**U-Pb-ESD-Calculator – User Manual (V1.0)**

**Quick guide for apatite U-Pb and trace elements with LA-ICP-MS:**   
  
1. Load folder with ICPMS data   
2. Remove outliers   
3. Correct for background

4. Define Laser Window

5. Select glass standards and estimate extra Poisson uncertainty (Uncertainty estimation)

6. Calculate average CPS

7. Select Cl-standards (e.g. Durango) and estimate Cl-concentrations

7. Select glass standard and calculate/plot element concentrations (spider diagram)  
8. Calculate uncorrected ages and ratios   
9. Use 'Hide Samples (no signal)' and select all standards (either Durango or McClure) and correct for common lead 'Common Pb corr - Based on 207Pb or 208Pb'   
10. Select all ratios   
11. Mass and down-hole fractionation correction: Select batches of same standards that follow on each other (usually 3-4) and fit spline function and save   
13. Repeat for all standard batches   
14. Unselect 'Hide Samples (no signal)' and afterwards select 'Correct Ratios - Complete graph'   
15. Now it’s time to look at samples in Terra-Wasserburg plots   
16. If you have exported TW plots for all samples do the common lead fractionation for all samples ('Hold On' and 'Hide Samples (no signal)' should be not selected)   
17. Correct for common lead 'Common Pb corr - Based on 207Pb or 208Pb'   
18. Now it’s time to plot samples and standards in concordia plots or calculate weighed mean ages

1. **Preface**

This program determines LA-ICP-MS U-Pb ages for apatite and zircon correcting for session drift and downhole fractionation of Pb/U ratios using matrix-matched age standards (e.g. 9150 or Plesovice zircon or McClure or Durango apatite). The program is written in Matlab and distributed as standalone application (U-Pb-ESD-Calculator).

1. **Load and Visualize Raw Data**

Go to *File/Load Raw Data File to l*oad the raw ICP-MS data (Agilent .b folder), which will load the BatchLog.csv file in the main folder and afterwards reads all subfolders and create a Matlab structure file (e.g. CPS of mass 238 of sample 012SMPL are saved under app.data.012SMPL.U238). You can choose between CPS and count data, in latter case the count data will be transferred to CPS data using the mass specific integration time (read from Method/AcqMethod.xml). It is assumed that measured counts are sampled from a Poisson and extra Poisson distribution, the latter is session dependent and mainly depending on the introduction system (e.g. Ulianov et al. 2015). The Poisson distribution and the standard deviation (***SD****Cm,t)* of measured counts can be approximated with:

Eq. 1

Where *m* and *t* are individual masses and measuring time, respectively. Note that when the ICP-MS data is imported as CPS, the original counts are used to calculate the standard deviation using the mass specific integration times. The standard deviation of the raw counts are stored in ‘app.data(iSample,iTime).Masssd’.

If loaded successfully, available samples are shown in the list box on the left. Clicking on the sample in the list box will show the time resolved analyses of selected mass/isotopes. By default all measured masses will be shown. Simple unselect masses you do not want to be plotted. By default the uncertainties are not displayed in figures. Check the *Plot Errorbar* below the CPS figure to show uncertainties of CPS and ratios.

1. **Remove Outliers**

There are two possible ways to remove outliers, semi-automatic or fully-automatic. By default all measured CPS (counts per second) that are more than three scaled median absolute deviations away from the median are marked as outliers (black filled circle in the CPS-figure). Note that this value can be changed in *ESD U-Pb/Constants*. Deleting outliers can be done (i) for each sample separately by clicking the button *Remove Outlier (this sample)* at the bottom of the sample list box, or (ii) for all samples at ones by clicking in the menu bar *Steps/Remove All Outliers*. Automatically detected outliers can be deselected by clicking on them (they change color from black to green). Clicking on yet not selected points will mark them as manually selected outliers (blue filled circle). Ones selected or deselected points can be deselected or selected again.

1. **Define Background CPS**

The background CPS need to be subtracted from the ablation CPS and therefore background is usually measured before ablation is starting (e.g. 30 sec). The time window of background CPS used for this purpose can be changed in the *Bkg* edit fields below the CPS figure. Changing these values for one sample will apply it to all other samples.

Clicking on *Steps/Bkg correction* will calculate the average background for each mass and sample and subtract this from the corresponding ablation signal. The average sample specific background (*bkgm*) and of mass *m* in cps (counts per second) is calculated with:

Eq. 2

Where *T1* and *T2* is the start and end of the used background measurements and *N* is the number of sweeps in this background time window.

