Quick Guide on the RESTREX routine

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Contents

Part I
Guide

1 RESTREX

For the evaluation of the Neptune results, the pre-installed Neptune *Eval* software was delivering on-line results for signals and corrected isotope ratios, without standard bracketing though. With the reasoning of gaining insight and control over the calculations performed, a custom Python routine named *RESTREX* (Retzbach Strontium Examinator) was coded as well, which is presented in this section. It can be retrieved on the author's GitHub page under https://AchimRetzbach.github.io/RESTREX/, and its code is licensed under CC-BY 4.0 for use by other researchers. Because of this better transparency and confidence in the calculation, usually the custom results for the isotope ratios were used instead of the Neptune's ones.

Input of the files is achieved by simply specifying the path of the folder in which the mass spectrometer stores its output files. The routine automatically searches for the relevant .exp-files and tries to filter the file for the relevant data (i.e. without prefix and suffix lines) by trial-and-error. That is, systematically trying out different prefix-suffix-line combinations until no error message is delivered. This had to be done since their number seems to vary from file to file. Theoretically, no additional information needs to be given, although the script allows the setting of different options, e.g. which plots to show, if to perform a blank correction, which sigma clipping to use (standard: 2σ) and more. Also note that the assumed-to-be-constant quantities like the masses of the measured isotopes and the natural isotope ratios used for corrections can be specified in the beginning of the file as set variables. Within this thesis, they were set the following:

Quantity	Value (error)	Source
$m_{^{83}\mathrm{Kr}}$	82.91412716(32)	NIST website
$m_{^{84}\mathrm{Kr}}$	83.9114977282(44)	NIST website
$m_{^{84}\mathrm{Sr}}$	83.9134191(13)	NIST website
$m_{^{85}\mathrm{Rb}}$	84.9117897379(54)	NIST website
$m_{^{86}\mathrm{Kr}}$	85.9106106269(41)	NIST website
$m_{^{86}\mathrm{Sr}}$	85.9092606(12)	NIST website
$m_{^{87}\mathrm{Rb}}$	86.9691805310(60)	NIST website
$m_{^{87}\mathrm{Sr}}$	86.9088775(12)	NIST website
$m_{^{88}\mathrm{Sr}}$	87.9056125(12)	NIST website
$\left(\frac{^{83}\mathrm{Kr}}{^{84}\mathrm{Kr}}\right)_{norm}$	0.201750	-TODO-
$\left(\frac{^{83}\mathrm{Kr}}{^{86}\mathrm{Kr}}\right)_{norm}$	0.664740	-TODO-
$\left(\frac{^{85}\mathrm{Rb}}{^{87}\mathrm{Rb}}\right)_{norm}$	2.592310	-TODO-
$\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{norm}$	8.375209	Nier 1938

Table 1: Set isotope masses and natural isotope ratios

Note that the isotope ratios are given without error since their objective is to be used as fixed, error-less constants to which our measurement is being normalized, than actual physical quantities.

Finally, the output isotope ratios are stored in a `.csv`-table in a corresponding sub-folder to the script.

The aim of the now presented evaluation routine is, to perform the necessary steps to get from the raw isotope signals, given by their voltage measured at the amplifier, to the final isotope ratio involving all corrections presented. To illustrate its functionality, a flow chart depicting the main technical steps inside of the script is given and the most important corrections employed by the routine are described in further detail.

neptune_auswertung.py – Program Chart

main method

evaluateSequence(...):
- Preparation of output directory
- Selection of correct files in input directory
- Setting measurement types *(if not given)* (i.e. blank/wash/ standard/sample)
- Getting data of individual measurements, determining & setting blank correction
- Performing standard bracketing
- Possible plots & tables:

$$\left(\frac{^{84}Sr}{^{86}Sr}\right) \quad \left(\frac{^{87}Sr}{^{86}Sr}\right) \quad \left(\frac{^{88}Sr}{^{86}Sr}\right)$$

$$\Delta\left(\frac{^{84}Sr}{^{86}Sr}\right) \quad \Delta\left(\frac{^{87}Sr}{^{86}Sr}\right) \quad \Delta\left(\frac{^{88}Sr}{^{86}Sr}\right)$$

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{own} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{nep}$$

- Writing bracketing-corrected, Non-bracketing-corrected and Neptune results of each measurement in respective files for further examination

major methods

evaluateMeasurement(...):
- Reading-in and sorting of data
- Conversion to float-values
- Double-checking Neptune outliers and re-formatting them back to numbers (for plots)
- Option to take absolute value
- Calculation of raw isotope ratios
- Calculation of mean signals
- Blank correction (if previous mean signals given)
- Linear isotope correction (LIC)
- Iterative isotope correction (EIC) *(if not a wash/blank measurement)*
- Mass fractionation correction *(if not a wash/blank measurement)*
- Calculation of σ-clipped means and errors
- Comparison with Neptune ratios
- Calculation of Allan variances *(if enabled)*
- Possible plots & tables:

$$^{82}Kr \quad ^{83}Kr \quad ^{84}Sr \quad ^{85}Rb \quad ^{86}Sr \quad ^{87}Sr \quad ^{88}Sr$$

$$\left(\frac{^{84}Sr}{^{86}Sr}\right) \quad \left(\frac{^{87}Sr}{^{86}Sr}\right) \quad \left(\frac{^{88}Sr}{^{86}Sr}\right)$$

$$\left(\frac{^{84}Sr}{^{86}Sr}\right)_{own} - \left(\frac{^{84}Sr}{^{86}Sr}\right)_{nep}$$

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{own} - \left(\frac{^{87}Sr}{^{86}Sr}\right)_{nep}$$

$$\left(\frac{^{88}Sr}{^{86}Sr}\right)_{own} - \left(\frac{^{88}Sr}{^{86}Sr}\right)_{nep}$$

over cycle, Rb and Kr signals

$$\sigma_{Allan}\left(\frac{^{84}Sr}{^{86}Sr}\right) \quad \sigma_{Allan}\left(\frac{^{87}Sr}{^{86}Sr}\right)$$

$$\sigma_{Allan}\left(\frac{^{88}Sr}{^{86}Sr}\right)$$

- Outputting ratios & errors as means or full arrays

standardBracket(...):
- Determining samples and standards around them in the obtained data set using measurement types
- *Option do do this cycle-wise (usually not enabled)*
- Calculation of bracketing-corrected sample ratios
- Outputting bracketing-corrected sample ratios

minor methods

outlierCheck(...):
- Searching for Neptune outliers, re-formatting them to float values
- Calculation of own outliers
- Checking if they match
- Outputting error code and re-formatted Neptune ratios

linearIsotopeCorrection(...):
- Calculating and outputting LIC-corrected isotope ratios from raw signals
(EIC does not have a comparable function because calculation between ratios is interdependent)

thermoMassFractionation(...):
- Calculating and outputting fractionation-corrected isotope ratios based on LIC-/EIC-corrected ones (usually EIC-option is chosen)

