes with extremely high values or in case of generally low counts).

(b) Searching and testing the possible outliers by the Grubbs tests. In this procedure UranOS is testing always the most extreme value and if it is an outlier at the given significance level of the test it is rejected and the average re-calculated. This method works in an iterative way until a user determined number of cycles.

2) Drift & fractionation correction

Fractionation factor

$$FF_{6/8} = MRstd_{6/8} / {}^{nom}Rstd_{6/8}$$

[same procedure also for other ratios]

where

FF_{6/8}: fractionation factor
^{nom}Rstd_{6/8}: nominal isotope ratio of the standard
 MRstd_{6/8}: measured isotope ratio in the standard (mean or Tzero according to the preference of the user)

Error of correction factor

As one of the most reliable approximation of the interpolation error we can use the prediction interval of the applied regression method:

$$erFF_{6/8} = t_{\alpha} * s * \sqrt{1 + \frac{1}{n} + \frac{(x - \bar{X})^2}{\sum (x - \bar{X})^2}}$$

[same procedure also for other ratios]

ERROR OF AGE STD ISOTOPE RATIO

where

erFF_{6/8}: error of correction factor for 206Pb/238U

t_α: t-statistics value for a 1-α confidence interval

n: number of total standard analyses in the measurement session

X: average of serial numbers of standard measurements

s: standard deviation from the expected value y at co-ordinate x

$$s = \sqrt{\frac{\sum (y_i - Y)^2}{n - 2}}$$

where

y_i: measured value at x

Y: calculated value by the regression

Fractionation corrected isotope ratio

$$FcR_{6/8} = MR_{6/8} / FF_{6/8}$$

[same procedure also for 207Pb/206Pb ratio]

where

FcR_{6/8}: fractionation corrected isotope ratio

MR_{6/8}: measured isotope ratio in the sample (mean or Tzero according to the preference of the user)

FF_{6/8}: fractionation factor

Fractionation corrected isotope 207Pb/235U ratio

It can be calculated as above or from the corrected 207/206 and 206/238 ratios:

$$FcR_{207/235} = FcR_{207/206} * FcR_{206/238} * I_{235/238}$$

where

FcR: fractionation corrected isotope ratios

I_{235/238}: ratio of uranium isotopes

Remark: in this case the MR_{7/5} presented on main window and exported into output files is *not* used to calculate the fractionation corrected ratio and age.

3) Error propagation

Error of fractionation corrected 206Pb/238U and 207Pb/206Pb isotope ratios

$$erFcR_{6/8} = FcR_{6/8} * \sqrt{\left(\frac{erFF_{6/8}}{FF_{6/8}}\right)^2 + \left(\frac{erMR_{6/8}}{MR_{6/8}}\right)^2 + \left(\frac{erStd}{Std}\right)^2}$$

[same procedure is used also for 207Pb/235U ratio if it is not calculated from the corrected isotope ratios, see below]

where

erFcR_{6/8}: error of the corrected isotope ratio of the sample

FcR_{6/8}: fractionation corrected isotope ratio

erFF_{6/8}: error of fractionation factor

FF_{6/8}: fractionation factor

erMR_{6/8}: error of measured isotope ratio

MR_{6/8}: measured isotope ratio

erStd: error of the nominal isotope ratio of the standard

Std: nominal isotope ratio of the standard

Error of corrected 207Pb/235U isotope ratio

If the corrected 207Pb/235U ratio is calculated by the two other corrected isotope ratios, then:

$$erFcR_{7/5} = FcR_{7/5} * \sqrt{\left(\frac{erFcR_{6/8}}{FcR_{6/8}}\right)^2 + \left(\frac{erFcR_{7/6}}{FcR_{7/6}}\right)^2}$$

where

erFcR_{7/5}: error of the corrected isotope ratio calculated from the two other isotope ratios

FcR_{7/5}: fractionation corrected isotope ratio

erFcR_{6/8}, erFcR_{7/6}: errors of corrected isotope ratios

FcR_{6/8}, FcR_{7/6}: corrected isotope ratios

Remark: probably here we can neglect the contribution to the error from the uncertainty of 235U/238U isotope ratio.

References

Bonett, D. G. & Price, R. M. (2002): Statistical inference for a linear function of medians: Confidence intervals, hypothesis testing and sample size requirements. Psychological methods, 7(3), 370-383.