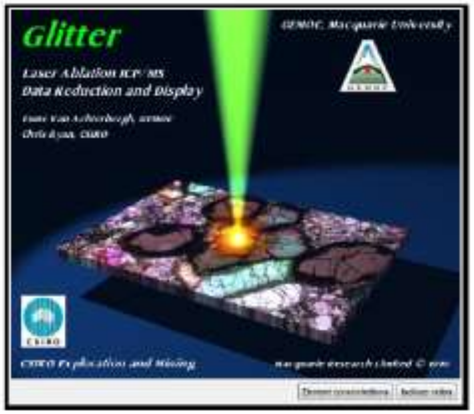
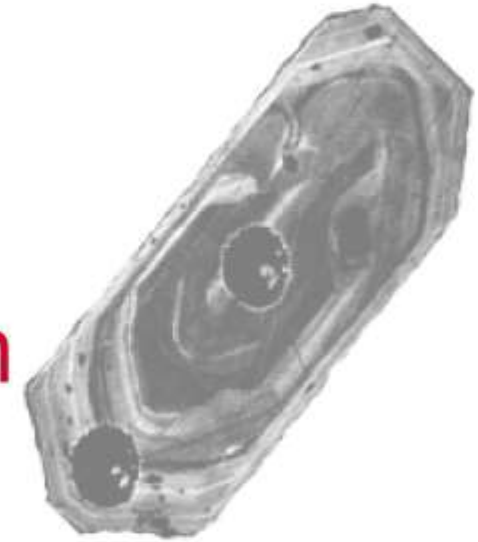


Glitter:
U-Pb data reduction and error propagation



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CCFS

MACQUARIE UNIVERSITY
Curtin University
THE UNIVERSITY OF WESTERN AUSTRALIA
Achieve International Excellence

U-Pb Workshop, Charleston SC, 2013

Glitter

CCFS

Current commercial release (version 4.4.4)

Features in GEMOC lab 'beta-testing'
- automatic loading of new data
- loading of internal standard data from a user-defined file
- TE mode: user defined plotting orders
- TE mode: entry of IS values as ppm (v4.4.4 requires wt% oxide)
- Ratio mode: moving of the rise-time indicator with the mouse
- Ratio mode: default option is for "Tie Standard Markers to Analyses"
- improved support for MassHunter output - automatic loading of dwelltime information

Features under development
- TE mode: multi-stage fitting to the standards
- Ratio mode: individual uncertainties for standard ratios
- Ratio mode: calculation by mean of ratios or ratio of means
- support for Nu AttoM and Nu Plasma output
- early work on support for the Neptune
- support for Qtegra output (Thermo Fisher)
- improved signal rise detection and better marker detection

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propagation of uncertainties

Isotopic analysis of unknown • error of raw ratio	**Within-spot error** (counting statistics)
Internal corrections • mass bias corrections • overlap corrections	**Internal precision** (corrected within-spot error)
External corrections • absolute correction using calibration standard • drift corrections	**Within-run/session error** (reproducibility of standard within session)
Cumulative error • calculate uncertainty in mass bias and overlap corrections for calibration standard • calculate uncertainty in calibration constants	**External precision** (reproducibility of standard beween sessions)

propagation of uncertainties

CCFS

Isotopic analysis of unknown
- error of raw ratio

Within-spot error
(counting statistics)

Internal corrections
- mass bias corrections
- overlap corrections

Internal precision
(corrected within-spot error)

External corrections
- absolute correction using calibration standard
- drift corrections

Within-run/session error
(reproducibility of standard within session)

Glitter
1σ error

Cumulative error
- calculate uncertainty in mass bias and overlap corrections for calibration standard
- calculate uncertainty in calibration constants

External precision
(reproducibility of standard beween sessions)

GEMOC

uncertainty

Internal (random)

- measurement of signals of isotopes of interest (counting statistics)
- correction for mass bias and/or elemental fractionation (analytical uncertainty on measured ratio used for normalization)
- correction for instrument drift (time relationship with standards)

External (systematic)

- corrections for detector response and calibration (gain, deadtime)
- correction procedures for mass bias and/or elemental fractionation
- correction for instrument drift (best-fit through standards)
- 'true' value of calibration or reference standard
- decay constants used in age calculation

isotope ratio

$$R_{unk}^{corr} = R_{unk}^{meas} \bullet \left(\frac{R_{std}^{true}}{R_{std}^{meas}} \right)$$

normalization factor

R_{unk}^{corr} is the corrected ratio of masses M2 and M1 in the unknown sample

R_{unk}^{meas} is the measured ratio of masses M2 and M1 in the unknown sample

R_{std}^{true} is the true ratio of masses M2 and M1 in the calibration standard

R_{unk}^{meas} is the measured ratio of masses M2 and M1 in the calibration standard

calculation of isotope ratio – 1

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Ratio of the mean signals in the integration interval

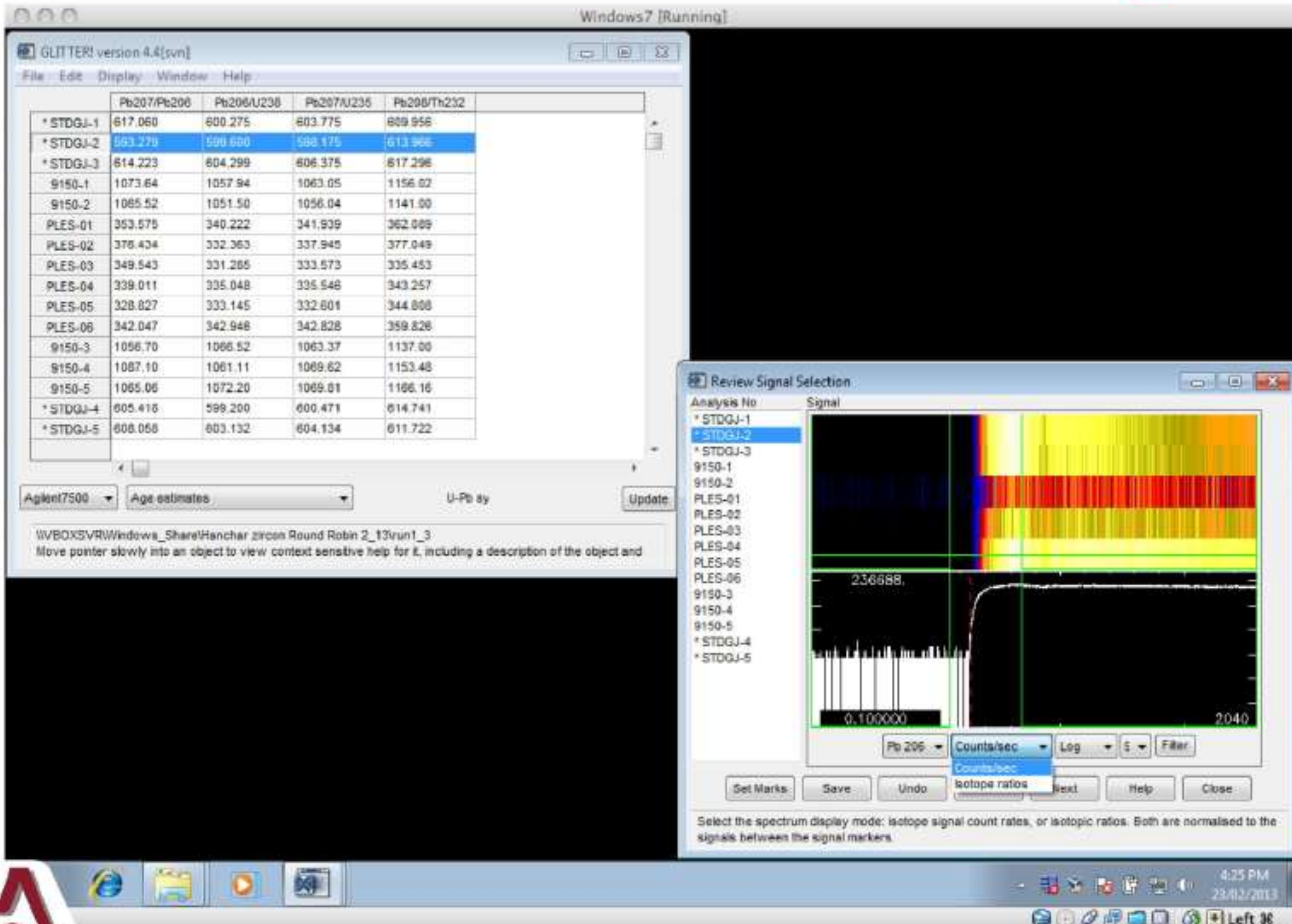
- selection of background and signal integration intervals
- calculation of mean signal and mean background
- background subtraction