clippedMeanError(...):
- Generating isotope ratio array without outliers *(or use mask if given)*
- Outputting its mean and error

ratioCheck(...):
- Checking if σ-clipped isotope ratios correspond to those of the Neptune up to a specific digit
- Error messages if they do not

allanVariance(...):
- Calculating and outputting the Allan variance of a given array

utility methods

std(...):
- Calculating and outputting the **empiric** variance of an input array *(needed because uses statistical variance)*

outlierMask(...):
- Generating and outputting a boolean mask array indicating if each value of an input array is an outlier or not

ripPath(...):
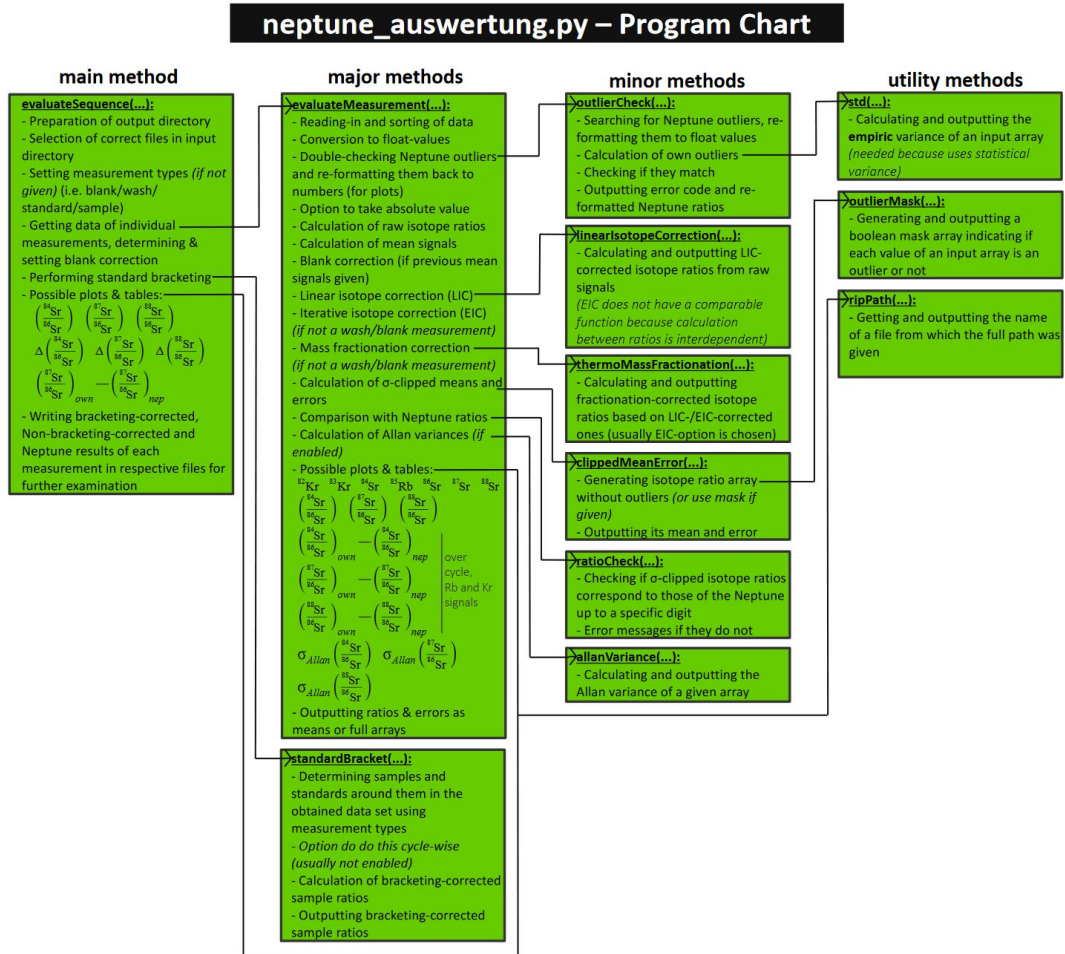- Getting and outputting the name of a file from which the full path was given

Figure 1: Flow chart of Neptune evaluation routine

1.0.1 Blank correction

In order to minimize the influence of memory effects (i.e. leftover signals from previous measurements), other contamination in the machine or systematic electronic signals, a blank correction was performed with each standard or sample measurement. This was achieved by subtracting the mean of the previous blank measurement for each cycle in each cup's signal individually before using them for further calculations. In cases where there was no such blank measurement (i.e. due to file corruption) zero was being subtracted. While technically the subtracted blank signal as a mean of individual blank measurements has an error, the data shows that for even (comparably) low concentrations as 5-10 ppb Sr the mean error of the blank is several magnitudes smaller than the observed scatter within standard/sample measurements. To give an example, for the first sample of the following 'reference sample measurement', the ^{88}Sr signal intensity was about 8.02799 ± 0.04429 V while the same signal for the previous blank measurement is at 0.00498 ± 0.00017 V, leading to a signal-to-noise ratio of about 1600. Similar orders of magnitude are observed for the other isotopes. Therefore the conclusion is that calculating the error from the standard deviation of many blank-corrected single measurements is sufficient for a physical error estimation.

1.0.2 Interference Isotope Correction

One of the main challenges in determining precise Strontium isotope ratio measurements are the corrections for interference isotopes, most notably Rubidium (contained in some samples or introduced through contamination) and Krypton (introduced as residual gas in the Argon input of the machine). Therefore, the routine is able to correct for the interference of ^{84}Kr, ^{86}Kr and ^{87}Rb based on the measured ^{83}Kr and ^{85}Rb signals and their assumed natural ratios specified in table 1. This can be achieved using two different methods, both described in Thermo Fisher Scientific [2008]:

- **Linear Element Interference Correction (LIC):** The measured ^{83}Kr and ^{85}Rb signals and the known isotope ratios for both elements are used to calculate the corresponding ^{84}Kr, ^{86}Kr and ^{87}Rb signals, which are conclusively subtracted from the measured (i.e. total) signal at the respective mass. This is done cycle-wise, i.e. for each single measurement. For those, the corrected Sr intensities therefore look as follows:

$$^{84}\text{Sr}_{lic} = {}^{84}\text{Sr}_{meas} - \frac{{}^{83}\text{Kr}_{meas}}{\left(\frac{{}^{83}\text{Kr}}{{}^{84}\text{Kr}}\right)_{norm}} \tag{1}$$

$$^{86}\text{Sr}_{lic} = {}^{86}\text{Sr}_{meas} - \frac{{}^{83}\text{Kr}_{meas}}{\left(\frac{{}^{83}\text{Kr}}{{}^{86}\text{Kr}}\right)_{norm}} \tag{2}$$

$$^{87}\text{Sr}_{lic} = {}^{87}\text{Sr}_{meas} - \frac{{}^{85}\text{Rb}_{meas}}{\left(\frac{{}^{85}\text{Kr}}{{}^{87}\text{Kr}}\right)_{norm}} \tag{3}$$

Afterwards, the corrected intensities are used to calculate the Sr isotope ratios of interest.