The standard deviation of the background (*SDbkgm*)is calculated with:

Eq. 3

The resulting mean and standard deviation of the background is stored in ‘app.bkg\_mean(iSample,iMass)’ and ‘app.bkg\_std(iSample,iMass)’. The background corrected sample signal (*CPSt,m*) is simply:

Eq. 4

The uncertainty of each individual measurement (*CPSt,m*) is derived by error propagation:

Eq. 5

The resulting background corrected CPS and associated standard deviations are stored in ‘app.data(iSample,iTime).Mass’ and ‘app.data(iSample,iTime).Masssd’. Note that we do overwrite data from earlier steps (intermediate steps data could be exported by saving data to a mat-file using *File/Save Current State*.

1. **Determine the ablation time window**

We have to define the ablation time window used for further calculations (such as average CPS). Similar to the background, the ablation time window can be set using the *Laser* edit fields below the CPS figure. This is working in case the ablation signal didn’t dropped (e.g. caused by shooting through the grain) for some samples. Therefore the end of the ablation time window is set three seconds before the CPS is dropped to within three standard deviations of the blank level of a user-defined mass. The mass can be chosen from the *Mass* drop-down menu below the CPS figure. In addition a higher/lower CPS threshold can be defined in the *CPS* edit fieldinstead of the background level. Clicking on *Steps/Define End Laser Window* will apply the user-defined setting and will show the sample specific end of the ablation time window in the *CPS figure* and also in the *Laser* edit field. If results are not satisfying, this step can be repeated with other masses or CPS. Experimenting with some masses have shown that Th232 is working well for apatite (e.g. using 100000 CPS as threshold). The resulting ablation time windows need to controlled for each sample and adjusted. This can be done by clicking on the sample in the sample list box and change the time window with the *Laser* edit fields. Alternatively, move the mouse to a plane area and use the up- and down-arrow to scroll through samples and the right- and left-arrow to decrease or increase the laser end time. The start and end of the ablation time window is further on named *T3* and *T4* (*T1* and *T2* are the start and end of the background time window).

1. **Extra Poisson uncertainty**

The extra Poisson uncertainty in the count data is coming mainly from processes in the introduction system, the torch and cones (e.g. Ulianov et al. 2015). The glass standard is used to estimate the extra Poisson uncertainty. Simply select (‘Hold on’) all glass standards and select ‘Steps/Uncertainty estimation’. This will do the following steps:

First, any trend in the CPS data of individual masses is removed by fitting a smooth spline. Second, the CPS are transferred back to counts using the individual integration times. Third, the mean and standard deviations of count data is calculated. Fifth, the Poisson standard deviation of the mean count is calculated with Eq. 1 and subtracted from total standard deviation:

Eq. 6

Sixth, the remaining extra Poisson standard deviations of counts is fitted with linear least-square fitting forced through the origin. According to the data, a simple linear increase with counts does explain 99% of the variability in standard deviation. The mean slope of all fitted standard glasses is used to estimate the uncertainty of individual count data simply by adding the extra Poisson uncertainty to the Poisson uncertainty (cf. Eq. 6).

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1. **Calculation of average CPS**

Average sample derived CPS for each mass within the user-defined time window can be calculated by clicking on *Steps/Avg laser CPS*. The calculation is similar to those done to determine the average background CPS (Eq. 2). Note that this value is not yet corrected for mass fractionation and session drift and gives only a rough estimate of the sample specific composition. Mass specific CPS that are within the detection limit (three times blank level) are shown in red all other average CPS are shown in black. Mean and standard deviations of masses are stored in ‘app.laser\_mean(iSample,iMass)’ and ‘app.laser\_std(iSample,iMass)’.