  I_{unk}^{M1} is the mean signal of mass M1 in the unknown sample

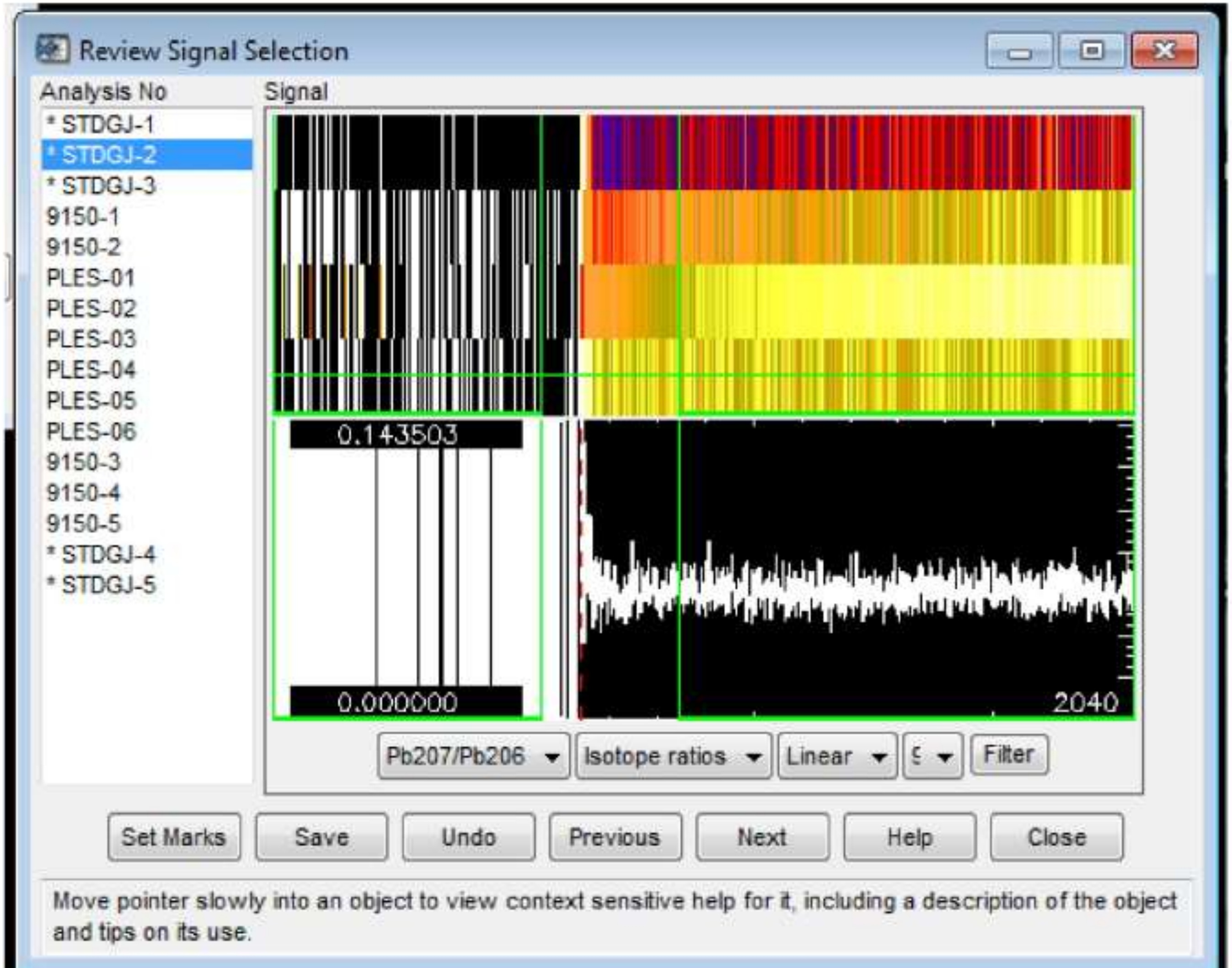
- uncorrected ratio

$$R_{unk}^{meas} = \frac{I_{unk}^{M2}}{I_{unk}^{M1}}$$

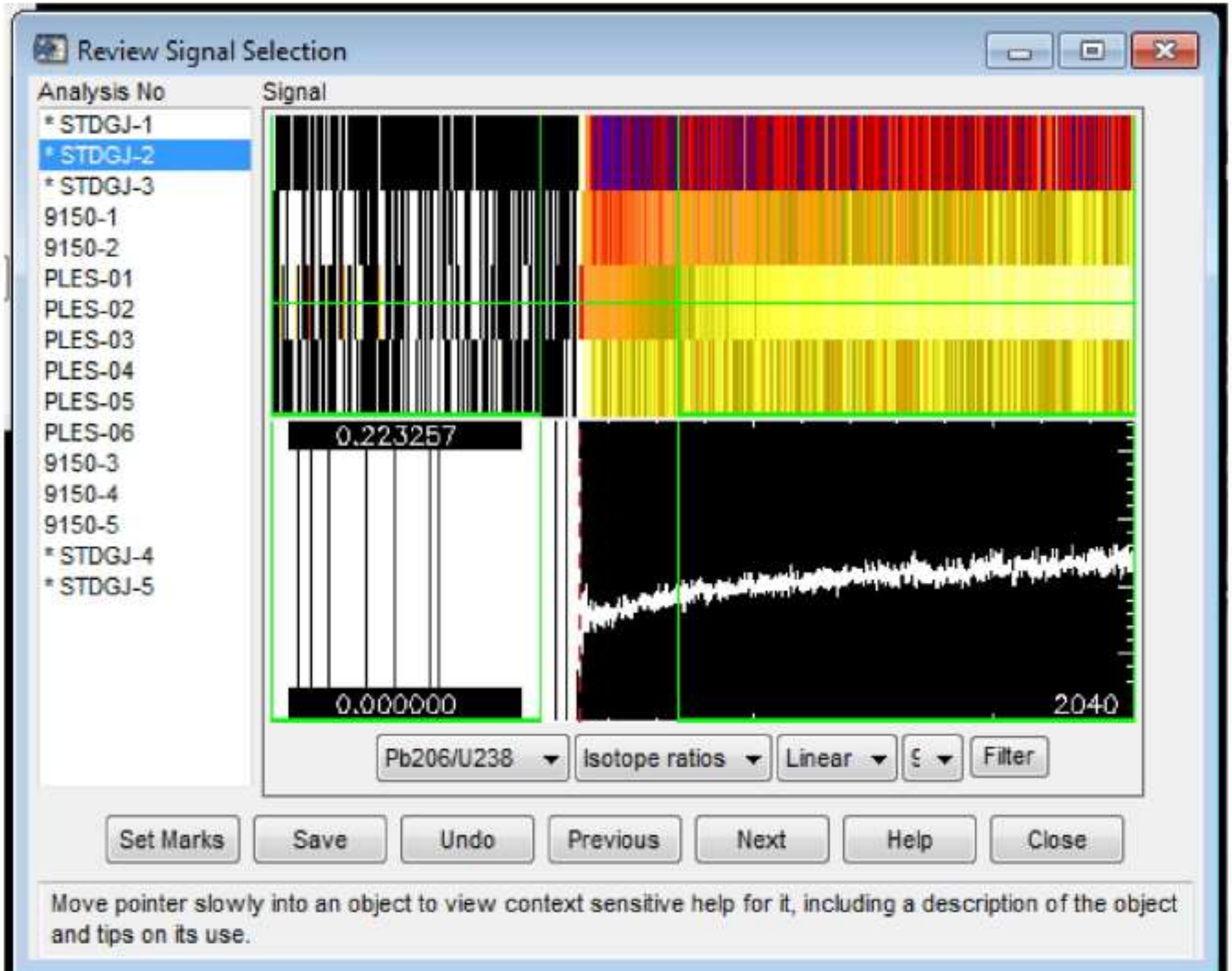
Glitter – selection interval



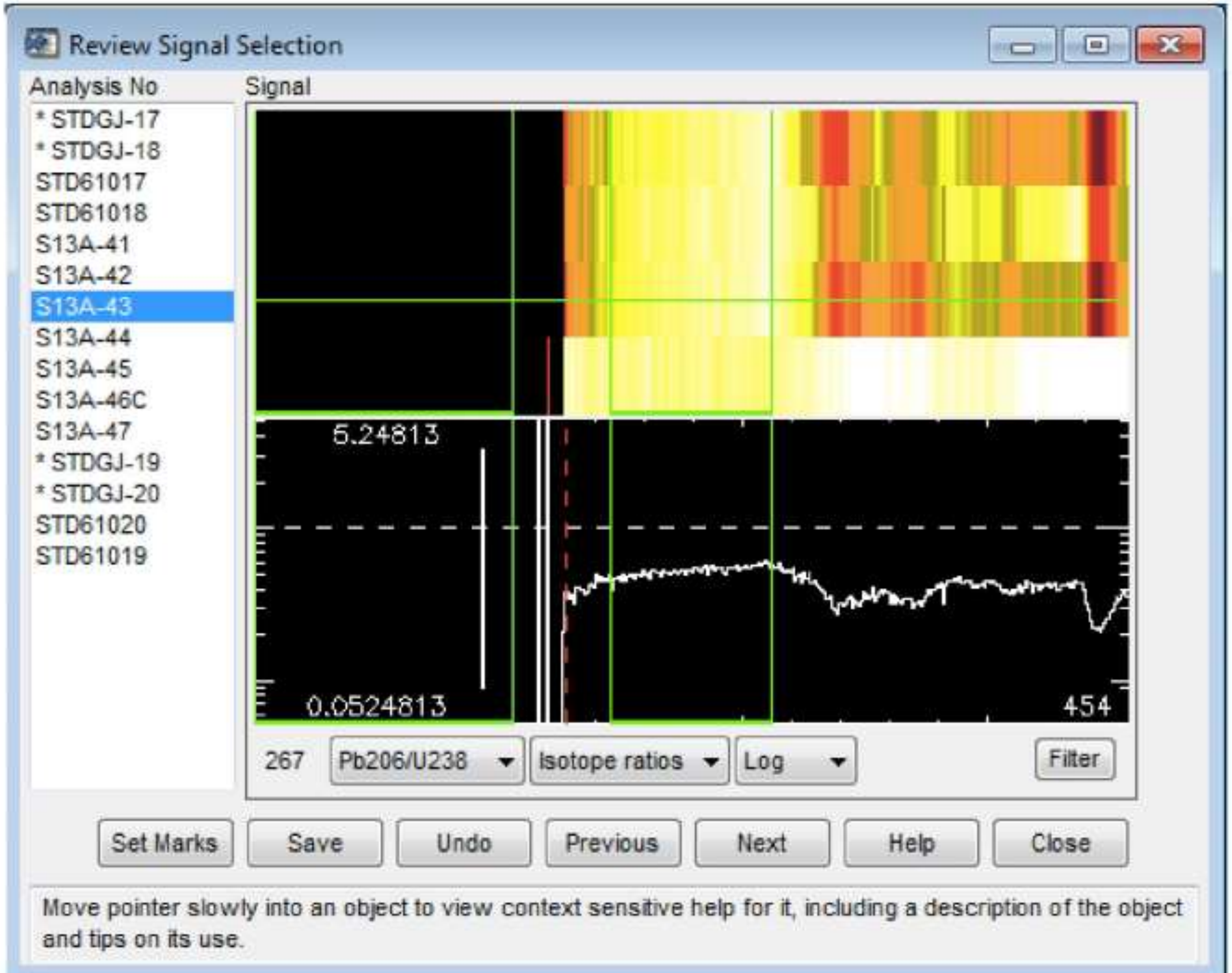
Glitter – selection interval



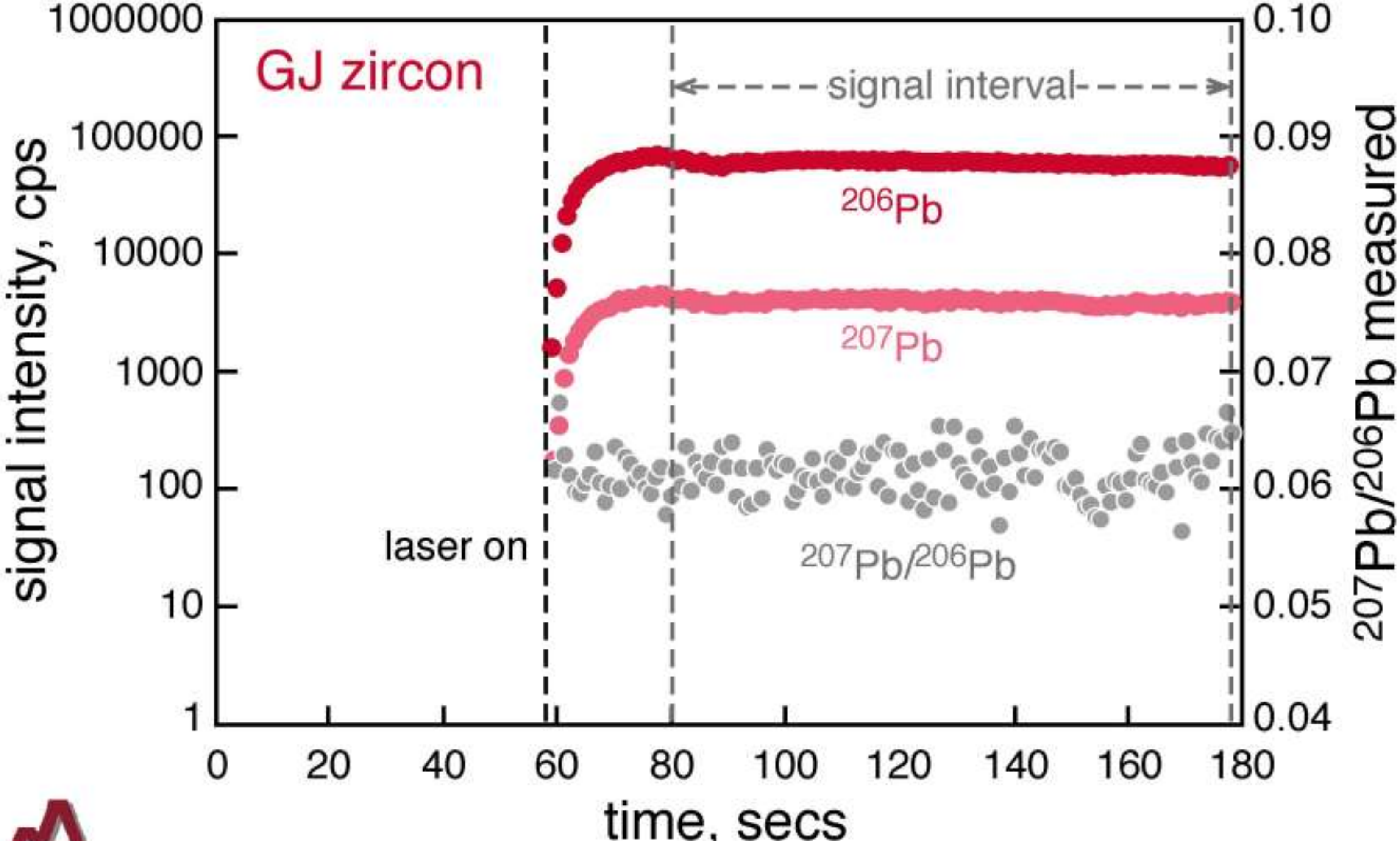
Glitter – selection interval



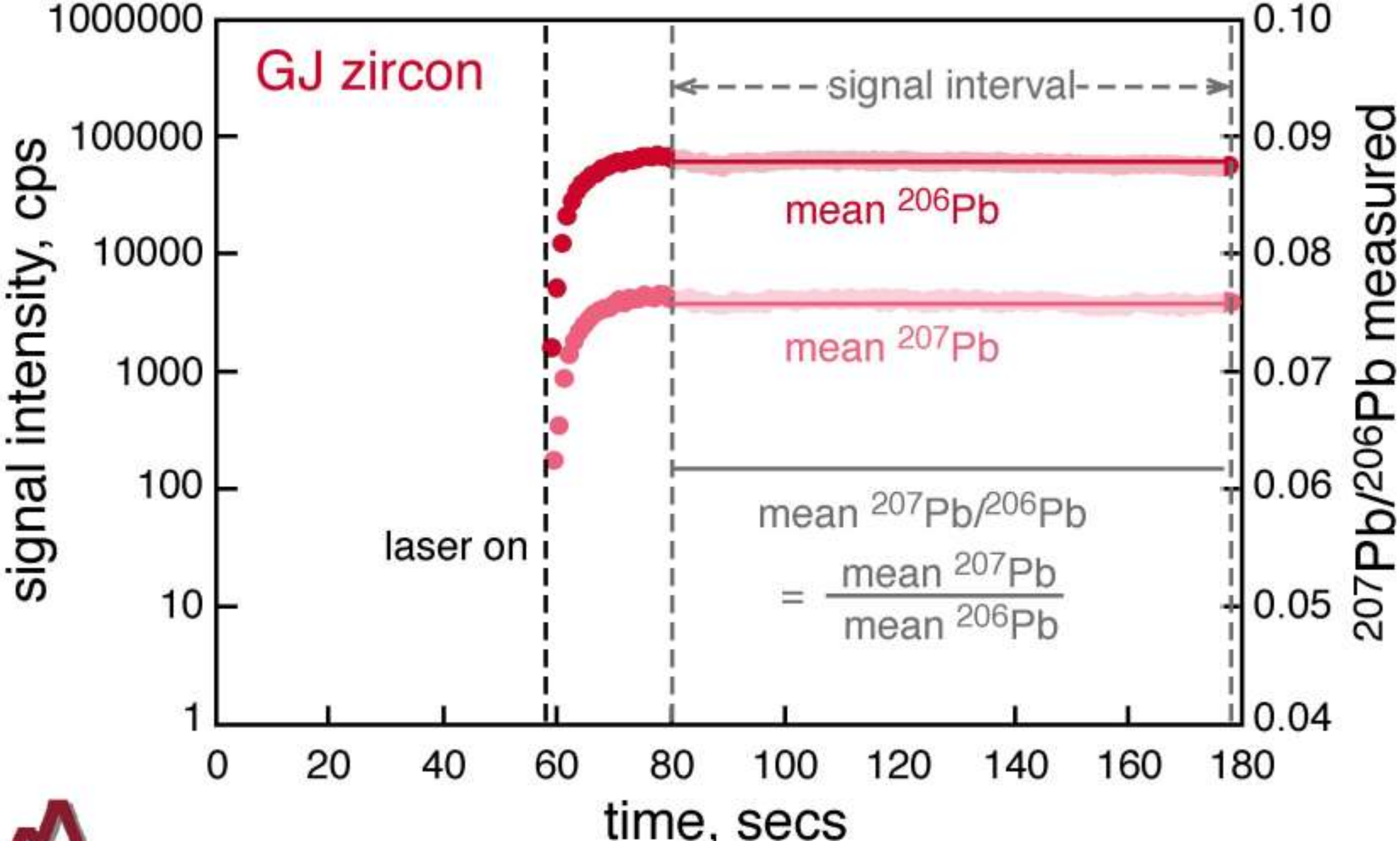
Glitter – selection interval



fractionation – $^{207}Pb/^{206}Pb$



isotope ratio – $^{207}Pb/^{206}Pb$



uncertainty – isotope ratio – 1

Ratio of the mean signals in the integration interval

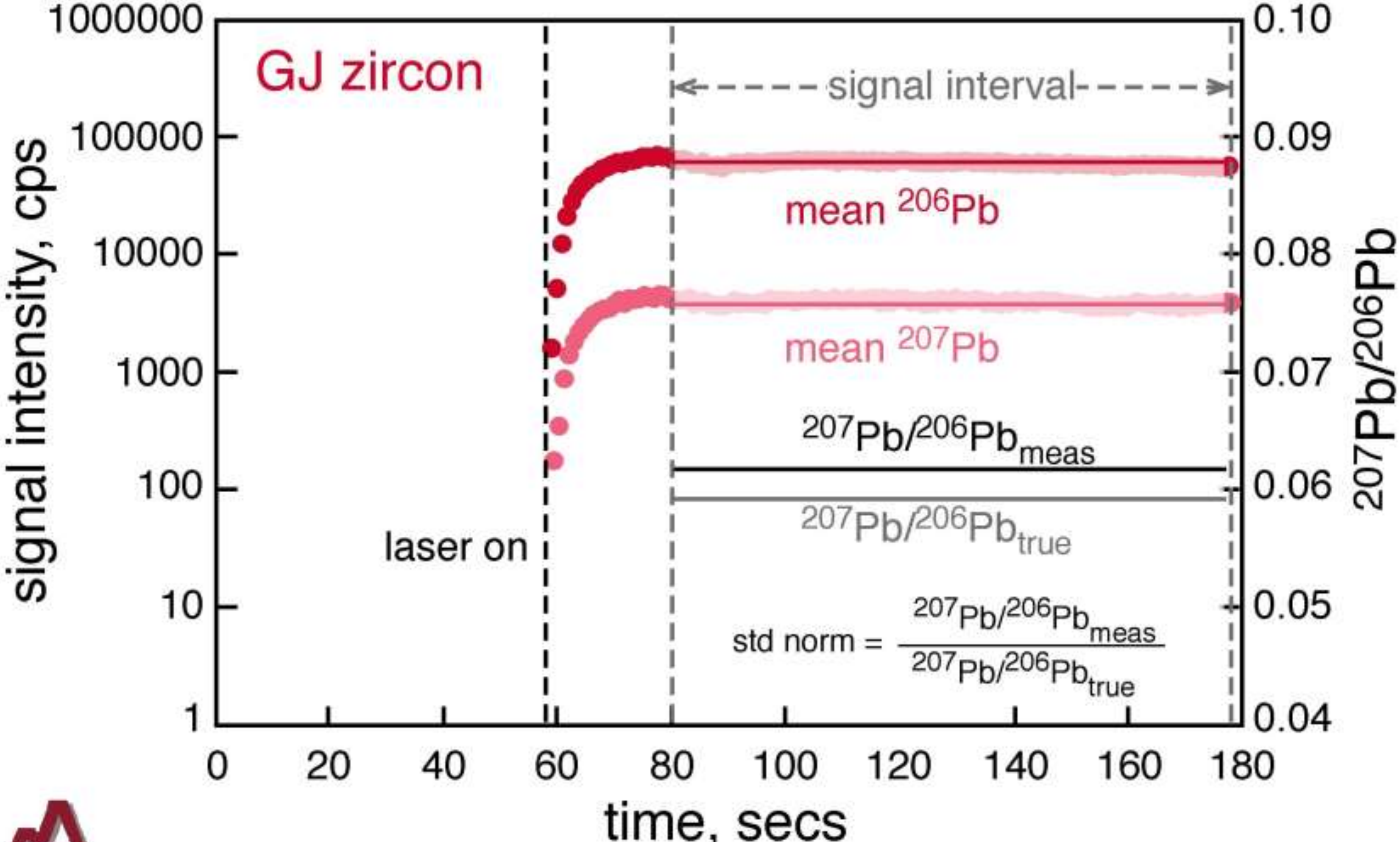
$$R_{unk}^{meas} = \frac{I_{unk}^{M\,2}}{I_{unk}^{M\,1}}$$

$$u(I) = \sqrt{\left(\frac{\text{counts per second}}{\text{time}}\right)}$$

$$u(I) = \sqrt{\left(\frac{\text{counts per replicate}}{\text{no. of replicates}}\right)}$$

$$u(R_{unk}^{meas}) = R_{unk}^{meas} \bullet \sqrt{\left[\left(\frac{u(I)_{unk}^{M\,1}}{(I)_{unk}^{M\,1}}\right)^2 + \left(\frac{u(I)_{unk}^{M\,2}}{(I)_{unk}^{M\,2}}\right)^2\right]}$$

normalization – $^{207}Pb/^{206}Pb$



standard normalization factor

$$normalization\ factor = \frac{\left(\dfrac{I_{std}^{M2}}{I_{std}^{M1}}\right)}{R_{std}^{true}}$$

standard normalization factor incorporates:

- instrumental mass bias
- laser-induced isotopic fractionation where M2 and M1 are isotopes of the same element
- laser-induced elemental fractionation where M2 and M1 are isotopes of different elements

uncertainty – external correction

Uncertainty on *standard normalization factor* needs to take into account:

- drift of instrumental mass bias with time
  – interpolation of yield values between groups of standards

- laser-induced isotopic/elemental fractionation
  – assume that standards and unknowns behave in the same way
  – Glitter enables the automatic linking of the same signal integration intervals for standards as selected for unknowns

uncertainty – standard normalization

$$stdnorm = \frac{\left(\frac{I_{std}^{M2}}{I_{std}^{M1}}\right)}{R_{std}^{true}}$$

$$u(I) = \sqrt{\left(\frac{\text{counts per replicate}}{\text{no. of replicates}}\right)}$$

$$u\left(R_{std}^{true}\right) = \%\text{ of reference value}$$

$$u(stdnorm) = stdnorm \bullet \sqrt{\left[\left(\frac{u(I)_{std}^{M1}}{(I)_{std}^{M1}}\right)^2 + \left(\frac{u(I)_{std}^{M2}}{(I)_{std}^{M2}}\right)^2 + \left(\frac{u(R)_{std}^{true}}{(R)_{std}^{true}}\right)^2\right]}$$

uncertainty – standard normalization

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$$R_{unk}^{corr} = R_{unk}^{meas} \bullet \underbrace{\left(\frac{R_{std}^{true}}{R_{std}^{meas}} \right)}_{\textit{standard normalization factor}}$$

$$u(stdnorm) = stdnorm \bullet \sqrt{\left[\left(\frac{u(I)_{std}^{M1}}{(I)_{std}^{M1}} \right)^2 + \left(\frac{u(I)_{std}^{M2}}{(I)_{std}^{M2}} \right)^2 + \left(\frac{u(R)_{std}^{true}}{(R)_{std}^{true}} \right)^2 \right]}$$

$$u(R_{unk}^{corr}) = R_{unk}^{corr} \bullet \sqrt{\left[\left(\frac{u(I)_{unk}^{M1}}{(I)_{unk}^{M1}} \right)^2 + \left(\frac{u(I)_{unk}^{M2}}{(I)_{unk}^{M2}} \right)^2 + \left(\frac{u(stdnorm)}{stdnorm} \right)^2 \right]}$$