- **Iterative Element Interference Correction (EIC):** This method works as the LIC in the first step (i.e. also cycle-wise), but instead of simply returning the linearly corrected isotope ratios as-is, the $\frac{{}^{88}\text{Sr}}{{}^{86}\text{Sr}}$ ratio is used further on to calculate the fractionation of the $\frac{{}^{83}\text{Kr}}{{}^{86}\text{Kr}}$ ratio, which is then in turn used to get a new $\frac{{}^{88}\text{Sr}}{{}^{86}\text{Sr}}$ and start another iteration i:

$$\left(\frac{{}^{83}\text{Kr}}{{}^{86}\text{Kr}}\right)_{norm,i} = \left(\frac{{}^{83}\text{Kr}}{{}^{86}\text{Kr}}\right)_{norm} \cdot \left(\frac{\left(\frac{{}^{88}\text{Sr}}{{}^{86}\text{Sr}}\right)_{eic,i}}{\left(\frac{{}^{88}\text{Sr}}{{}^{86}\text{Sr}}\right)_{norm}}\right)^{a_1} \tag{4}$$

$$^{86}\text{Sr}_{eic,i+1} = {}^{86}\text{Sr}_{eic,i} - \frac{{}^{83}\text{Kr}_{meas}}{\left(\frac{{}^{83}\text{Kr}}{{}^{86}\text{Kr}}\right)_{norm,i}} \tag{5}$$

$$\left(\frac{{}^{88}\text{Sr}}{{}^{86}\text{Sr}}\right)_{corr,i+1} = \frac{{}^{88}\text{Sr}_{meas}}{{}^{86}\text{Sr}_{corr,i+1}} \tag{6}$$

with

$$a_1 = \frac{\log\left(m_{^{83}\mathrm{Kr}}/m_{^{86}\mathrm{Kr}}\right)}{\log\left(m_{^{88}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)} \tag{7}$$

$$^{86}\mathrm{Sr}_{eic,0} = {}^{86}\mathrm{Sr}_{meas} \tag{8}$$

$$\left(\frac{^{83}\mathrm{Kr}}{^{86}\mathrm{Kr}}\right)_{norm,0} = \left(\frac{^{83}\mathrm{Kr}}{^{86}\mathrm{Kr}}\right)_{norm} \tag{9}$$

Once this iterative approach comes to a halt at iteration j, its results are used to correct the other Strontium isotope ratios as well:

$$\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{eic} = \frac{{}^{84}\mathrm{Sr}_{meas} - \frac{{}^{83}\mathrm{Kr}_{meas}}{\left(\frac{^{83}\mathrm{Kr}}{^{84}\mathrm{Kr}}\right)_{norm,corr}}}{{}^{86}\mathrm{Sr}_{corr,j}} \tag{10}$$

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{eic} = \frac{{}^{87}\mathrm{Sr}_{meas} - \frac{{}^{85}\mathrm{Rb}_{meas}}{\left(\frac{^{85}\mathrm{Kr}}{^{87}\mathrm{Kr}}\right)_{norm,corr}}}{{}^{86}\mathrm{Sr}_{corr,j}} \tag{11}$$

with

$$a_2 = \frac{\log\left(m_{^{83}\mathrm{Kr}}/m_{^{84}\mathrm{Kr}}\right)}{\log\left(m_{^{88}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)} \tag{12}$$

$$\left(\frac{^{83}\mathrm{Kr}}{^{84}\mathrm{Kr}}\right)_{norm,corr} = \left(\frac{^{83}\mathrm{Kr}}{^{84}\mathrm{Kr}}\right)_{norm} \cdot \left(\frac{\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{corr,j}}{\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{norm}}\right)^{a_2} \tag{13}$$

$$a_3 = \frac{\log\left(m_{^{85}\mathrm{Rb}}/m_{^{87}\mathrm{Rb}}\right)}{\log\left(m_{^{88}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)} \tag{14}$$

$$\left(\frac{^{85}\mathrm{Rb}}{^{87}\mathrm{Rb}}\right)_{norm,corr} = \left(\frac{^{85}\mathrm{Rb}}{^{87}\mathrm{Rb}}\right)_{norm} \cdot \left(\frac{\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{corr,j}}{\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{norm}}\right)^{a_3} \tag{15}$$

6

The iterations are performed so long until either the result does not change anymore (usually 6-9 times on the 17-digit numbers used by Python) or the number of iterations reaches a pre-defined limit (in this work always set to 20).

The errors of a_1, a_2 and a_3 are, because of the precise mass determinations, assumed to be sufficiently small to neglect it. Note that the subscript *meas* refers to measured, and (if turned on) previously blank-corrected isotope signals or ratios thereof.
For standard and sample measurements, the EIC is being used, for washes and blanks the LIC.

1.0.3 Internal Mass Fractionation Correction

Furthermore, an internal mass fractionation correction is being performed. This is, according with the most common objective of determining precise $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ ratios, achieved by normalizing to the fixed $\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{norm} = 8.375209$ (Nier [1938], Banner [2004]).
The reasoning behind this is that, while $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ seems to be highly variable in nature because of the ^{87}Rb decay, $\frac{^{88}\text{Sr}}{^{86}\text{Sr}}$ is mostly not, at least not on the level that could have been resolved by previous generations of mass spectrometers (Banner [2004]). For the sake of completeness, this conclusion does not seem to be fully fixed (Fietzke and Eisenhauer [2006]) with contemporary techniques, a further elaboration on this is, however, not in the scope of this master thesis.
Given that, the correction is employed cycle-wise on the already interference-corrected isotope ratios and looks as follows (based on Thermo Fisher Scientific [2008]):

$$\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{frac} = \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{ic} \cdot \left(\frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{norm}}{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{ic}}\right)^{a_1} \tag{16}$$

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{frac} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{ic} \cdot \left(\frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{norm}}{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{ic}}\right)^{a_2} \tag{17}$$

with

$$a_1 = \frac{\log\left(m_{^{84}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)}{\log\left(m_{^{88}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)} \tag{18}$$

$$a_2 = \frac{\log\left(m_{^{87}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)}{\log\left(m_{^{88}\mathrm{Sr}}/m_{^{86}\mathrm{Sr}}\right)} \tag{19}$$

The subscript *ic* indicates the previously interference-corrected ratio (i.e. either *lic* or *eic*), while the subscript *frac* stands for the then derived mass fractionation-corrected one. Again, the errors of the masses are assumed small enough to be neglected.

Naturally, since the $\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}$ ratio is employed in the correction, it cannot be used to correct itself. Therefore, for the further analysis, the interference- and mass fractionation-corrected $\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}$ and $\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}$ are used, while the corresponding $\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}$ ratios are only interference-corrected. Still, for most of the experiments depicted later on, the $\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}$ will be depicted as well as a means of quality control and in order to provide additional insight. At this point in the script, the sigma-clipped means and its mean errors are calculated and forwarded to the next correction step.