1. **Calculate element concentrations**

Element concentrations of samples are calculated based on the comparison with Durango (chlorine) NIST612 glass standard (all other elements) and known concentrations based on independent determinations (Jochum et al. 2011). Unknown samples are bracket by element standards and to account for variations in-between brackets Calcium is used as internal standard. A CaO concentration of 11.9% and 56% is used for NIST612 and apatite, respectively. Correction factors (*cf*) are calculated with:

Eq. 7

Where *PPM* is the independently determined concentration of the measured mass and *Ca43* (0.00135\*Ca). The associated error can be derived by error propagation:

**SD**

Correction factors are averaged for batches of element standards and linearly interpolated in-between element standards (NIST612, Durango). First the chlorine concentration should be estimated by selecting Durango measurements and clicking *steps/CPS2PPM/Cl concentration*. An excel-sheet needs to be selected with Cl concentrations (Cl\_concent\_standards.xlsx). Afterwards all other element concentrations are estimated by selecting all NIST612 glass standards and clicking *steps/CPS2PPM/Element concentrations*.An excel-sheet needs to be selected with NIST612 concentrations (NIST612TraceElementConc.xlsx). Afterwards unknown concentrations are calculated with Eq. 7 (solving to *PPMmass*). Weighted mean concentrations are shown in the main figure, whereas values are either red (scatter is larger than predicted by the analytical uncertainty) or black (MSWD ~1).

Data of selected samples can be plotted with *steps/CPS2PPM/Spider Diagram*, whereas concentrations are normalized for CI chondrite concentrations (McDonough and Sun 1995). Results (mean, standard error and mswd) of all samples and elements can be exported with *steps/CPS2PPM/Export table*.

1. **Calculate raw Ratios and Ages**

Ratios and ages can be calculated as raw values (before corrections) or after corrections. We have used individual CPS measurements of masses the derive time-resolved ratios:

The ratios are stored in ‘app.data(iSample,iTime).Ratio’. The associated standard deviations of ratios are (example for Pb206/U238 ratio):

Eq. 6

The data is stored in ‘app.data(iSample,iTime).Ratiosd’. The weighted average and standard errors of ratios are calculated with:

Eq. 7

Eq. 8

Eq. 9

The average ratios and standard error are shown for each sample when selected in the list box and are used to calculate weighted average U-Pb ages with standard error (example for Pb206/U238 age):

Eq. 10

Eq. 11

1. **Common lead correction**

Common lead might be incorporated during mineral growth and together with potential U and Pb loss and gain will bias direct interpretation of U-Pb data/ages. If possible the U-Pb data should be corrected for common lead. Within the U-Pb-ESD-Calculator you can choose between (i) skipping the common lead correction, (ii) apply a common lead correction based on 202Hg, and (iii), apply an iterative correction based on 207Pb or 208Pb (e.g. Williams 1998).

**7.1 202Hg-based correction**

The most applied and powerful common lead correction is based on measuring 204Pb. Only choose this correction if you have a high ratio between mass 204/202, which is often true for zircons but not for apatite (due to lower overall U contents). Click on *Steps/Common Pb corr/Based on 202Hg* to do this correction.

The only stable Pb isotope is 204Pb which however suffers from interferences of Hg that comes from make-up gases (Ar, He and N) and all metallic materials (e.g. valves, regulators). Therefore 202Hg needs be measured to indirectly estimate 204Hg and this is subtracted from the *CPS204* to estimate the common lead content. The natural 202Hg and 204Hg content is 0.2986 and 0.0687 and therefore the correction is:

Eq. 12

The associated standard deviation is:

Eq. 13

The common lead correction is only done if *CPS204* is above the detection limit (*DL*), which is defined here as:

Eq. 14

Note that *CPS204* below DL are shown in red in the sample list box, and those are not corrected for common lead. In addition CALS (calibration standard) and CALB (calibration blank) sample types are also not corrected. Now that we know the 204Pb CPS of the sample, we do have to know the Pb isotopic composition to correct 206Pb, 207Pb and 208Pb. The Pb isotopic composition, however, was not constant throughout Earth’s history, but does follow a predictable trend estimated for instance by Stacey and Kramer (1975) using Pb minerals with known age. The Stacey and Kramer (1975) Pb evolution model is used here to derive the initial Pb isotopic ratios (*206Pb/204Pbi*, *207Pb/204Pbi*, *208Pb/204Pbi*). We used the background but not common Pb corrected *207Pb/206Pbage* (SEq. X) as initial guess for the age of initial Pb fixation. The Pb isotopic composition is derived for that initial age estimate from the Stacey and Kramer (1975) Pb model and used to correct masses 206, 207 and 208 (only shown for mass 206):

Eq. 15

The corrected masses 206 and 207 are used to recalculate the *207Pb/206Pbage* and initial Pb isotopic composition is recalculated and this process is iterated until the age is not changing anymore.

Following the approach of Chew et al. (2010) we assume that initial Pb isotopic ratios are associated with a 5% uncertainty (2σ) and the resulting absolute uncertainty on the corrected Pb isotopes are (only shown for mass 206):

Eq. 16

Note that the raw time resolved CPS and associated standard deviations will be overwritten ones the common lead correction has been done.