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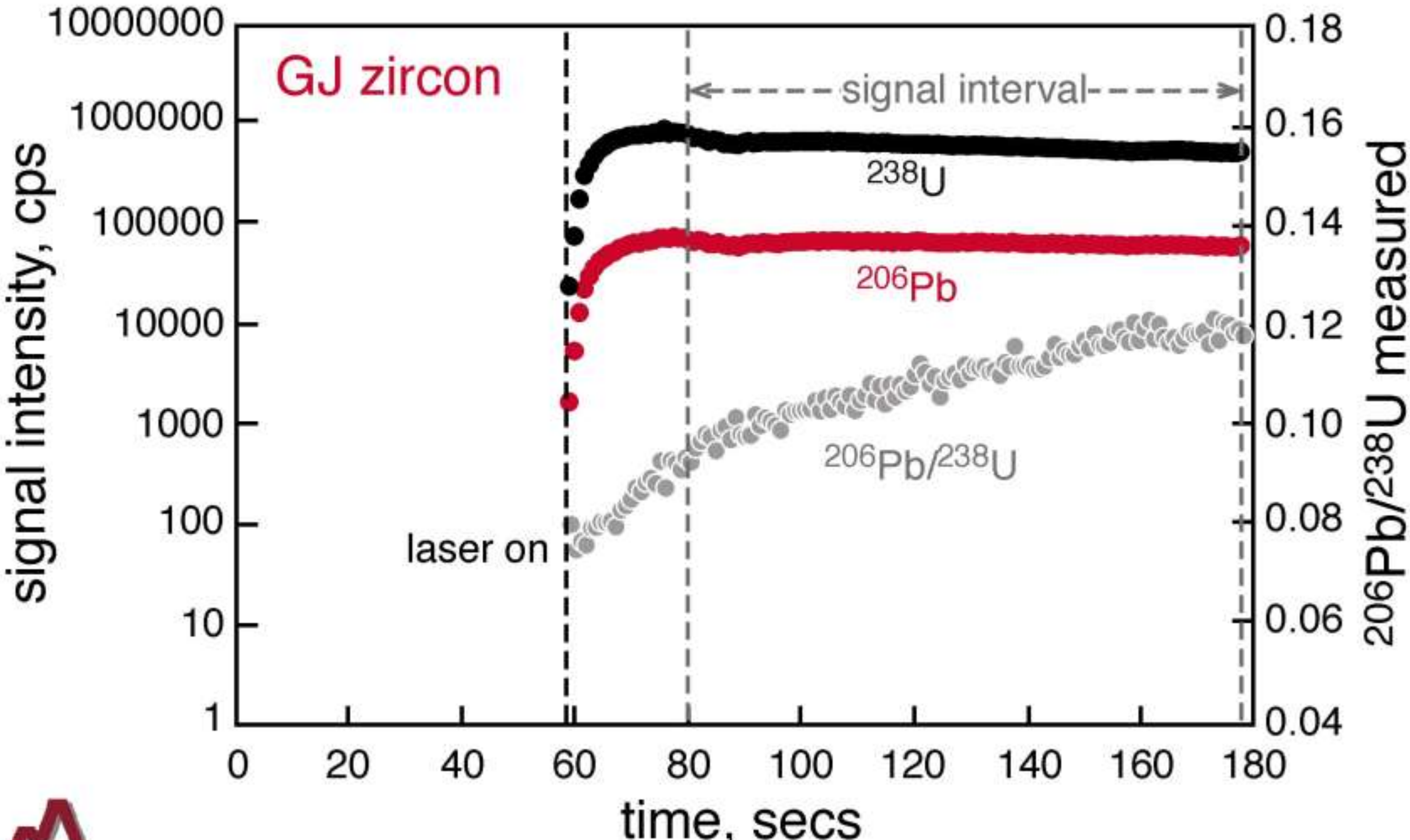
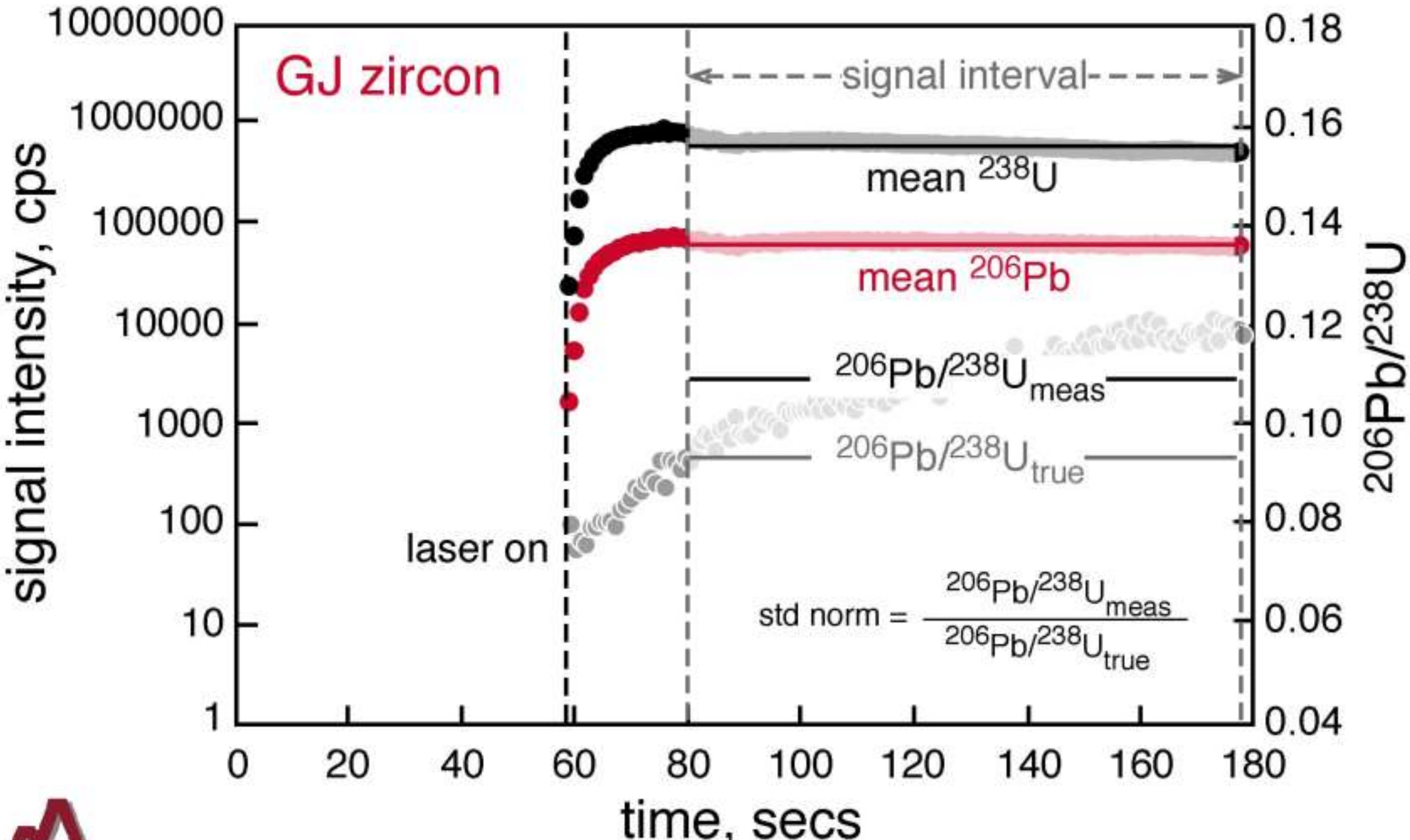
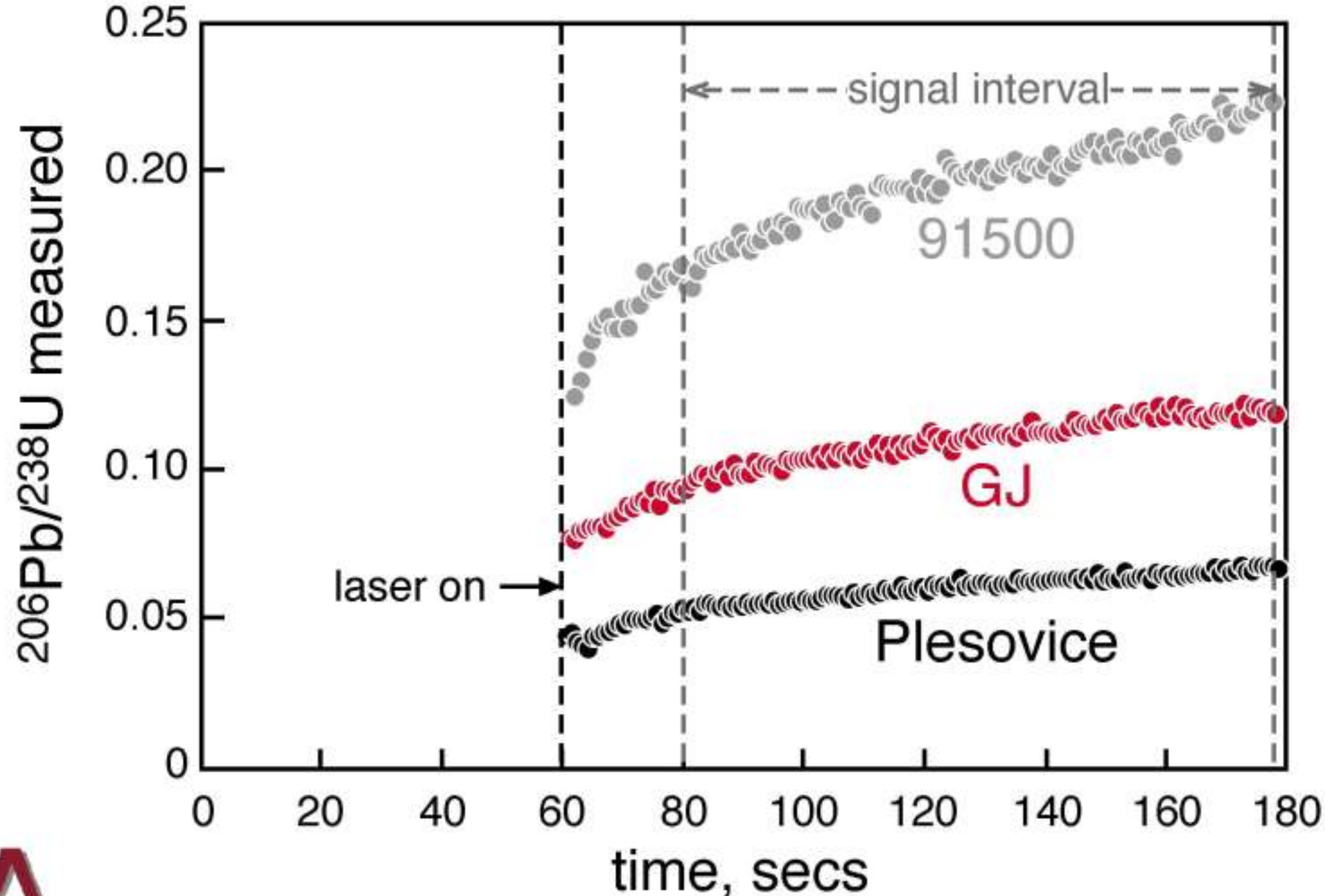
fractionation – $^{206}Pb/^{238}U$