1.0.4   Standard Bracketing

Following interference correction, mass fractionation correction (except $\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}$, see above paragraph) and mean calculation (with sigma-clipping) on the individual measurements' results, the method of so-called 'standard bracketing' is employed on standard and sample measurements following one another. The goal of this is to eliminate any deviations still left in the data by measuring a standards of known isotopic composition and using their measured deviations for the correction. As stated before, within this thesis, the calcium carbonate standard NIST SRM 987 was used. The calculation was done as follows (Krabbenhöft [2011], I.14):

$$\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{corr} = \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)_{known}}{\sqrt{\left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean} \cdot \left(\frac{^{84}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}} \qquad (20)$$

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{corr} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{known}}{\sqrt{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean} \cdot \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}} \qquad (21)$$

$$\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{corr} = \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{known}}{\sqrt{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean} \cdot \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}} \qquad (22)$$

The upscripts *smp, std1* and *std2* refer to the mean ratio of the sample measurement, the standard measurement right before the sample, and the one right after, respectively. The subscripts *known, mean* and *corr* refers to the known isotope ratios for the NIST SRM987, the sigma-clipped mean values as delivered after the previous correction step and the final result after the bracketing.

1.0.5   Error Determination

Errors are determined after the internal mass fractionation step by taking the collections of individually corrected isotope ratios, calculating their mean, removing 2σ outliers and then calculating the error of the new mean.
This makes sense when one considers that the correction are essentially aimed at reducing noise and therefore error, but already calculating errors before and propagating them would lead to higher errors instead. This logic does not hold for the standard bracketing anymore though, because instead of one continuous series of measurements of one sample, multiple distinct ones are compared. Therefore, the error in standard bracketing is calculated using Gaussian error propagation. Shown for the example of $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{corr}$, this looks as follows:

$$\Delta\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{corr} = \left[\left(\Delta\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{known}}{\sqrt{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean} \cdot \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}}\right)^2 \right.$$

$$+ \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{known} \cdot \Delta\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean}}{2 \cdot \sqrt{\left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean}\right)^3 \cdot \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}}\right)^2$$

$$\left. + \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{smp}_{mean} \cdot \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{known} \cdot \Delta\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}}{2 \cdot \sqrt{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std1}_{mean} \cdot \left(\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)^{std2}_{mean}\right)^3}}\right)^2\right]^{1/2}$$

1.1 Comparison of Own and Neptune Evaluation

Besides personal understanding of the calculations involved and having greater control over them, one of the aims in programming a custom evaluation routine was to check the plausibility of the results delivered by the ThermoFisher Neptune spectrometer software. This can be constantly done by plotting the deviations between Neptune-delivered values against own inside of the evaluation routine. Oone should note that the Neptune-values are not blank-corrected and therefore the custom blank correction should be turned of for meaningful comparison (the other corrections are set up as described). Here, it is presented exemplary for the SR2d.5 sample. The different correction methods are abbreviated as in section 1.

Starting with the sample, best agreement is achieved with EIC and mass fractionation correction (the latter naturally only for $\frac{^{84}Sr}{^{86}Sr}$ and $\frac{^{87}Sr}{^{86}Sr}$) turned on:

First of all, the better results for the EIC (compared to the LIC) do not come by surprise, since it was the method of interference correction set up in the files for Strontium measurements left by ThermoFisher at the installation of the spectrometer, which were not changed through the course of these experiments.
In terms of the overall precision, it can be observed, that for $\frac{^{84}Sr}{^{86}Sr}$ and $\frac{^{88}Sr}{^{86}Sr}$, the deviations are on the order of magnitude of 10^{-9} and 10^{-10}, respectively, this being on a much lower scale than the usual uncertainties. For $\frac{^{87}Sr}{^{86}Sr}$ however, the order of magnitude of the deviations is about 10^{-7}, which is in fact on a similar scale than the uncertainty of the measurements and therefore could potentially be relevant.
Given that this is still an admittedly small number, the deviations could be caused by otherwise irrelevant factors as different algorithms/approximation methods for the power term in the fractionation corrections, or by different values for the isotopic masses used by the Neptune software. With the largest deviations occuring for the $\frac{^{87}Sr}{^{86}Sr}$ ratio, an influence of the Rubidium interference correction could be suspected. This can be elaborated further on by a look into the correlation plot between $\frac{^{87}Sr}{^{86}Sr}$ ratio and ^{83}Kr or ^{85}Rb signals:
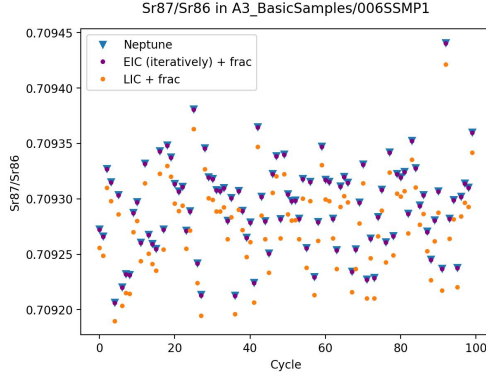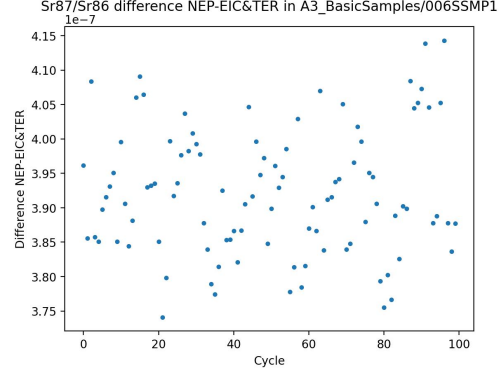
(a) Different calculation methods for $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ (SR2d.5 sample)
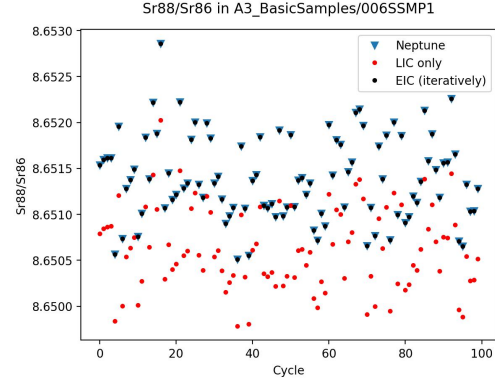
(b) Different calculation methods for $\frac{^{88}\text{Sr}}{^{86}\text{Sr}}$ (SR2d.5 sample)
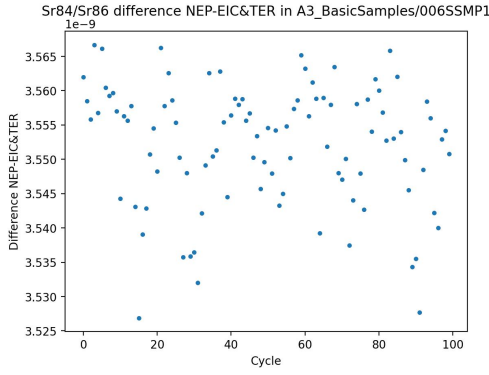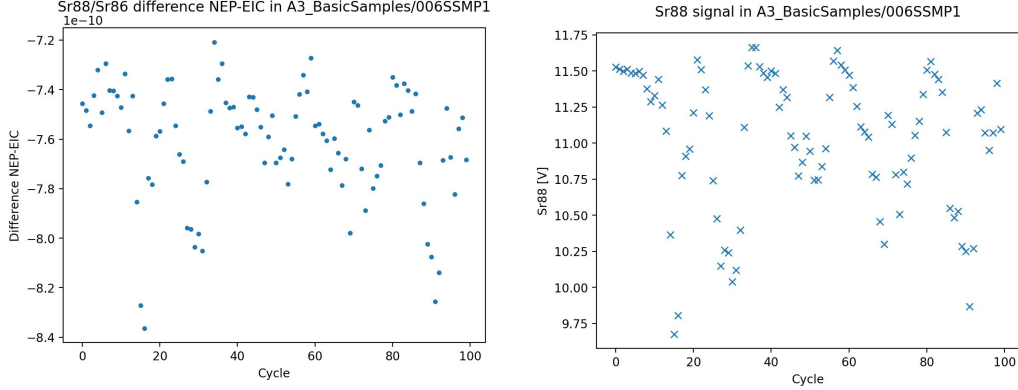