**7.2 208Pb/207Pb -based correction**

In case the 204Pb counts are low but common lead is significantly effecting Pb isotopes, such as in apatites a 207Pb or 208Pb correction can be applied (e.g. Williams 1998). The 208Pb correction works well for samples with 232Th/238U ratio below 0.5 which is rarely the case and therefore the 207Pb is applied more frequently. Both methods can be applied iteratively with the following steps:

1. The initial common lead composition is estimated based on the Stacey and Kramer (1975) Pb evolution model and the 207/235 age. The standard deviation of the latter was propagated in the estimation of the lead composition.
2. The theoretical common 207Pb/206Pb ratio is calculated with:

Eq. 17

The resulting standard deviation of the common lead ratio is:

Eq. 18

We assume an uncertainty of the initial common lead composition of 5% (2SD) or 2.55% (SD) (following the argumentation of Chew et al. 2011) and calculated the resulting uncertainty from the age uncertainty. The total uncertainty of the common lead ratio (e.g. 207/206) is:

Eq. 19

1. The radiogenic 207/206 ratio is calculated with

Eq. 20

The uncertainty of the radiogenic 207/206 ratio is simply derived by calculating the ratio with the mean age and associated standard deviation.

1. The fraction of common 206Pb (*f* 206 = 206PbC / 206Pbtotal) and 207Pb (*f* 207 = 207PbC / 207Pbtotal) can be derived from:

Eq. 21

Eq. 22

Where *C* is common*, M* is measured and *R* is radiogenic lead ratio. The resulting uncertainty of the fraction of common lead (e.g. *f206* from the total measured 206) is:

Eq. 23

The corresponding uncertainty for the 207 fraction is:

Eq. 24

1. The common 207 lead fraction (*f207*) is used to correct the lead concentration:

Eq. 25

The resulting 207/235 age is updated and steps 1…5 is repeated until age convergence (usually 5 steps are enough for convergence).

1. Afterwards the uncertainties of the common lead-corrected Pb206, Pb207, Pb208 counts are updated (example for Pb206):

Eq. 26

1. **Fractionation correction**

During ablation the LA-ICP-MS system produce some degree of elemental- and/or mass-related discrimination. There are typically two types of mass fractionations: (i) a slow drift in mass ratios and (ii) a shift in mass ratios during laser ablation also called ‘downhole fractionation’. Here we do follow the approach of Paton et al. (2010) and correct for the downhole fractionation by fitting a smoothed cubic spline to a well-characterized age standard (e.g. 91500, Plesovice). In practice we first merge a few ratios of repeated measurements of the standard and fit the mean of the ratios with the *scaps* Matlab-function and a user-configurable smoothing factor (can be adjusted in ‘ESD-U-Pb/Constants’). See Figure 1 and 2 for examples on a measured 206Pb/238U and 206Pb/207Pb data of five individual measurements of 91500 zircon fitted with a spline function and a smoothing factor of 0.5.