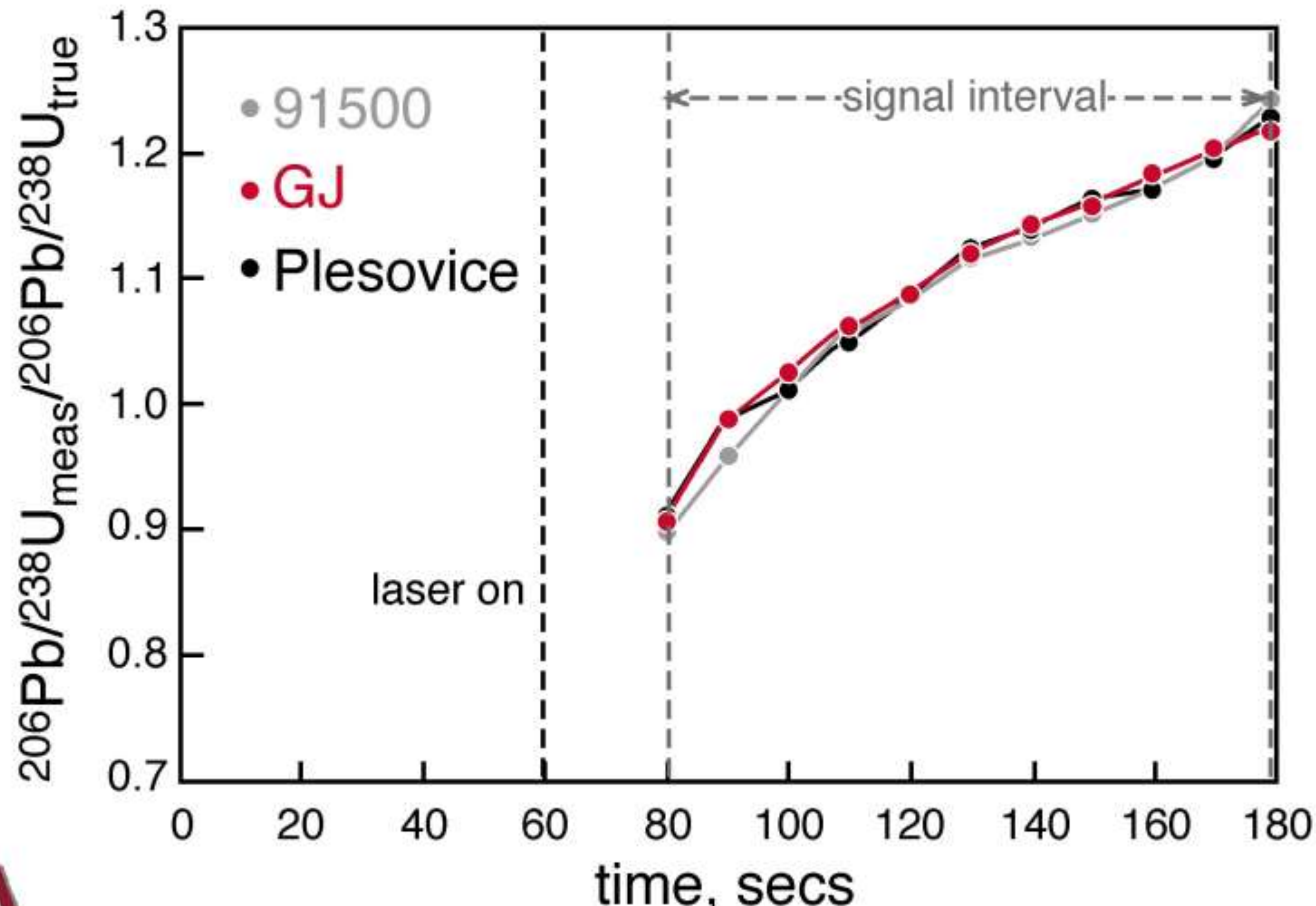
normalization – $^{206}Pb/^{238}U$



fractionation – $^{206}Pb/^{238}U$

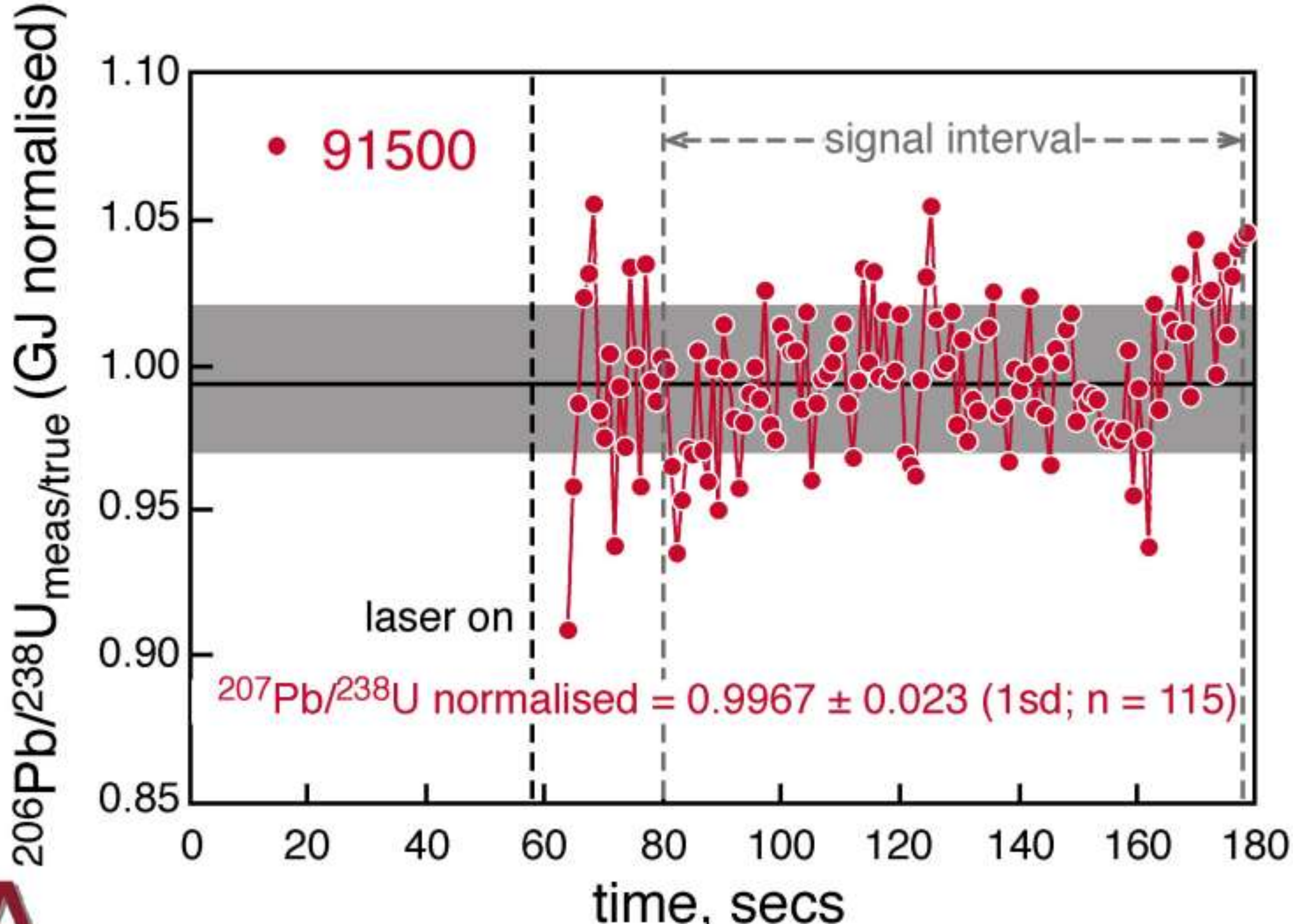


fractionation – $^{206}Pb/^{238}U$

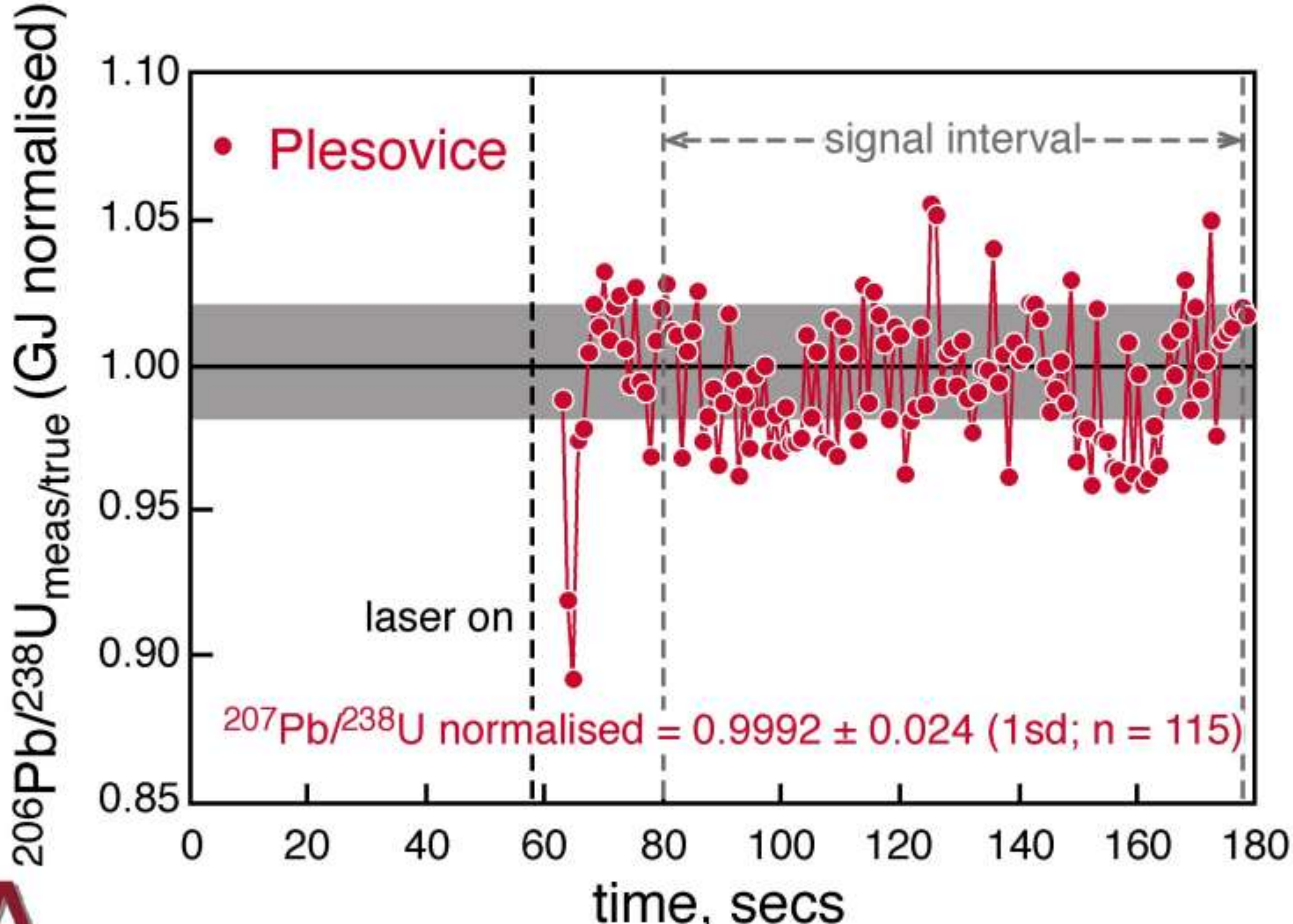


fractionation – $^{206}Pb/^{238}U$

CCFS



fractionation – $^{206}Pb/^{238}U$



calculation of isotope ratio – 2

Mean of all of the individual ratios in the integration interval

- selection of background and signal integration intervals
- calculate mean background
- calculate signals for each 'cycle' or 'replicate' (background subtraction)

$R_{unk,\,i}^{meas}$ is the measured ratio in the unknown sample in the i th cycle

- calculate corrected ratio for each 'cycle' or 'replicate'

$$R_{unk,i}^{corr} = R_{unk,i}^{meas} \bullet \underbrace{\left(\frac{R_{std}^{true}}{R_{std}^{meas}} \right)_i}_{stdnorm_i}$$

uncertainty – isotope ratio – 2

Mean of all of the individual ratios in the integration interval

- mean corrected ratio

$$\overline{R_{unk}^{corr}} = \frac{\sum_{i=1}^{n}\left(R_{unk,i}^{corr}\right)}{n}$$

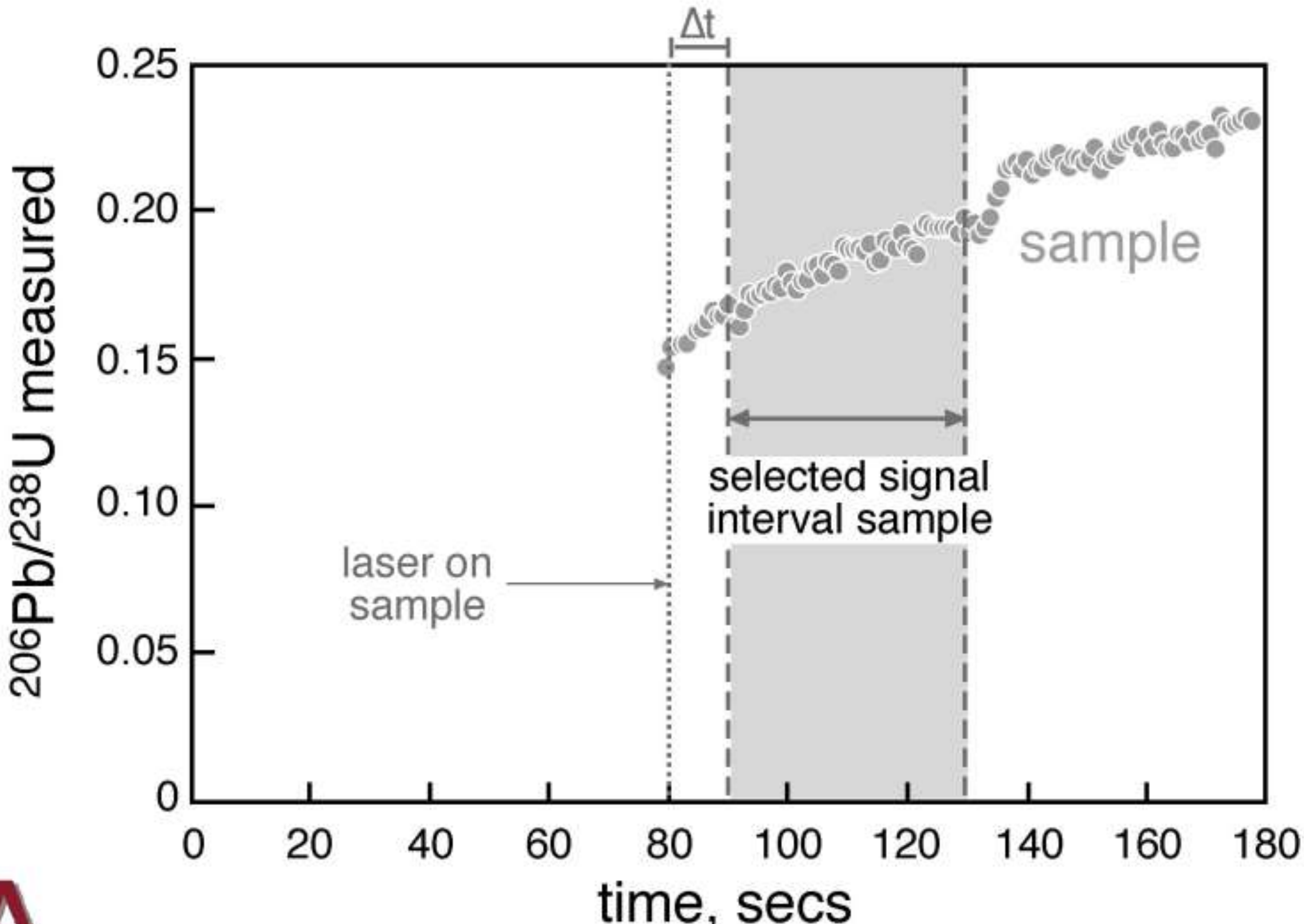
- standard deviation

$$u(R_{unk}^{corr}) = \sqrt{\left[\left(\frac{1}{n-1}\right)\sum_{i=1}^{n}\left(R_{unk,i}^{corr} - \overline{R_{unk}^{corr}}\right)^2\right]}$$

- standard error

$$u(R_{unk}^{corr})_{mean} = \frac{u(R_{unk}^{corr})}{\sqrt{n}}$$

ratio interval selection



interval selection – 'tied to standard'

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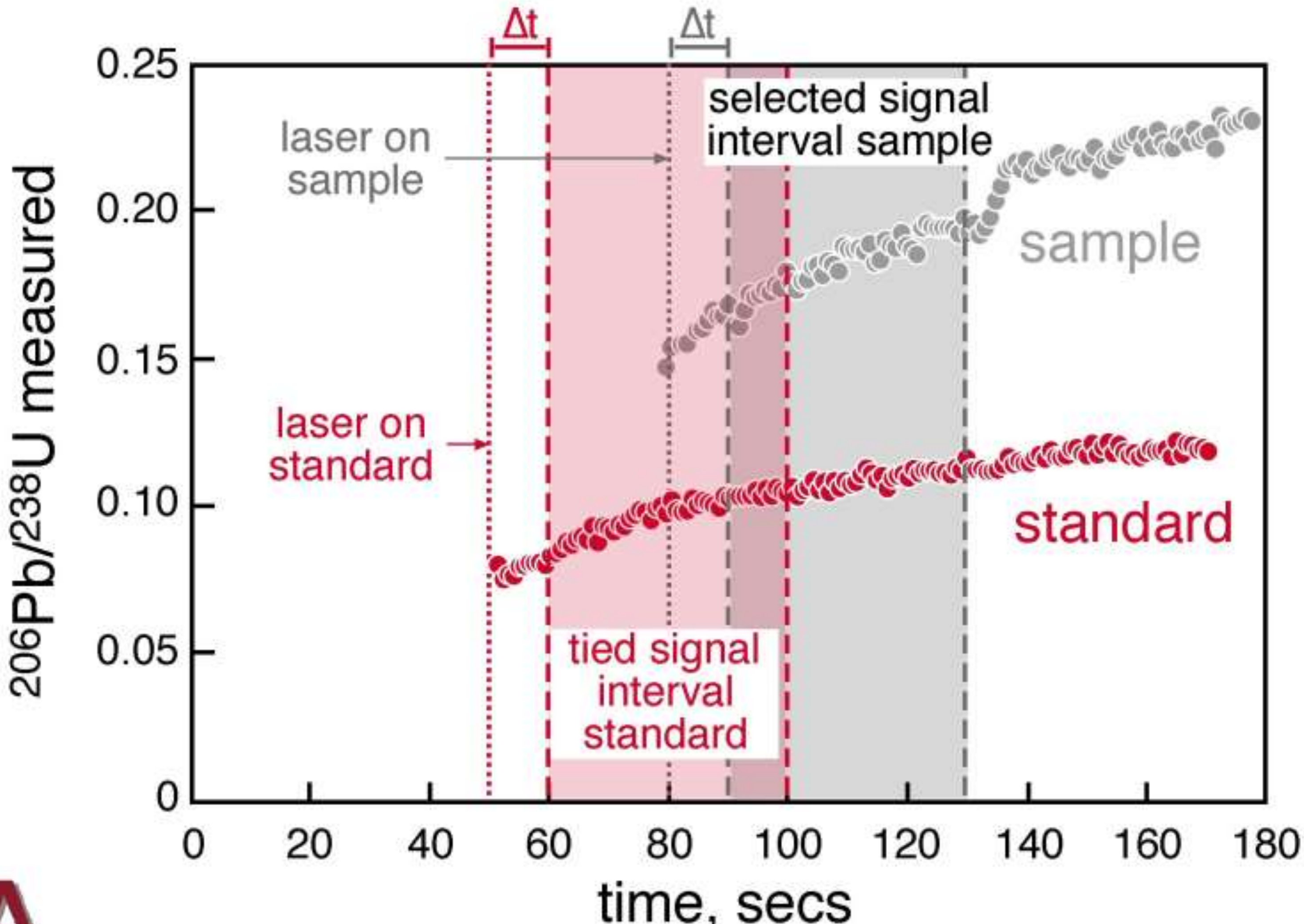