(c) Differences between own and Neptune's $\frac{^{84}\text{Sr}}{^{86}\text{Sr}}$ (SR2d.5 sample)

(d) Differences between own and Neptune's $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ (SR2d.5 sample)

As can be seen, this does not show any significant correlation at first. However, the following second standard measurement in the 'reference Samples' experiment does have an outlier with exceptionally high difference to the Neptune value, which can prove more insight:

(e) Differences between own and Neptune's $\frac{^{88}Sr}{^{86}Sr}$ (SR2d.5 sample)

(f) ^{88}Sr signal (SR2d.5 sample), for comparison

Figure 2: Differences between Sr isotope ratios from own and Neptune calculation (Sr2d.5 sample)

Here, the outlier seems to be correlated with the Rb signal for the $\frac{^{87}Sr}{^{86}Sr}$ ratio, which is being corrected for Rb interference. For the $\frac{^{84}Sr}{^{86}Sr}$ ratio, which is not influenced by the Rb correction in turn, the same outlier does not exhibit unusual isotopology. In the Kr correlation plots such effect cannot be observed with the outlier not having any raised ^{83}Kr. This is a hint towards the deviations mainly originating from the ^{85}Rb interference corrections, though it is recorded in one data point only.

A look into the same data for the wash immediately following the SR2d.5 sample from the reference sample experiment reveals the following, exemplarily shown for $\frac{^{87}Sr}{^{86}Sr}$:

As can be seen, the linear interference correction reproduces the Neptune output sufficiently well with all differences left being of pure numerical nature. This does even improve for the other isotope ratios and dismisses any need of EIC correction. In fact, the EIC fails in many of such because the exponential term's base in expressions 4 etc. can become negative for very low signals where the blank correction is frequently bigger than the signal itself. Possibly the ThermoFisher software stops the calculation at this point and therefore delivers the LIC-value as well.

This shows that the deviations observed previously can only occur as early as in the second iteration of the EIC where the mass fractionation power
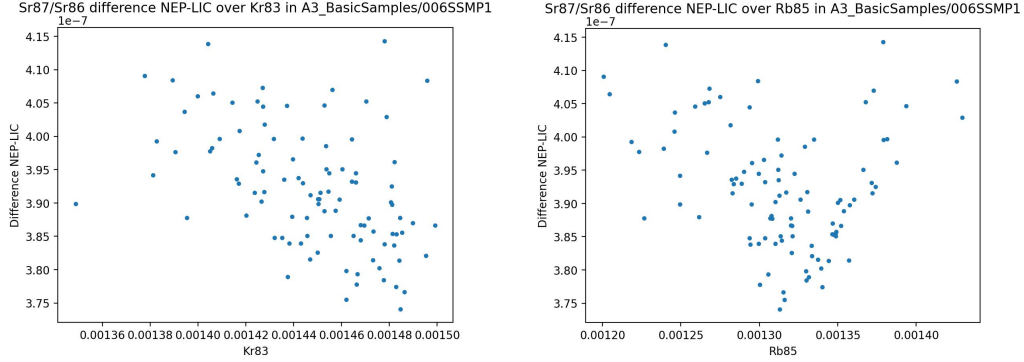
(a) Differences between own and Neptune's $\frac{^{87}Sr}{^{86}Sr}$ depending on ^{83}Kr signal (SR2d.5 sample)

(b) Differences between own and Neptune's $\frac{^{87}Sr}{^{86}Sr}$ depending on ^{85}Rb signal (SR2d.5 sample)

Figure 3: Calculated ratio differences depending on interference signals (Sr2d.5 sample)

term starts to play a role, backing up the previous thoughts on the source of error, which however, could not have been precisely determined as of today.

1.2 Hydride Influence

Another type of corrections that could have possibly been made in the Neptune evaluation routine would be corrections for possible molecular interferences. This would have required a similar approach as to the atomic interference correction presented so far. However, based on findings of other Sr measurements (e.g. Fietzke and Eisenhauer [2006], Konter and Storm [2014]) and backed up by own observations, it was concluded that this is not necessary.

In order to back this up, one needs to have a picture on which interferences would be expected in the first place. Because of the sample being dissolved in water and HNO_3 and consisting of large amounts of Sr, the most abundant molecule in the plasma is expected to be SRH, or, when considering the most abundant isotope, $^{88}Sr^1H$ at mass 89. A sensible way to quantify the amount of molecule interference is therefore to check the signal strength at a mass of 89 amu.