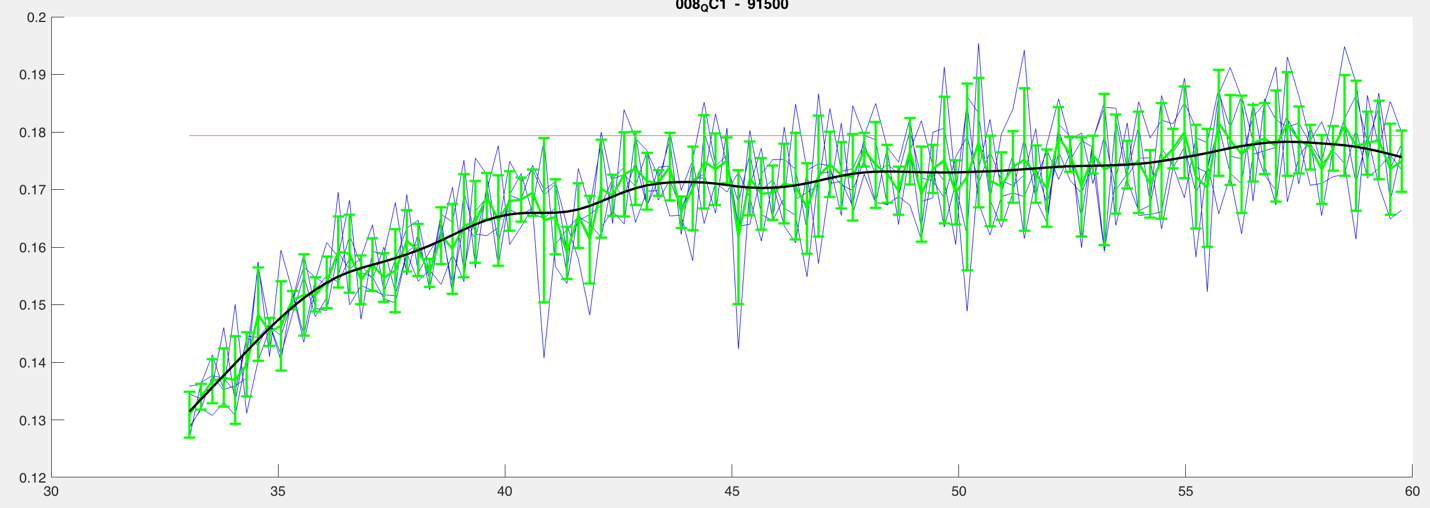


Fig. 1: Time resolved 206Pb/238U ratio of ablated 91500 zircon fitted with a smoothed cubic spline function. Blue lines are five individual measurements stacked on each other and the mean values (in green) are fitted with the spline function (black) with a smoothing factor of 0.5.



Fig. 2: Time resolved 207Pb/206Pb ratio of ablated 91500 zircon fitted with a smoothed cubic spline function. Red lines are five individual measurements stacked on each other and the mean values (in green) are fitted with the spline function (black) with a smoothing factor of 0.5.

Measurements and ratios that should be fitted are selected with ‘Hold on’, followed by pressing ‘Fit Ratio’. To save the spline fit press ‘Save Fit’. Ideally the saved spline fits to bracket all samples that should be corrected. Start fitting the first standard batch and continue sequentially with sample batches measured later. The correct standard ratios are saved in the *AgesRatiosStandards.*mat table and can be looked at and changed with ‘ESD-U-Pb/Constants’. Correction factors (*CF*) for each ratio are calculated with (example for 206/238 ratio):

Eq. 27

Where is the correct standard ratio and is the spline fitted ratio of an standard at time *t*. Correction factors are linearly interpolated between standards based on the absolute measurement time (*T*). Afterwards the measured ratio is multiplied with the correction factor to yield fractionation and drift corrected ratios:

Eq. 18

Where the standard deviation is:

Eq. 19

Where is the standard deviation of the ratio of the used standard. Note that we do neglect the uncertainty of the smoothed fitted ratio, since the uncertainty of the measured ratio which will be considered after the fractionation correction.

1. **Plotting**

**Concordia Diagram**

Selected measurements are plotted with their 2 sigma standard error on a Concordia diagram. Error ellipses of the 207Pb/235U and 206Pb/238U ratios are calculated following these steps:

1. Resampling 100 times from a normal distribution defined by the ratio and corresponding uncertainty
2. Calculate the 2 sigma standard error (2SE) from the random numbers, where *n* is the number of sweeps. The example for :
3. Calculate the correlation coefficient *r* between and
4. Calculate the covariance between and :
5. Construct the covariance matrix:
6. Calculate the eigenvalue and eigenvector for *covmat*
7. Create a vector *t* from 0 to 2pi
8. Construct the error ellipse (*xellipse*, *yellipse*):

For details on the calculation of the error ellipse look at the Matlab function ‘error\_ellipse\_flex.m’

**Intercept with Concordia**

Select samples (use ‘Hold On’) to be plotted and select ‘Plot/Concordia’ to plot the data in a Concordia diagram. Data selected and plotted in the Concordia can be fitted with the method described in York et al. (2012), the corresponding Matlab function is called ‘york\_fit’. The intercept with the Concordia is used the calculate corresponding ages and the standard deviation.

**Tera-Wasserburg Diagram**

Data can also be plotted with the Terra Wasserburg Diagram, which is useful in case samples have not yet been corrected for common lead (especially apatite). Samples can be selected with ‘Hold On’ and afterwards select ‘Plot/Tera-Wasserburg’ to plot the data. A table will open, which allows to select/deselect samples to be plotted. Click ‘Plot’ to plot the data. Least-squre linear fitting is used to find the intercept age with the Tera-Wasserburg line. The method is similar to that described for the Concordia diagram.

**References**

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