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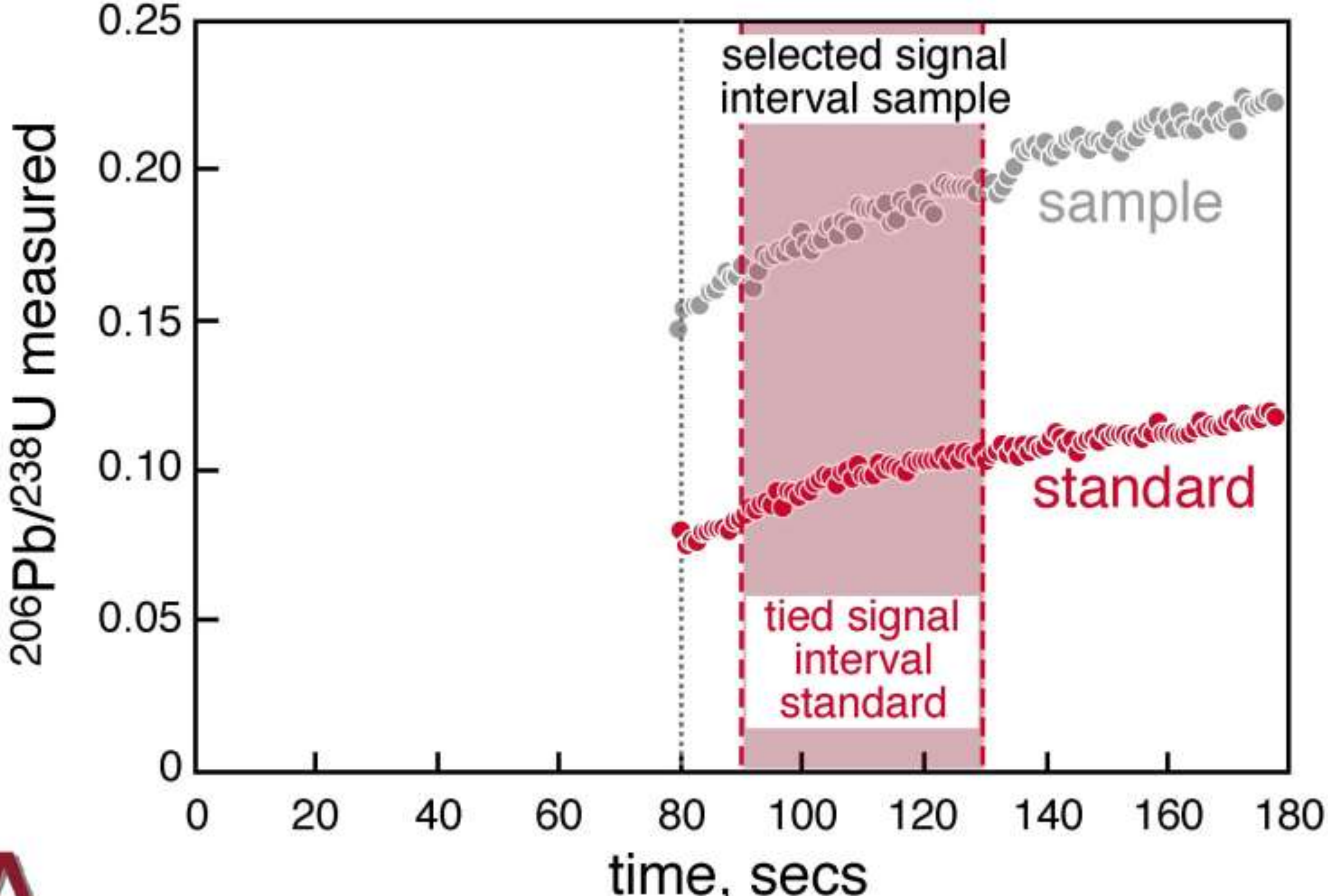
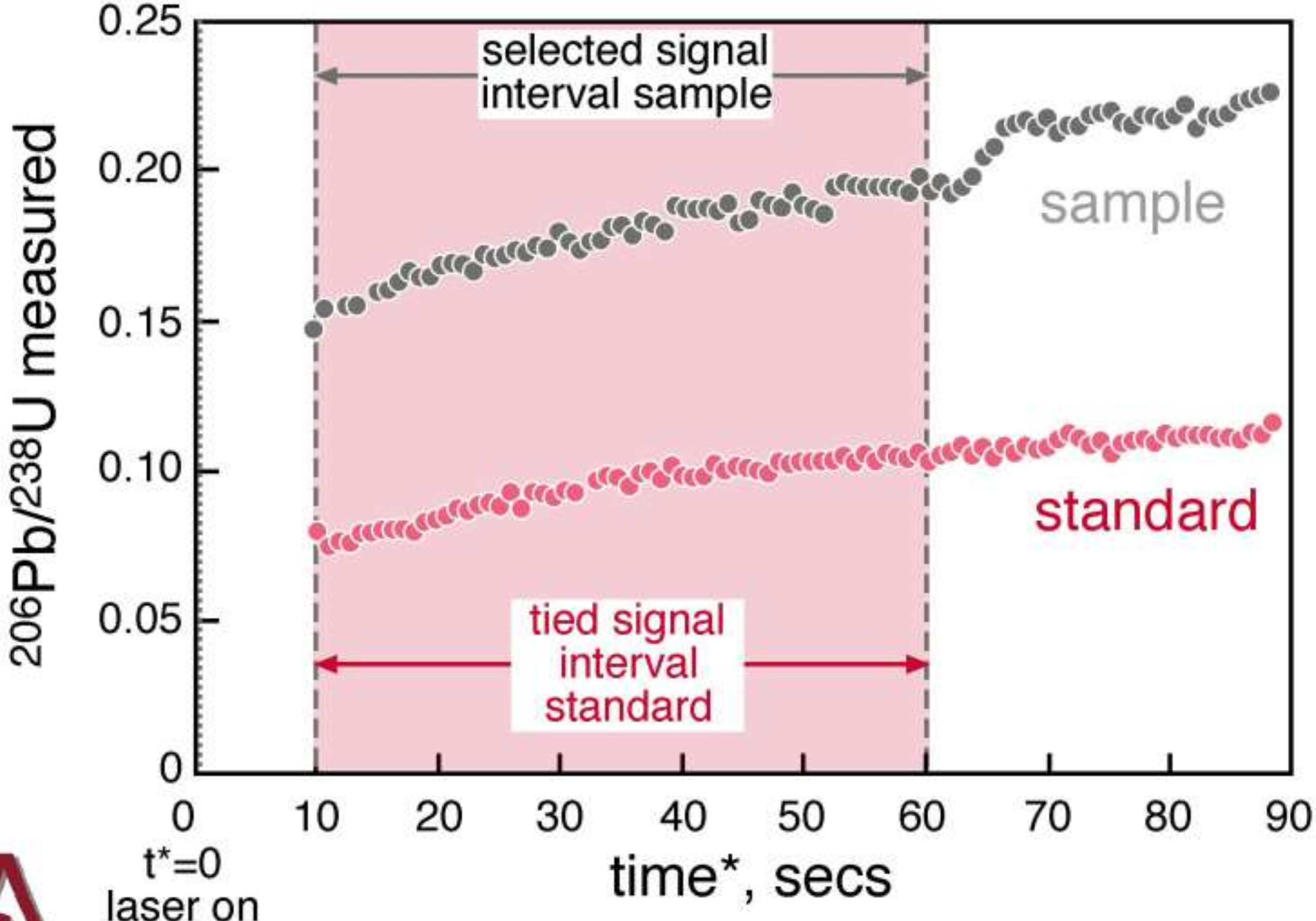
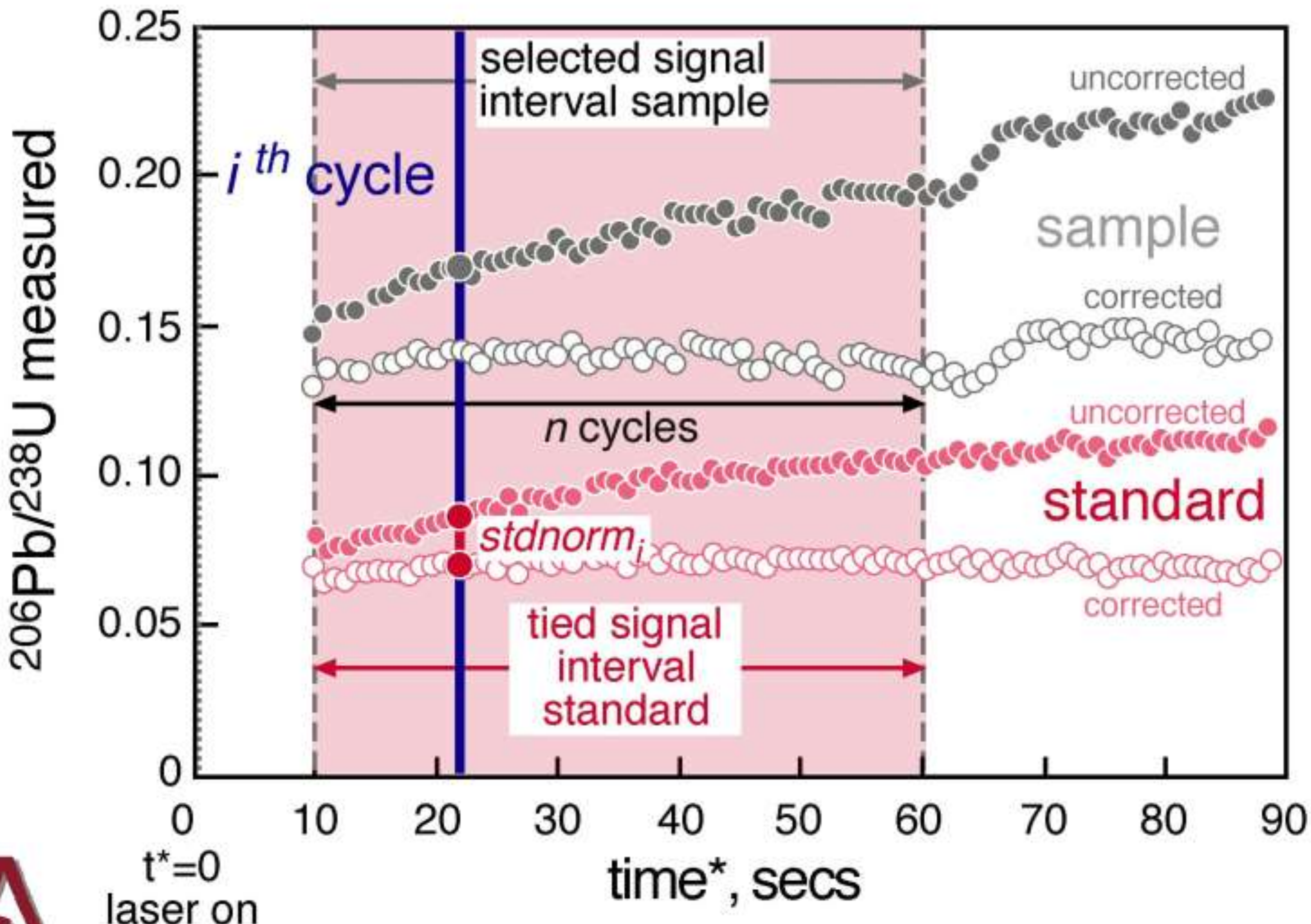
fractionation – $^{206}Pb/^{238}U$