14
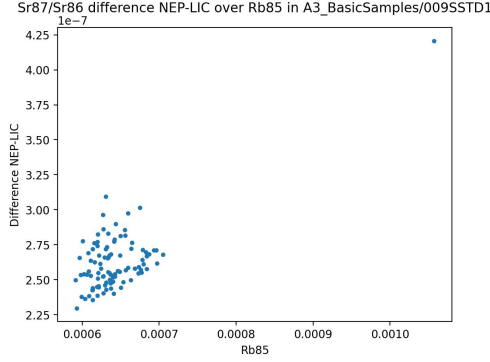
(a) Differences between own and Neptune's $\frac{^{87}Sr}{^{86}Sr}$ depending on ^{85}Rb signal (STD1, meas. 2)
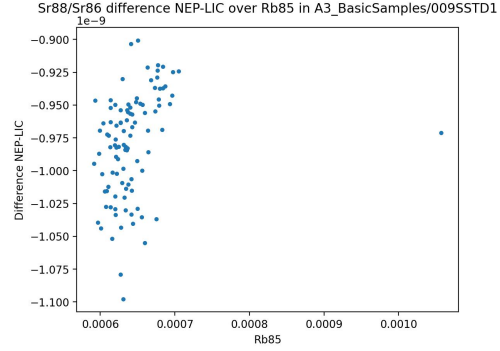
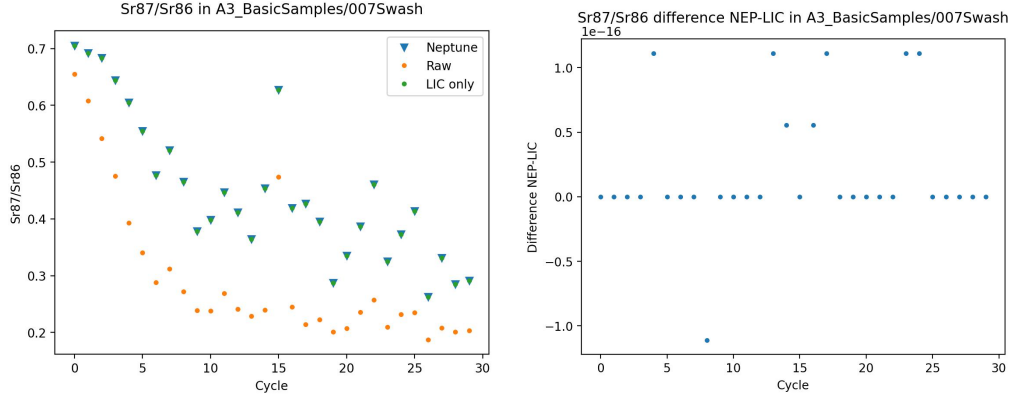(b) Differences between own and Neptune's $\frac{^{88}Sr}{^{86}Sr}$ depending on ^{85}Rb signal (STD1, meas. 2)

The intensity of this peak (if it is a real molecular peak and not some electronic artifact in the first place) is as low as about $3 \cdot 10^{-4}$V however. For comparison: the signal strength of ^{88}Sr is about 180V, the signal strength of ^{83}Kr about $1.5 \cdot 10^{-3}$V and the signal strength of ^{85}Rb about $5 \cdot 10^{-4}$V. This means that the possible influence of the most abundant molecule is about a factor 5 smaller than that one of the only relevant atomic interference correction and even smaller than the signal of an element that should not be present in any detectable amount in a coral sample in the first place.

Therefore, it is considered safe to assume that molecular interference plays no significant role for the results of the measurement.

(a) Own and Neptune results for $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ (wash3)

(b) Differences between own and Neptune's $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ (wash3)

2 RESTREX-Chemistry

While the iCAP's built-in software *QTegra* was already able of performing a concentration calibration, too (and, if it had been setup, the other corrections as well), for the sake of understanding and having better control of necessary drift and isobaric interference corrections, the *RESTREX-Chemistry* routine (Retzbach Strontium Examinator) was coded. It can be retrieved on the author's GitHub page under https://AchimRetzbach.github.io/RESTREX/, and its code is licensed under CC-BY 4.0 for use by other researchers. In the following, an overview of its functionality is given.

The input is specified by path to the `.csv`-file exported by *QTegra*. In order to start the evaluation, the user needs to specify this path and possibly the following basic parameters first:

- Isotope: The isotope that has to be evaluated, given by an identifier string like `ca44`, `Kr84`, `85rb` or `88Sr` (all these notations possible)

- Indices of the blank measurements in the `.csv`-file (i.e. line numbers starting from 0 not regarding prefixes/text lines)

- Indices of the drift measurements, format as blank indices

- Indices of the calibration measurements, as before

- Calibration concentrations: The concentrations exactly corresponding to the calibration measurements specified by the indices before

- Calibration errors: The errors of the calibration concentrations from before. These are mostly an approximation of the error coming from the concentration standards and their dilution. If not otherwise stated, they are assumed to be 10% of the corresponding concentration for the rest of this thesis. This may seem large for a gravimetric standard treated with micropipettes, but later results indicate that this is in fact the right order of magnitude, possibly due to multiple dilution steps and imprecise tube label scales.

- Plots: Identifier strings of plots that have to be shown, for example `calib`, `calib_log`, `drift`. A detailed list and explanation can be found in the code documentation.

In case blank and drift indices were not given, the routine will fill them up by itself according to the measurement label. To allow for this, `BLK` or `HNO3` must appear there for the blanks and `Drift` for the drifts. Similarly, if concentration calibration indices and concentrations are not given, they are retrieved by the program. All measurements with labels containing `Sr` as well as `ppt`, `ppb` or `ppm` are chosen as standards then and the number in front of the concentration unit is taken as concentration.
To start evaluation, the main function `examineChem()` needs to be run (see flow chart in figure 8). It employs the following steps after retrieving the parameters described above:

1. **Sorting** of the data according to type (intensity, intensity error, concentration, concentration error) and isotope (isotope composition varies from experiment to experiment) into different arrays. Also most of the string-to-float conversion happens here, if needed.

2. **Blank correction** (optional): The blank correction is applied for correcting for the signal present when no sample is introduced. It is achieved by taking the mean of all blank measurements of the sequence $\bar{b}$ and subtract it from all the other measurements (taking the absolute

value to prevent negative counts here):

$$s_i' = \text{abs}(s_i - \bar{b}) \tag{23}$$

$$\Delta s_i' = \sqrt{\Delta s_i^2 + \Delta \bar{b}^2} \tag{24}$$

s_i is the signal (i.e. count number) of measurement i before blank correction while s_i' is the same afterwards. For the calculation of $\bar{b}$ and its error.

If no blank indices are given/generated, it can also be performed during concentration calibration using a computational ansatz. If not otherwise stated, the first method was chosen because it relies on actual measured blank samples instead of a computationally derived value.

3. **Drift correction**: Based on the before-mentioned drift measurements of known concentration, a drift correction was performed. This was done by calculating the ratio between each drift measurement and the first one of them (=: "scaling factor" $\kappa_{d_0,\dots,j,k,\dots}$) and subsequently linearly interpolating the scaling factors κ_i of the measurements in between. Finally, dividing each measurement by its corresponding scaling factor yielded the drift-corrected data:

$$s_i'' = \frac{s_i'}{\kappa_i} \tag{25}$$

$$\kappa_i = \frac{i - d_j}{d_k - d_j} \cdot \kappa_{d_k} + \frac{d_k - i}{d_k - d_j} \cdot \kappa_{d_j} \tag{26}$$

$$\kappa_{d_j,k} = \frac{s'(d_{j,k})}{s'(d_0)} \tag{27}$$

$$\Delta s_i'' = \sqrt{\left(\frac{\Delta \kappa_i}{\kappa_i}\right)^2 + \left(\frac{\Delta s_i'}{s_i'}\right)^2} \cdot \frac{s_i'}{\kappa_i} \tag{28}$$

$$\Delta\kappa_i = \sqrt{\frac{i - d_j}{d_k - d_j} \cdot \Delta\kappa_{d_k} + \frac{d_k - i}{d_k - d_j} \cdot \Delta\kappa_{d_j}} \qquad (29)$$

$$\Delta\kappa_{d_j,k} = \kappa_{d_j,k} \cdot \sqrt{\left(\frac{\Delta s'(d_{j,k})}{s'(d_{j,k})}\right)^2 + \left(\frac{\Delta s'(d_0)}{s'(d_0)}\right)^2} \qquad (30)$$