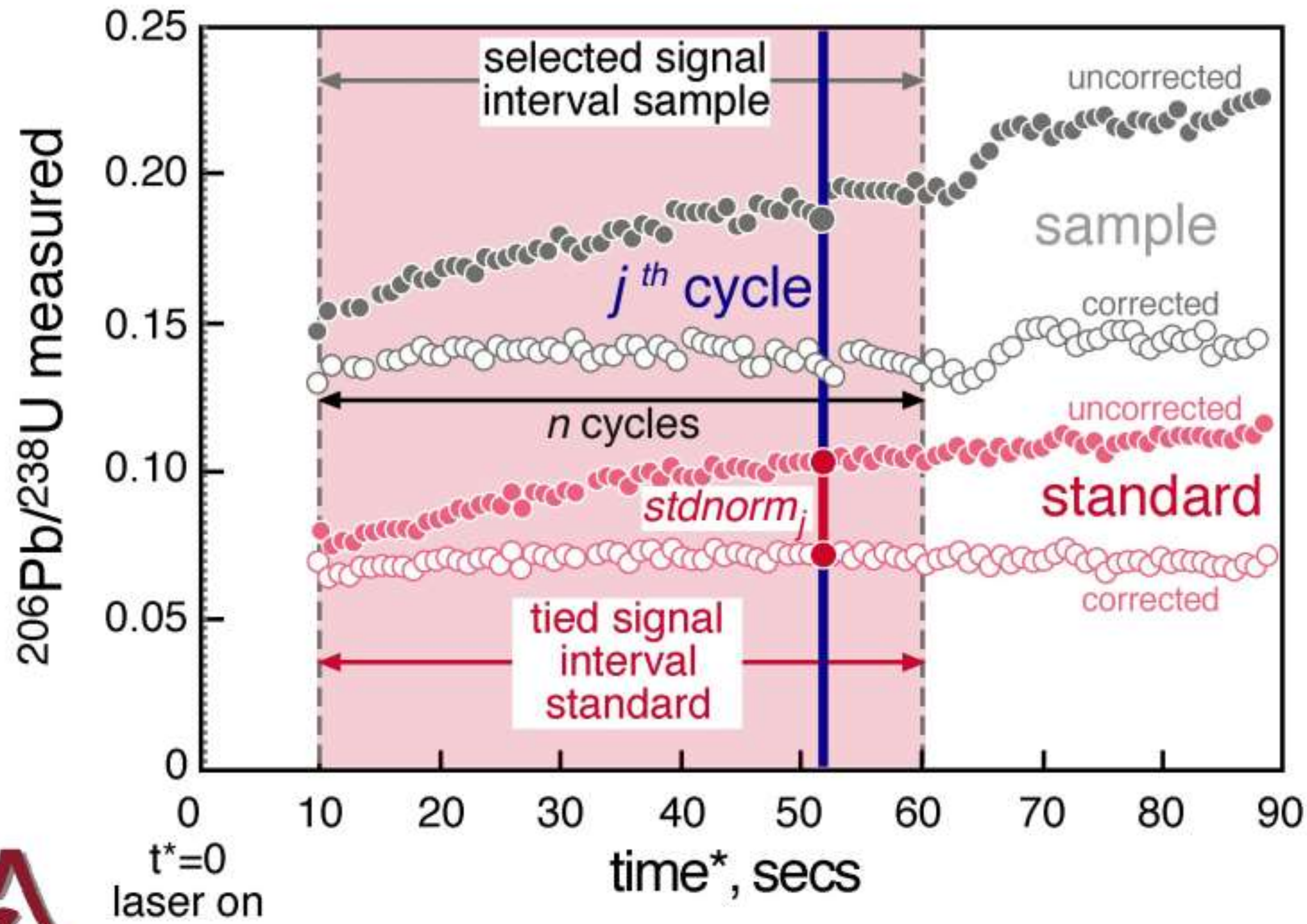
fractionation correction



fractionation correction

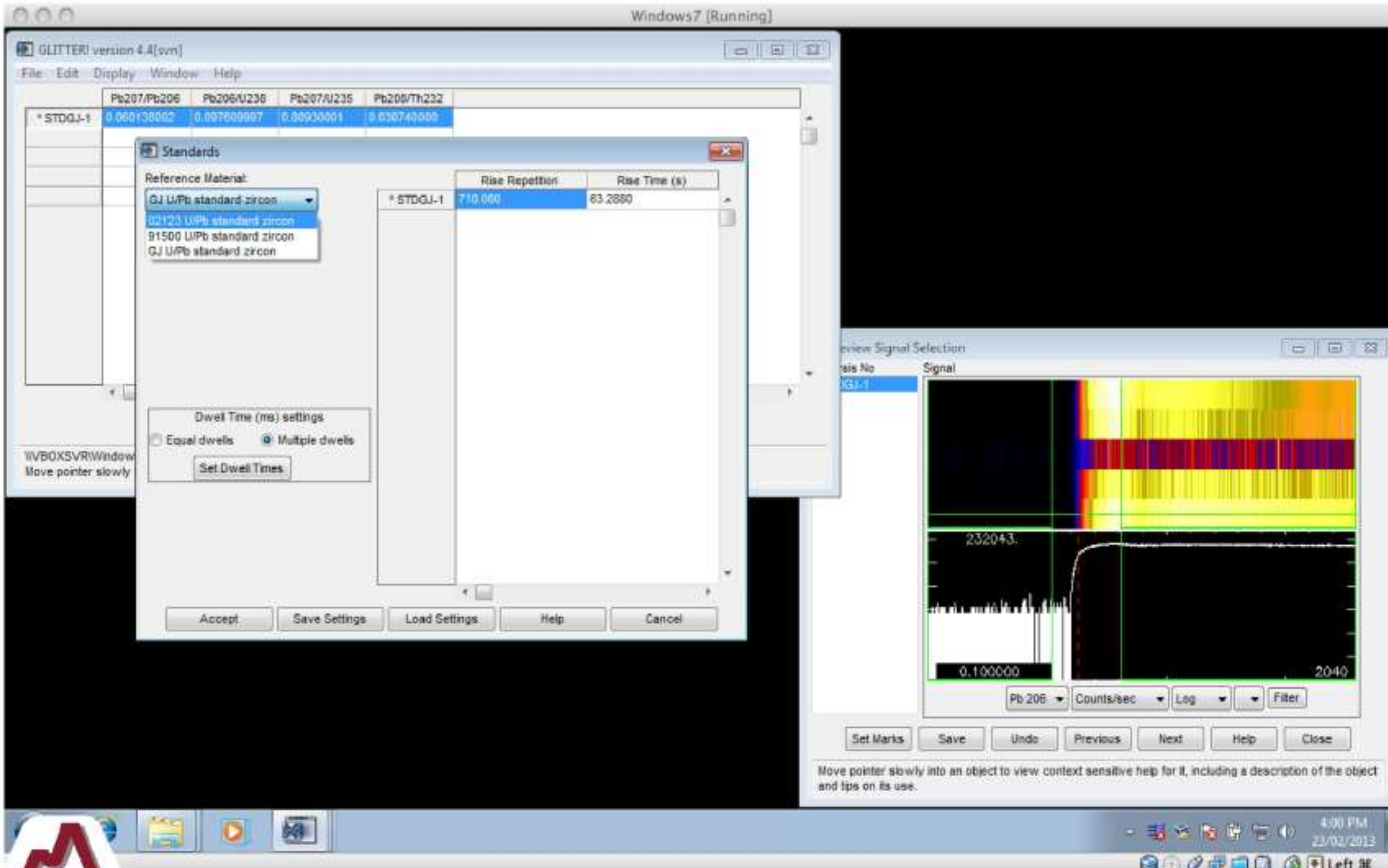


fraction correction

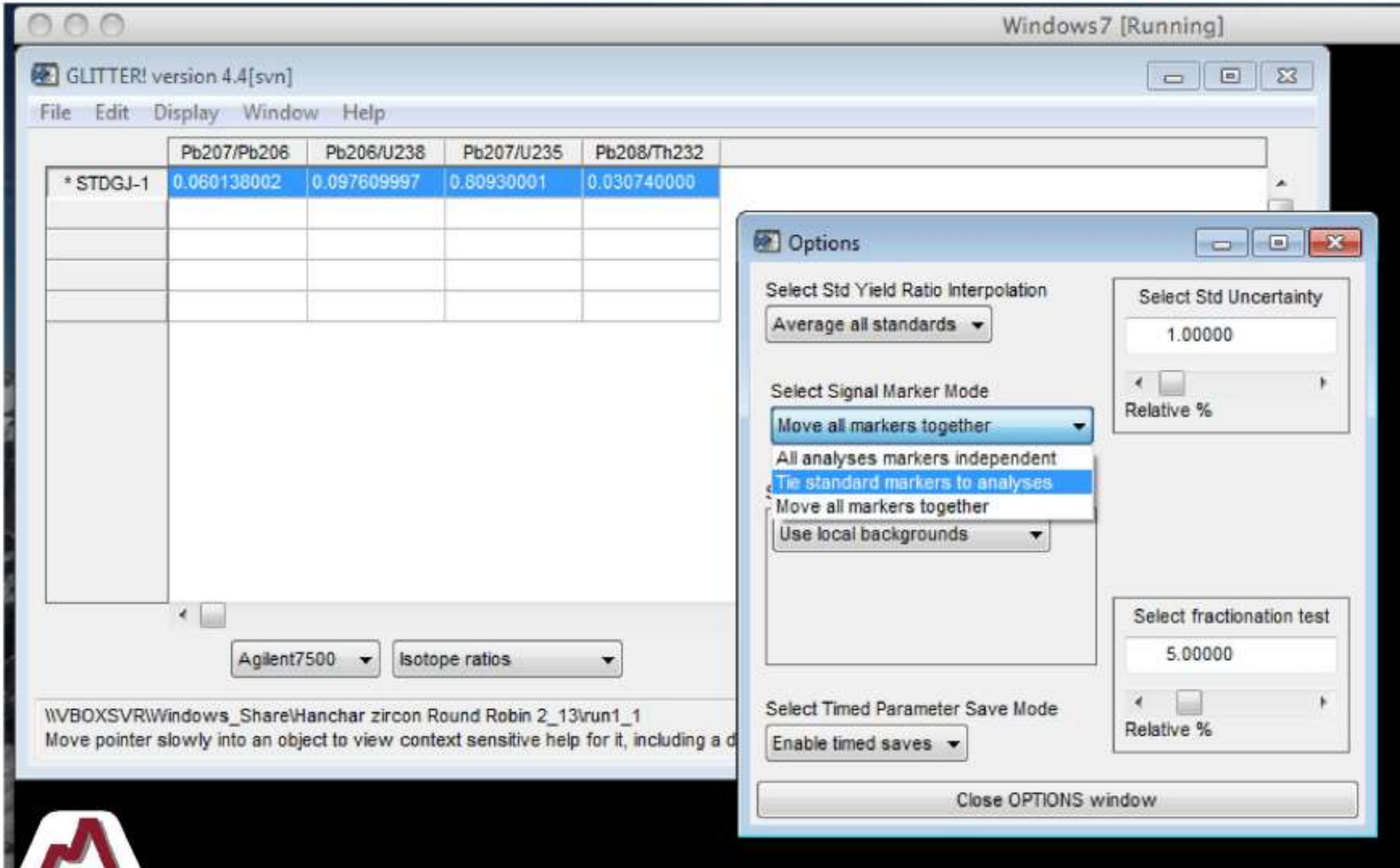


GEMOC

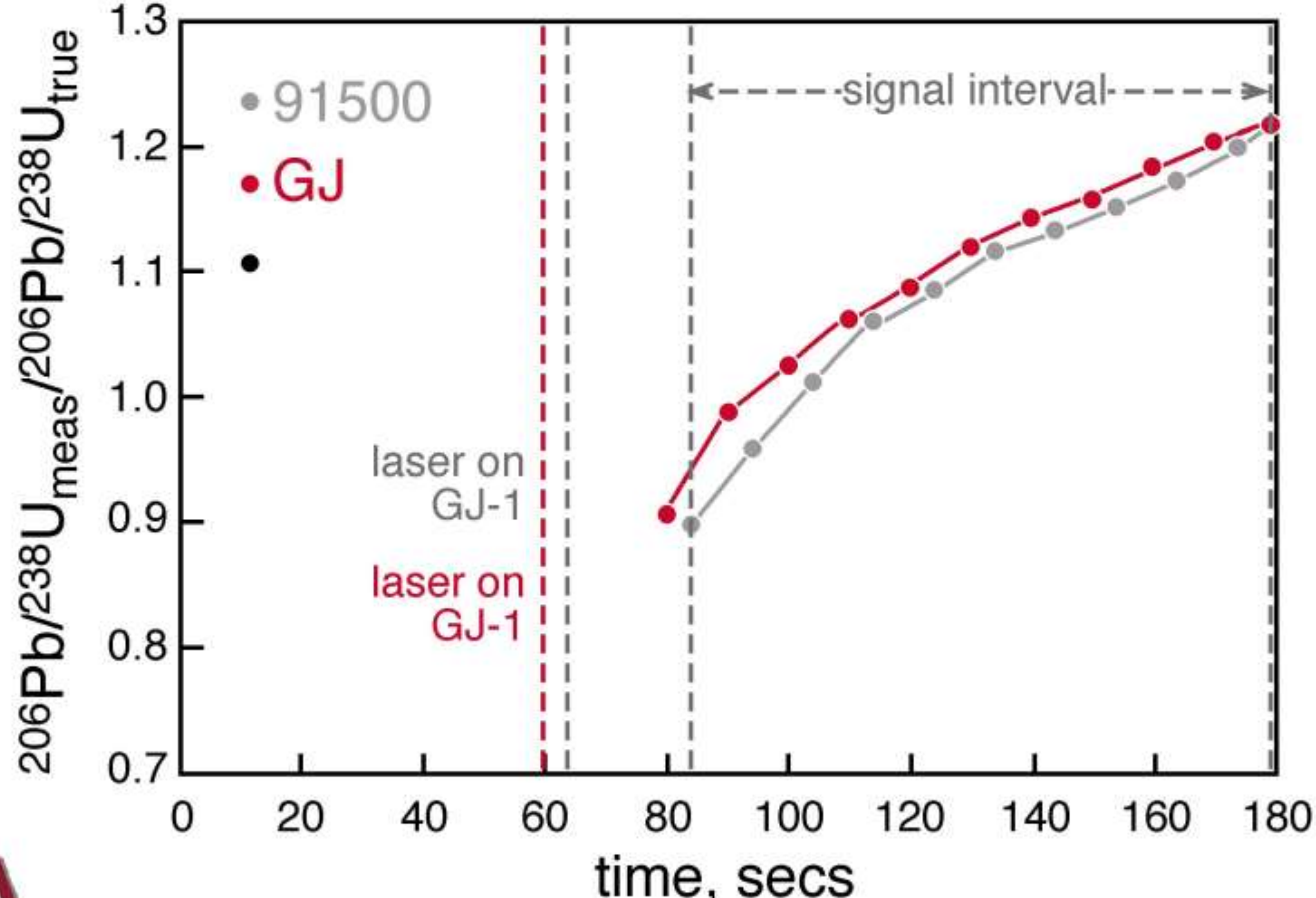
Glitter – rise time (laser on)