The subscripts d_0, d_j and d_k refer to the index of the first drift measurement overall, and the nearest drift measurement before and after the index i of the respective measurement. Note that instead of the blank-corrected s' the uncorrected s is taken here if no blank correction has taken place (yet).
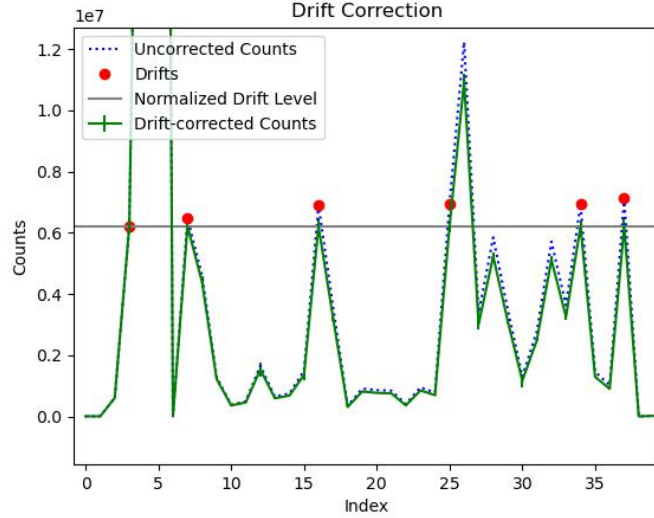

Figure 6: Example of a drift-correction (from Sr test experiment; zoomed in)

4. **Concentration calibration**: Given that a blank correction was performed before, the calibration is achieved by fitting proportional function (i.e. without any intercept) to the concentration-over-count rela-

tion:

$$c_i(x) = a \cdot s_i''\tag{31}$$

$$\Delta c_i(x) = \sqrt{(\Delta s_i'' \cdot a)^2 + (s_i'' \cdot \Delta a)^2}\tag{32}$$

$c(x)_i$ represents the concentration here while a is the fit coefficient. Its error Δa is returned by the fit routine.

If no blank correction was performed previously, a linear function is fit to the uncorrected data and its intercept is subtracted as zero-concentration signal afterwards:

$$c_i(x) = a \cdot s_i'' + b\tag{33}$$

$$\Delta c_i(x) = \sqrt{(\Delta s_i'' \cdot a)^2 + (s_i'' \cdot \Delta a)^2 + \Delta b^2}\tag{34}$$

b is now the y-intercept of the function, which is interpreted as the mean blank level. Its error Δb is returned by the fit routine as well and the blank correction is then treated as in expression 23 again, using b instead of $\bar{b}$.

As stated previously, the first method was used predominantly. An exemplary employment of it is shown in figure 7.

(a) calibration (linear)   (b) calibration (logarithmic)

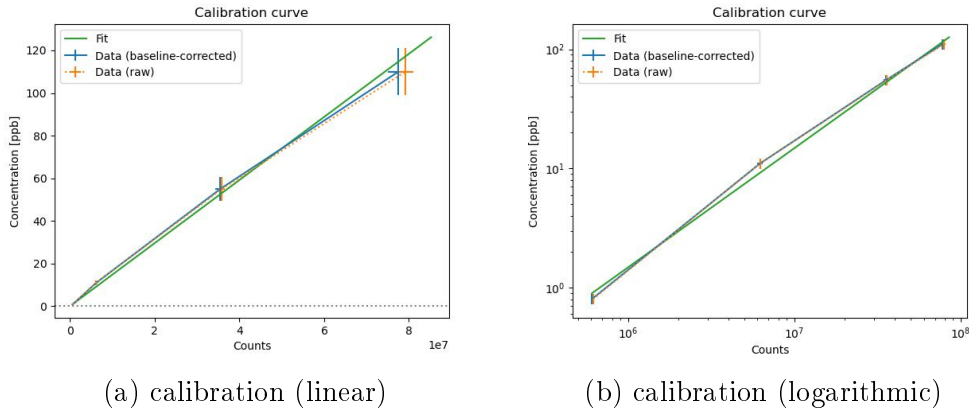Figure 7: Exemplary calibration plots (chemistry test experiment)

After running the main method, the output is stored in a table in a corresponding subfolder to the script.

The functionality of the whole column chemistry evaluation routine is illustrated in the following flow chart shown in figure 8.

A technical, even more 'in-depth' description of the program can be found in its documentation.

column_auswertung.py – Program Chart

major methods

evaluateChemistry(...):
- Preparation of output directory
- Importing Qtegra Query Export data
- Generating indices of blank/drift measurements (if neither given)
- Generating calibration slice array and retrieving concentrations (if not given)
- Blank correction / drift correction / recalibration (if enabled)
- Dilution correction (if enabled)
- Printing results to table
- Possible plots & tables:
  - *dilution-corrected concentration
  - *concentration (x-axis given as list of values in list of graphs in list of plots)
  - *counts (x-axis given as list of values in list of graphs in list of plots)

minor methods

getData(...):
- Function to import, sort and output the data exported by Qtegra in a more organised way

applyCorrections(...):
- Applying blank correction by mean blank *(if enabled)*
- Applying drift correction *(if enabled)*
- Applying concentration calibration *(if enabled)*
- Applying blank correction by calibration y-intercept *(if not previously done)*
- Possible plots:
  - *drift correction visualization
  - *calibration curve
  - *calibration curve (log-log)
  - *count-to-count comparison of blank/drift correction
- Outputting corrected counts and concentration *(depending on corrections)*

correctDilution(...):
- Scaling an array (e.g. of concentrations) by a provided corresponding array of (dilution) factors, outputting the scaled array
Not needed for the most part, remainder from test runs

utility methods

linear(...):
- Linear function used for the fit routine (f(x) = a·x + b)

proportional(...):
- Proportional function used for the fit routine (f(x) = a·x)

stringToFloat(...):
- Converting and outputting a string to a float-value, outputs 0 if the built-in float() does not work