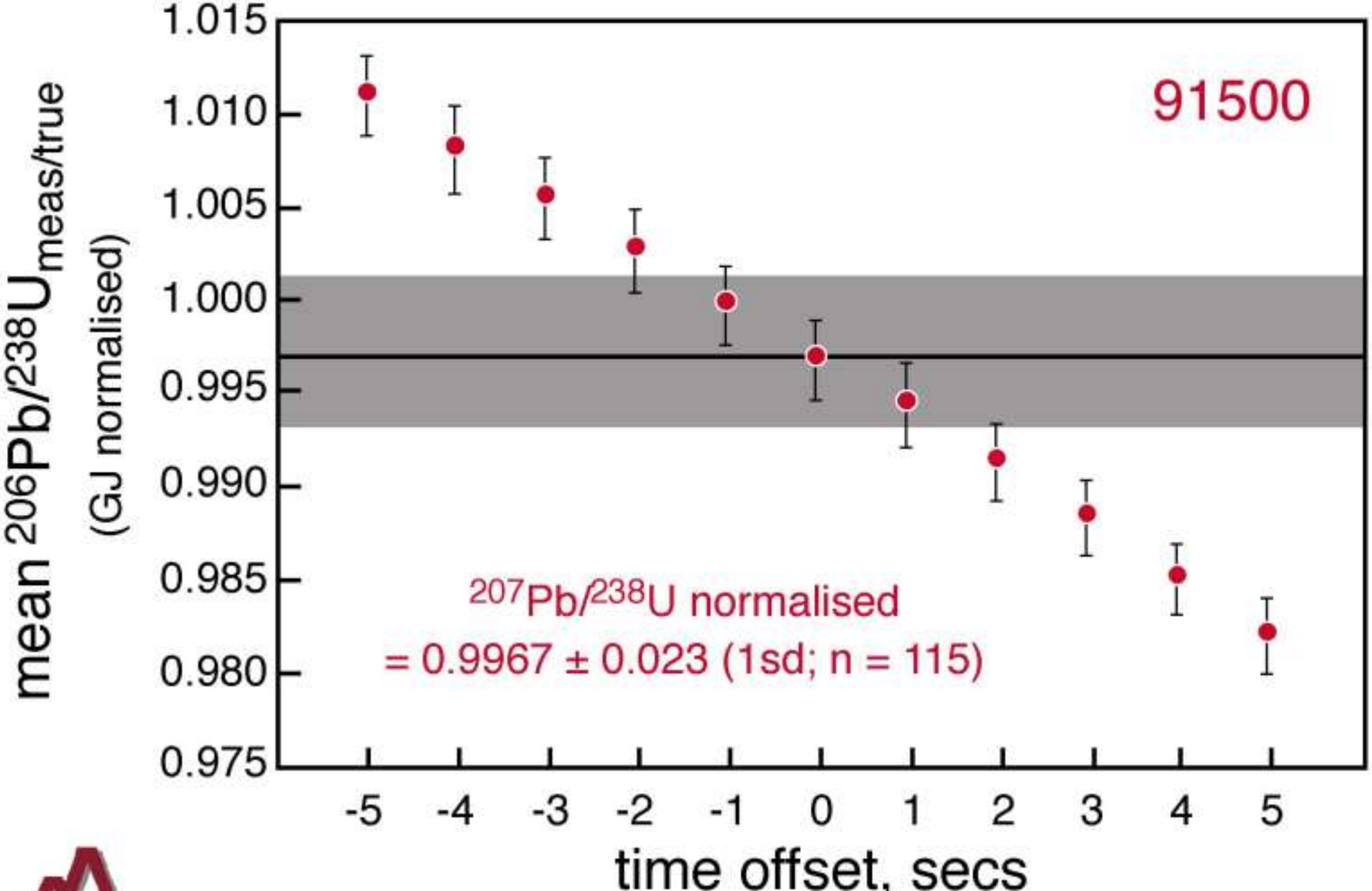
Glitter – tied selection interval



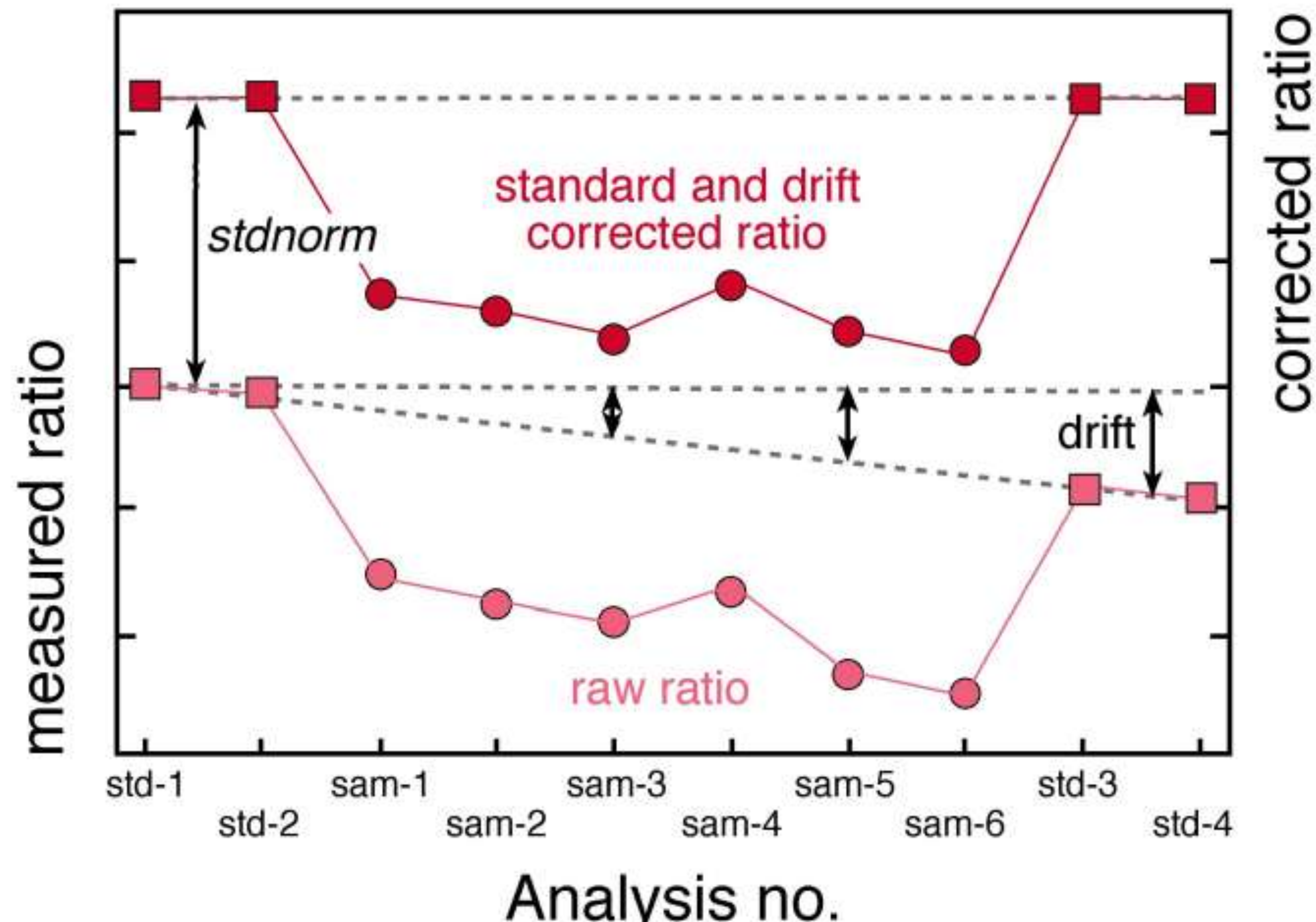
fractionation – $^{206}Pb/^{238}U$



fractionation – $^{206}Pb/^{238}U$

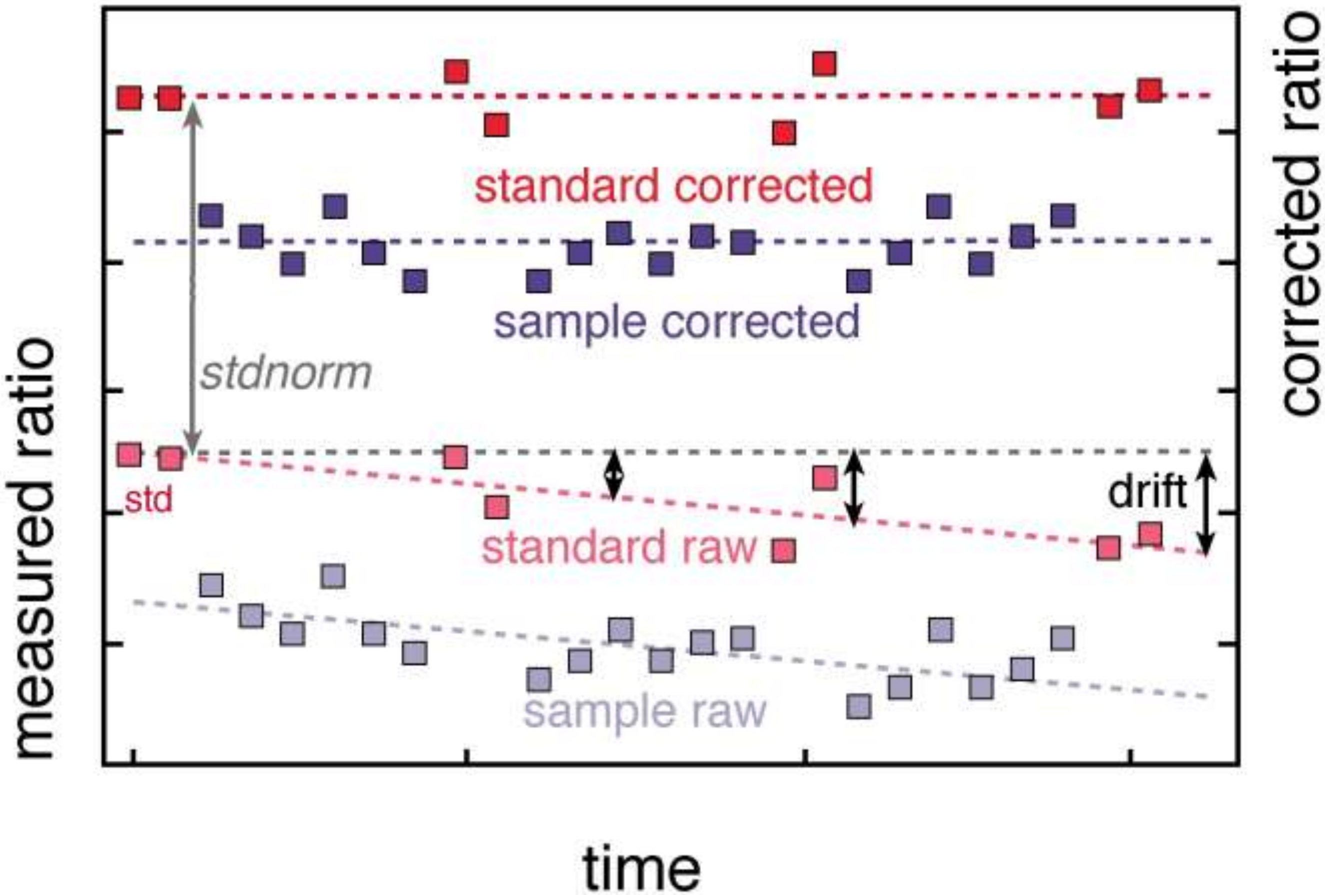


drift correction



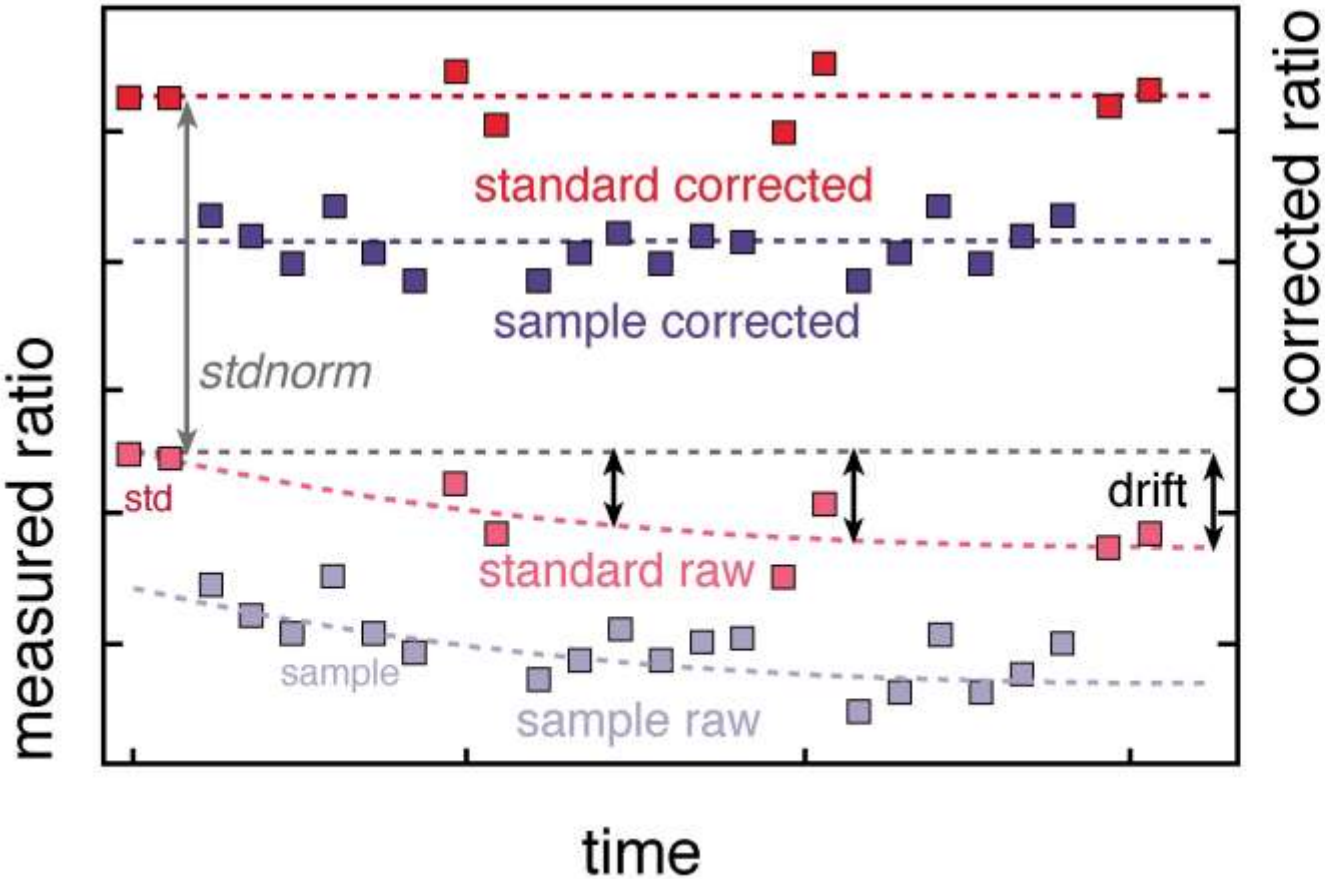
drift correction

linear



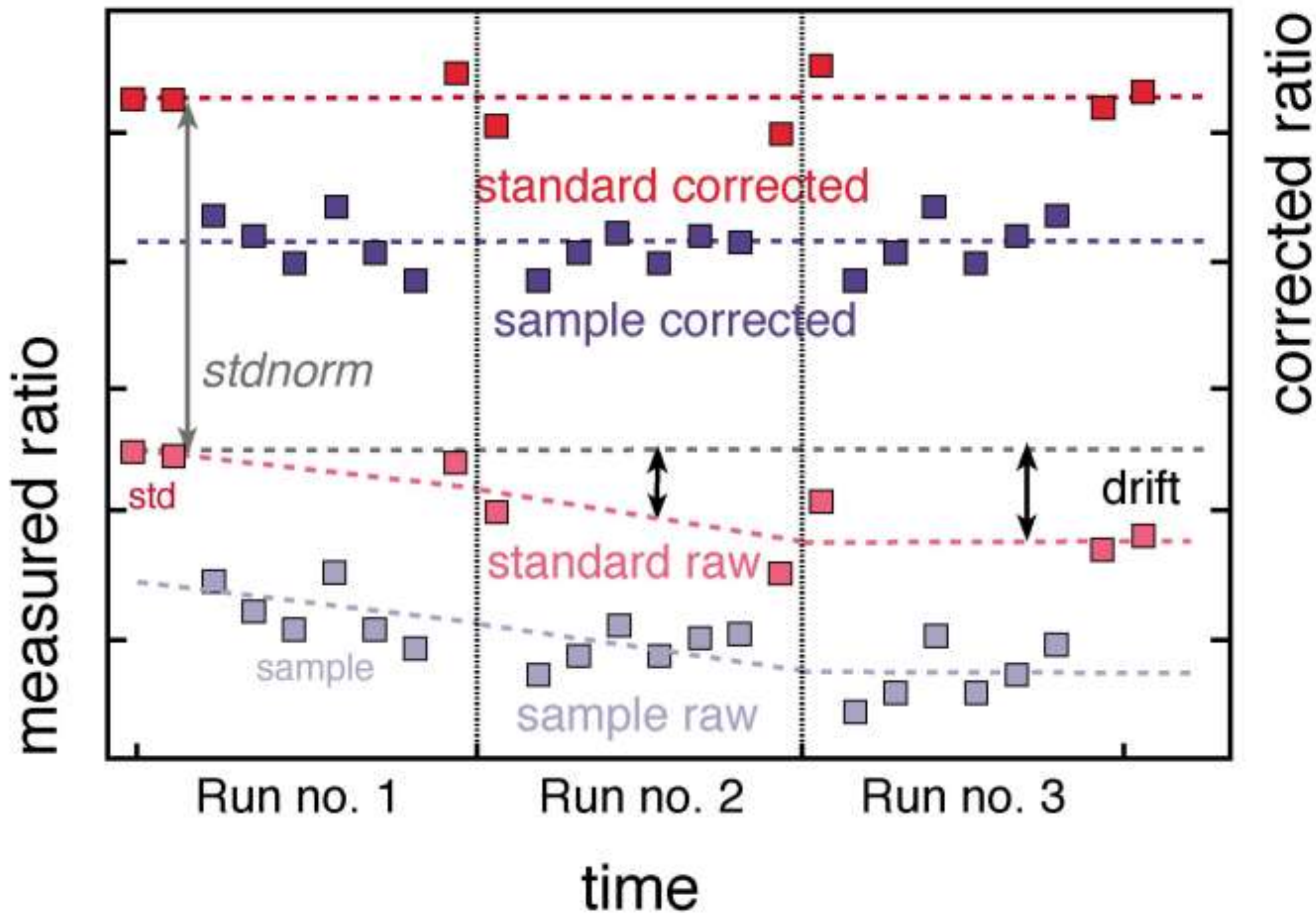
drift correction

polynomial curve fit

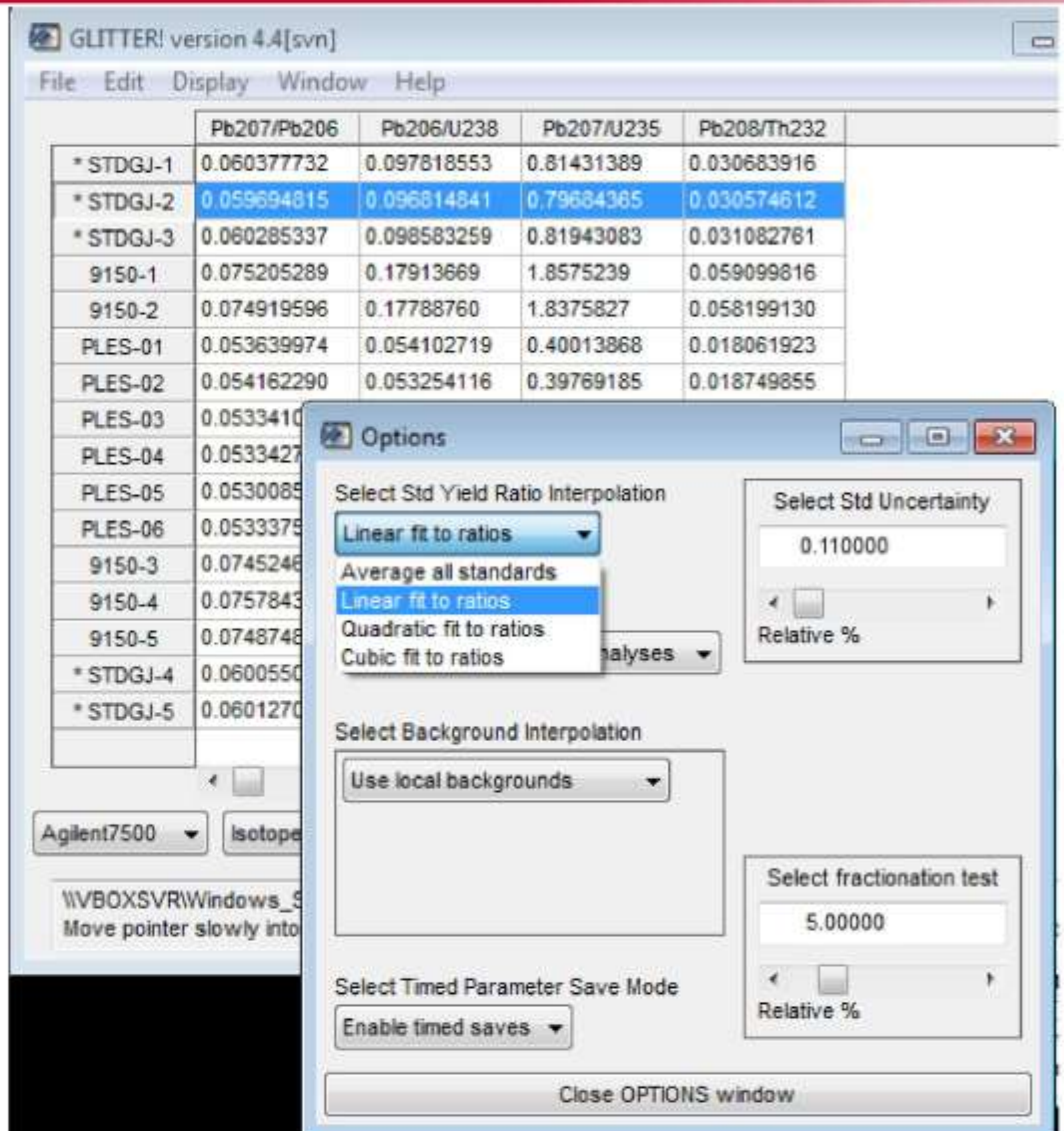


drift correction

linear segments – 'runs'



Glitter – drift correction



drift correction

For multiple groups of standards interpolated yield values are calculated for intermediate analyses.

There are several options for the interpolation:

- average all standards
- linear
- polynomial

For a linear drift correction:

$$stdnorm_{unk}^{n} = stdnorm_{std}^{0} + m \bullet n + b$$

where $stdnorm_{unk}^{n}$ is the interpolated yield value of the nth analysis

$stdnorm_{std}^{0}$ is the yield value for the first standard

n is the analysis number

m is the slope of the line of best fit

b is the intercept of the line of best fit

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uncertainty – drift correction

$$R_{unk}^{n,corr} = R_{unk}^{n,meas} \bullet \left(\frac{R_{std}^{true}}{R_{std}^{meas}} \right)$$

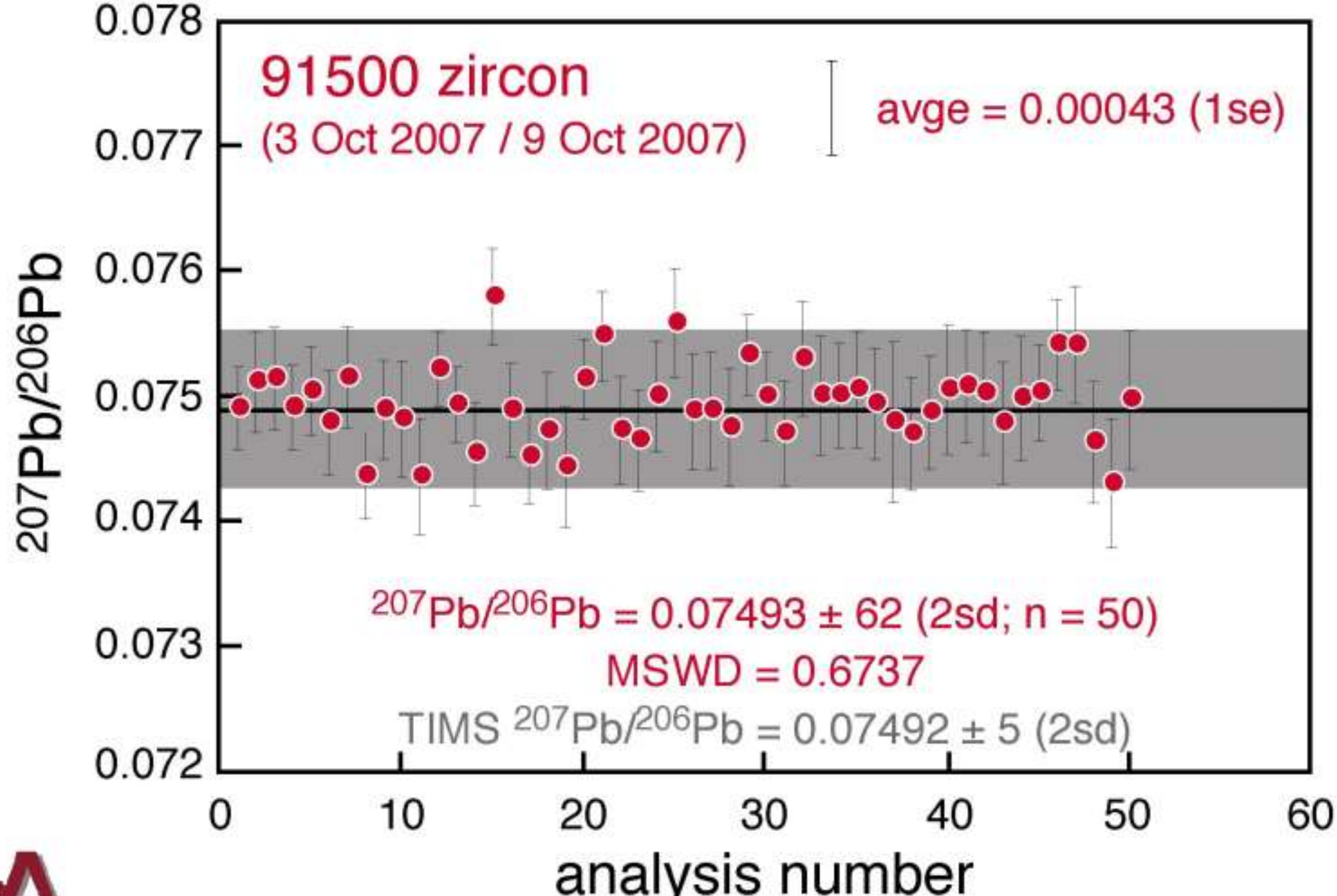
standard normalization factor

$$u(R_{unk}^{n,corr}) = R_{unk}^{n,corr} \bullet \sqrt{\left[\left(\frac{u(I)_{unk}^{n,M1}}{(I)_{unk}^{n,M1}} \right)^2 + \left(\frac{u(I)_{unk}^{n,M2}}{(I)_{unk}^{n,M2}} \right)^2 + \left(\frac{u(stdnorm_{unk}^{n})}{stdnorm_{unk}^{n}} \right)^2 \right]}$$

$$u(stdnorm_{unk}^{n}) = stdnorm_{unk}^{n} \bullet \sqrt{\left[\left(\frac{u(I)_{std}^{M1}}{(I)_{std}^{M1}} \right)^2 + \left(\frac{u(I)_{std}^{M2}}{(I)_{std}^{M2}} \right)^2 + \left(\frac{u(R)_{std}^{true}}{(R)_{std}^{true}} \right)^2 + u(m)^2 \bullet n^2 + u(b)^2 \right]}$$