sliceArray(...):
- Outputs an array sliced according to a given slice array: Single integers mean to take the array element at corresponding index, two-element arrays of integers mean to take the elements with indices between the first integer (inclusively) and second integer (exclusively)
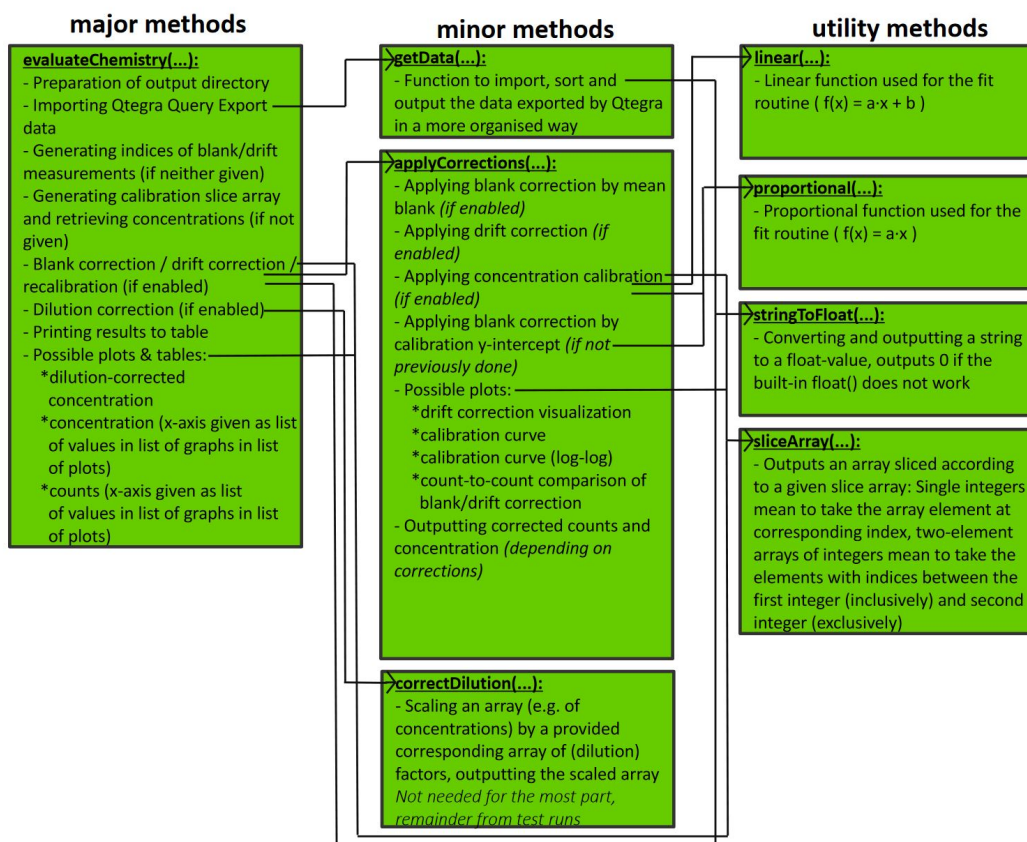
Figure 8: Flow chart of column evaluation routine

2.1 Comparison of Own and QTegra Evaluation Routine Results

As a means of quality control for both evaluation routines, the concentrations as delivered by *QTegra* are saved as well as the own routine's results. The general pattern that is visible when comparing them is that the results delivered by the custom routine usually deliver much higher concentrations.
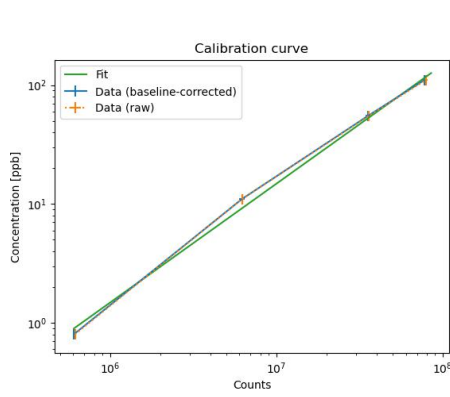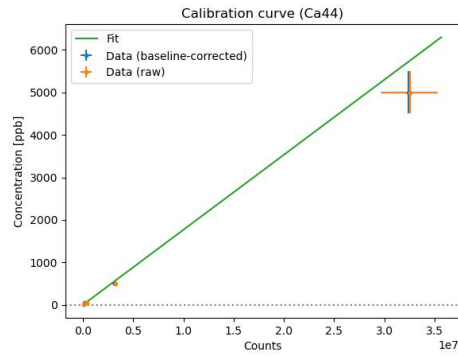

(a) Sr Calibration for SR1a-c samples
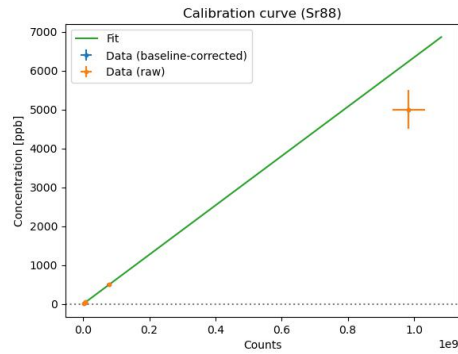
(b) Sr Calibration for SR3 samples (Angolan cold-water corals)
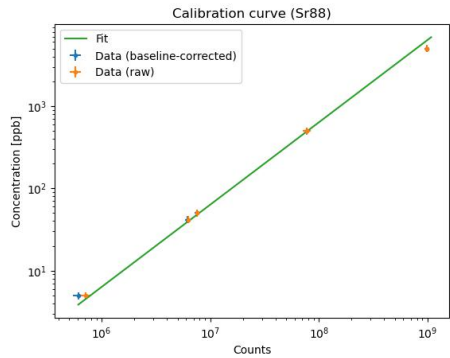
(c) Sr Calibration for SR3 samples (Angolan cold-water corals, logarithmic)

(d) Ca Calibration for SR3 samples (Angolan cold-water corals)

Figure 9

The origin of this was traced back to the calibrations which often show

a non-linear behavior, as can be seen in figure 9a. This continues in varying strength for all experiments, including the Angolan cold-water coral samples, whose calibration is depicted in figure 9b. Interestingly, when presented in a logarithmic plot, the calibration makes much more sense, as visible in figure 9c. Since higher concentrations also have higher errors, this leads to higher deviations, but the logarithmic plots shows that the deviations in fact scale according to their corresponding order of magnitude. This does show for other elements apart from Sr as well, as demonstrated in figure 9d. Changing the fitting procedure to the option with y-intercept does not resolve this and is therefore not done, and analogously disabling drift correction.

A possible explanation to this is that concentration standards with low concentrations (and unnaturally low count numbers, possibly due to having more dilution steps) are over-represented in the calibration, which is due to the logarithmic scaling of the standards. Possibly a linear calibration would make more sense for the future. The question why the *QTegra* results are smaller still remains unanswered though. While *QTegra* only performs a blank and no drift correction, this does not seem sufficient to explain the full magnitude of deviations. However, it is known that *QTegra* not only subtracts a blank before calibration, but also fits a linear function with a y-intercept to the data, which was purposefully not done in the custom approach due to practically double-correcting for blank this way. Also, from other works with other evaluation scripts in the group, similar problems are reported (Schreiber [2023], in progress). It was found out that *QTegra* apparently still includes a (0,0)-data point in the calibration routine that is not fixed however. Since the chemistry evaluation routine is not the main focus of this thesis though, the reader is referred to the other work for more information on the calibration problems. Here, the results delivered by the custom routine are taken for the sake of better knowledge about the calculation.

Part II
Appendix

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