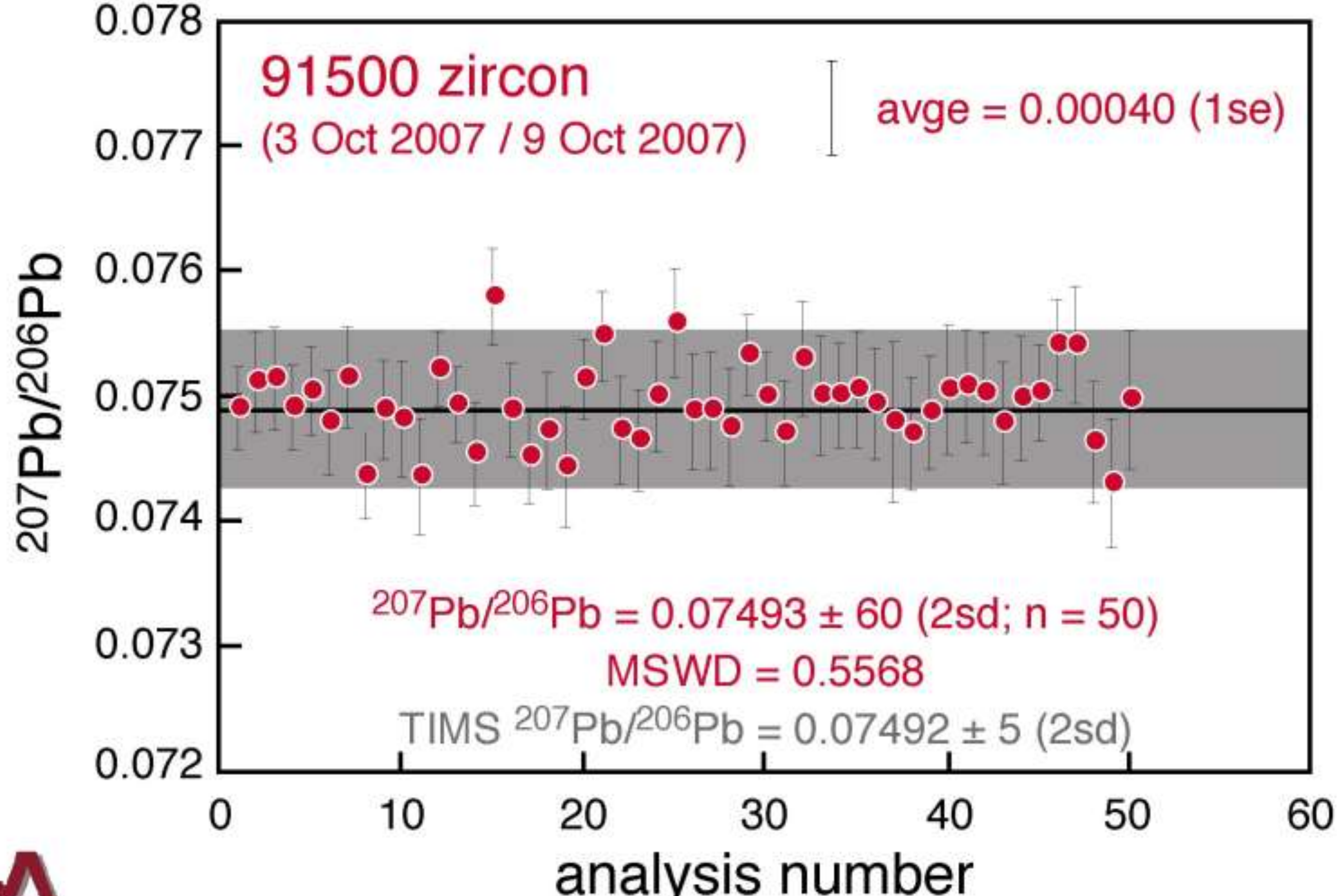
external precision – short-term

ratio of means



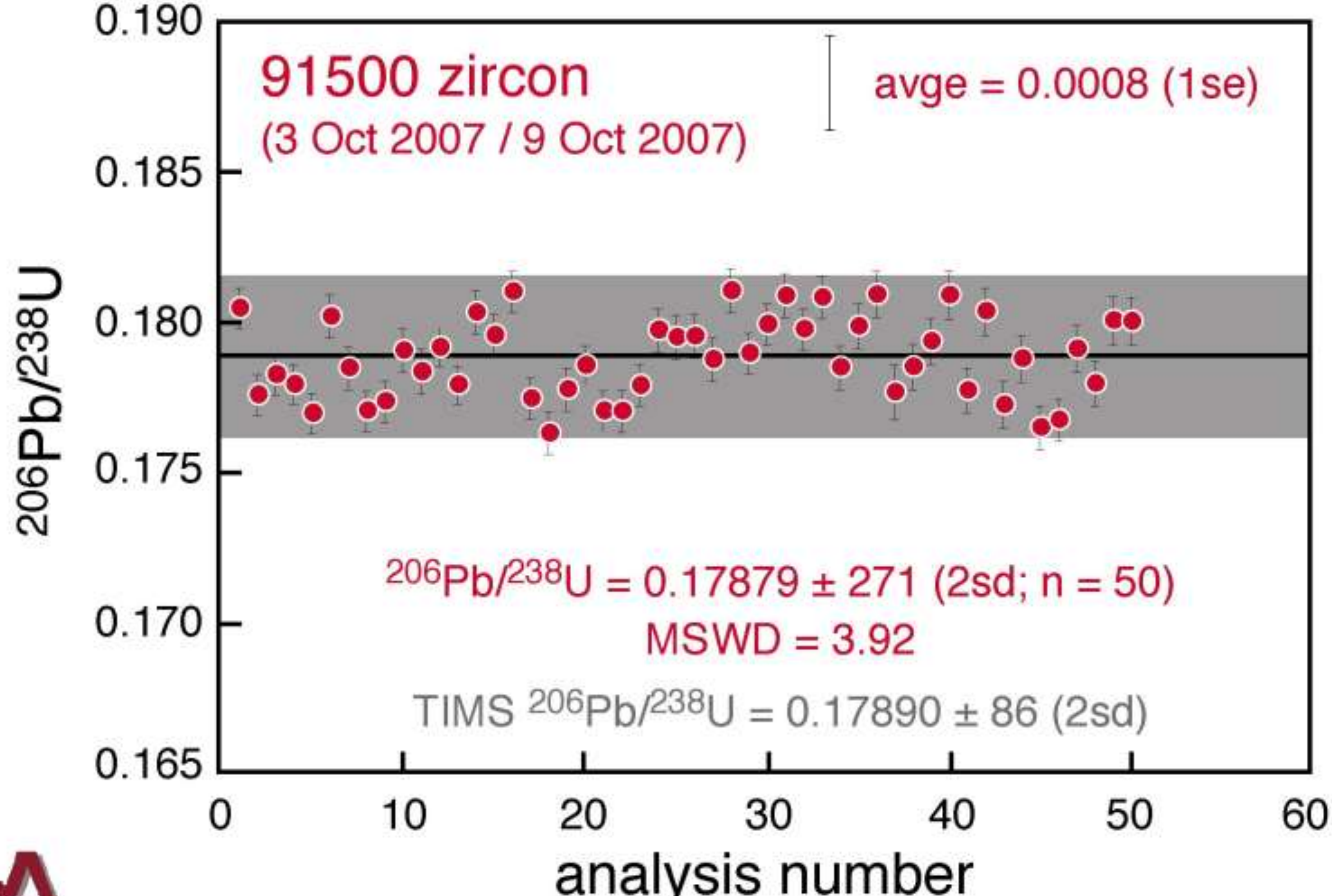
external precision – short-term

mean of ratios



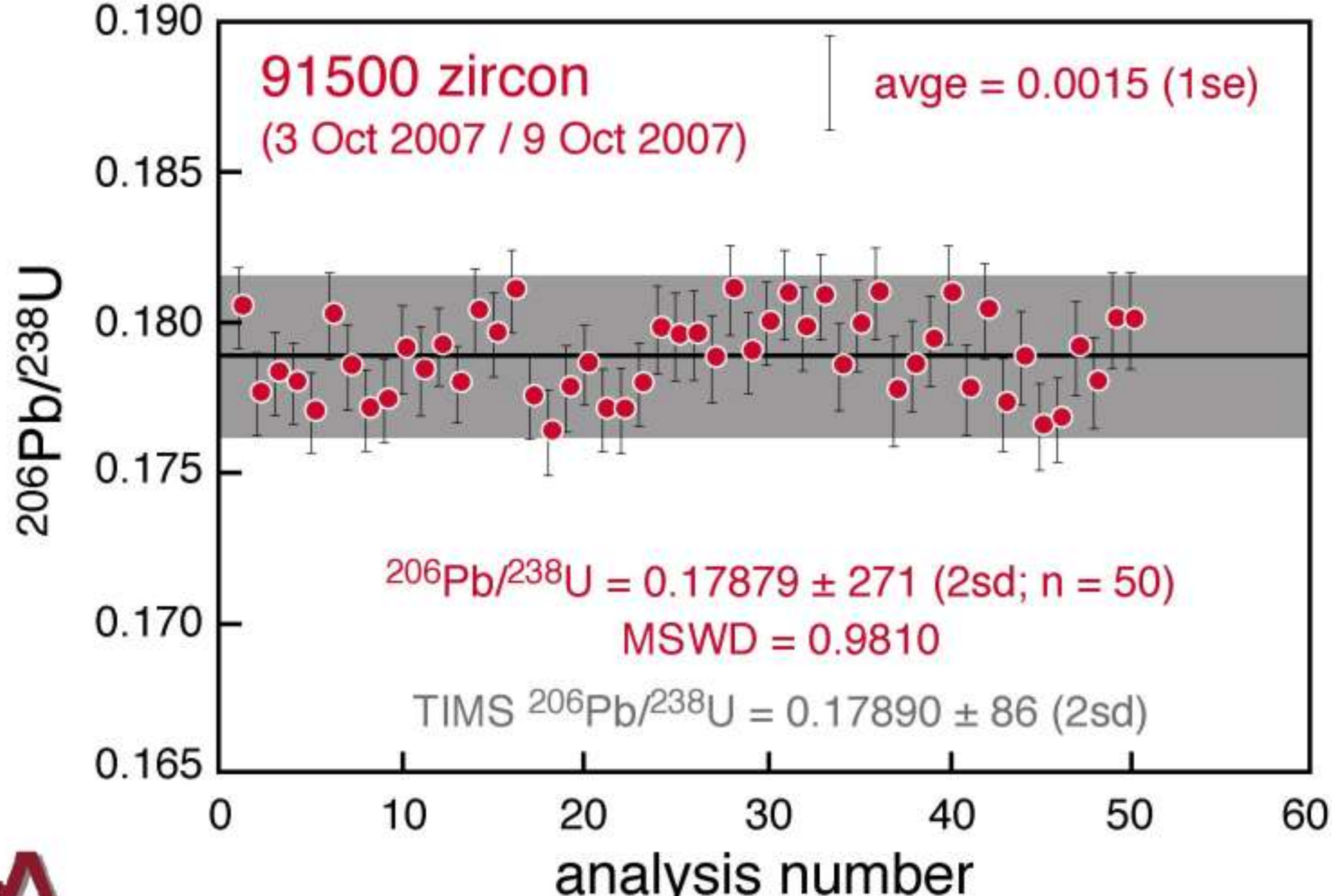
external precision – short-term

ratio of means

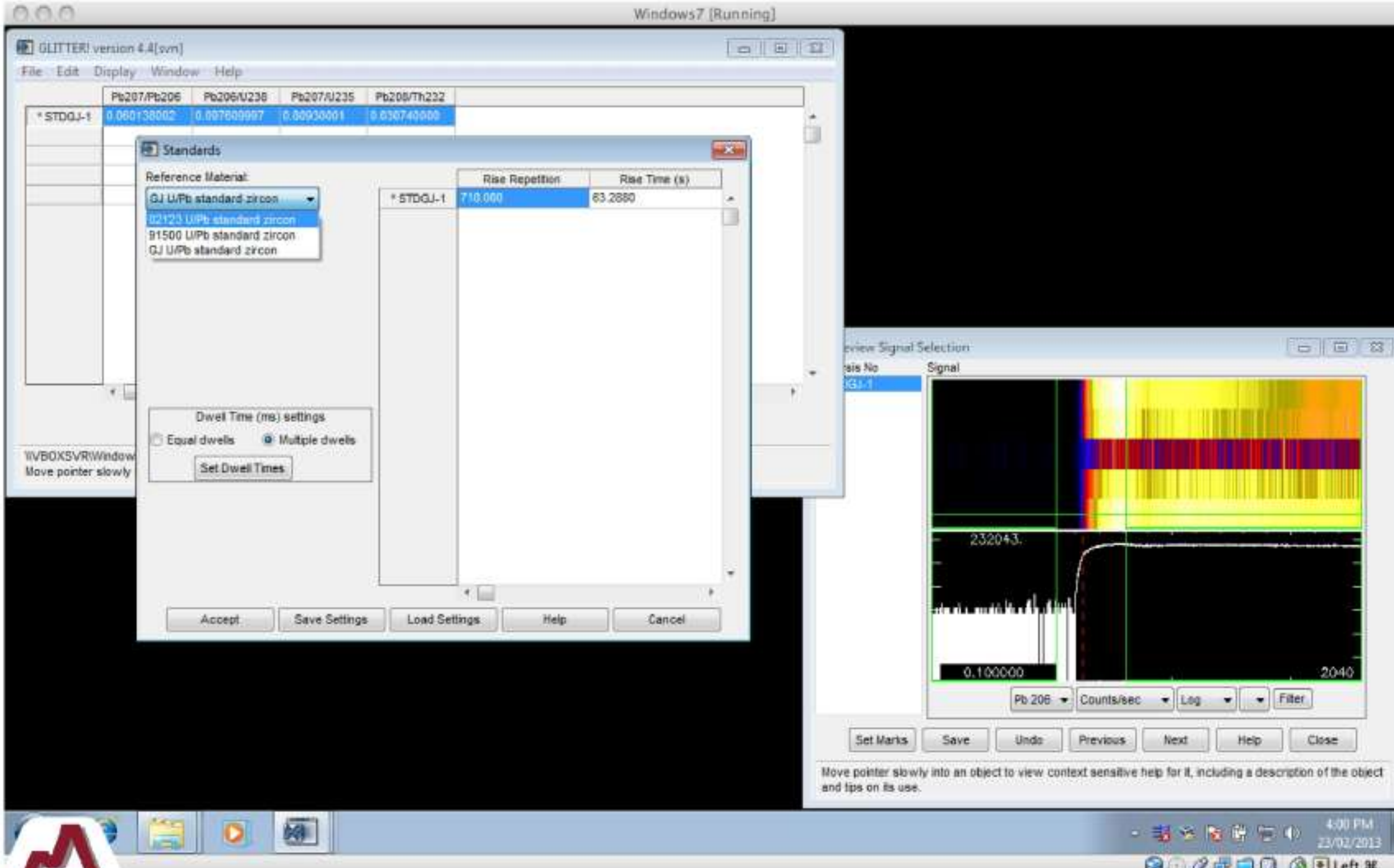


external precision – short-term

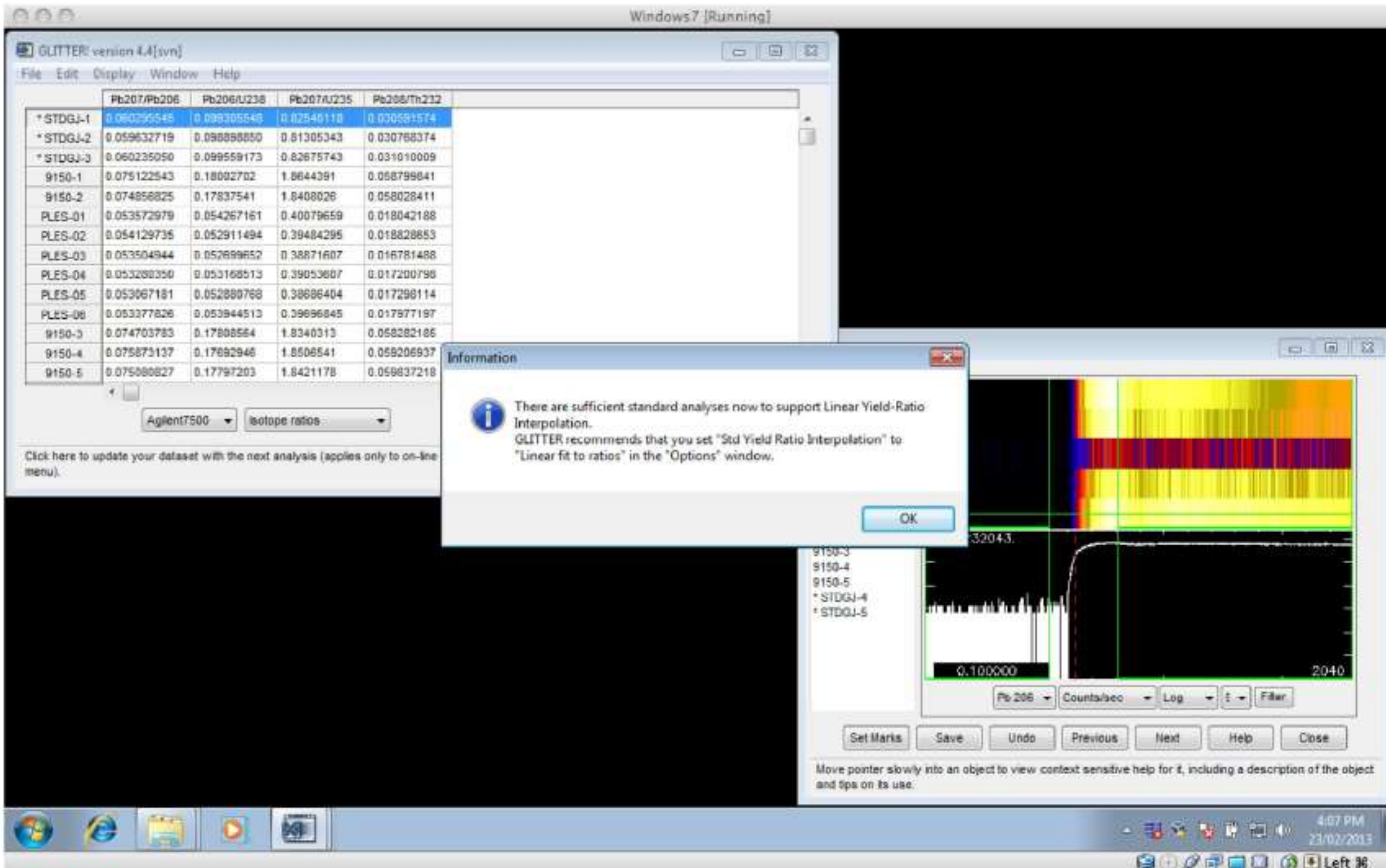
mean of ratios



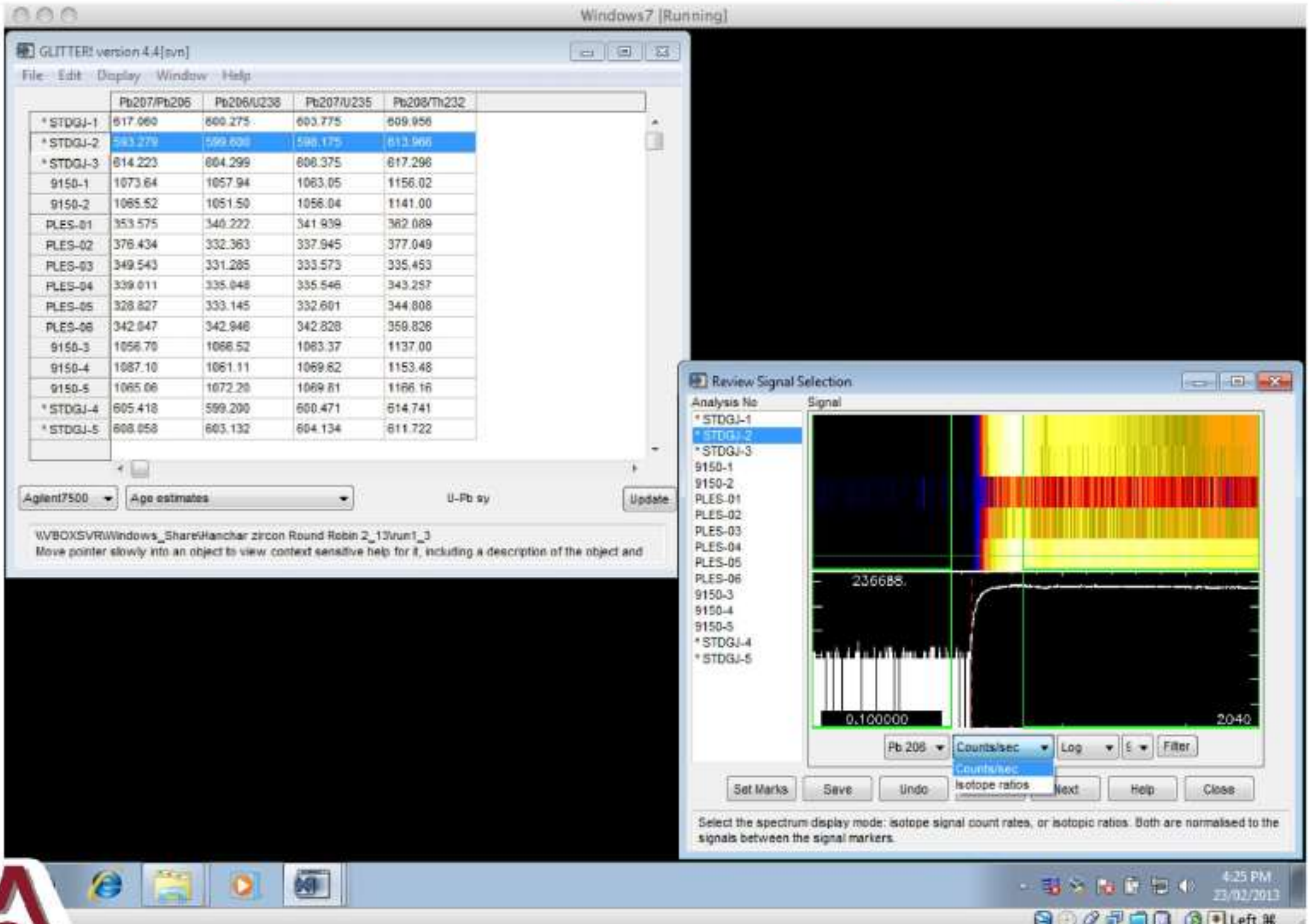
Glitter – calibration standard



Glitter – drift correction



Glitter – age results



Glitter – drift correction