Appendix 2.

Sample calculation of the correction procedure for adjusting measured isotope data to accepted IAEA reference scales.

There are a number of factors which lessen the measured spread between the isotopic composition of two samples with very different isotopic ratios. Leaking of changeover valves, memory, blanks, etc. could all cause the apparent isotopic difference between two samples to be less what it actually is. A correction for the compression effects can be made by 'stretching' all data so that they conform to a universally accepted scale. The problem is most severe for hydrogen isotope determinations. Two standards with very different compositions, VSMOW = 0 ‰ and SLAP = -428‰, were developed to allow each laboratory to correct for the compression unique to their system. For the hydrogen example, the difference between VSMOW and SLAP must be 428 ‰. If the difference measured in the laboratory is less than 428‰, a stretching factor needs to be applied to the data. Similar stretching factors can be applied to all isotope systems. The example below is for sulfur.

Consider the measured $\delta^{34}S$ values of SO_2 gas samples given in Table A2-1.

Table A.2.1 *Sample stretching factor calculations*

Sample	Measured $\delta^{34}S$ value	Measured × stretching factor*	Shifted to VCDT scale	Accepted $\delta^{34}S$ value
1	-14.2	-14.83	-14.61	
2	+2.3	2.40	2.62	
IAEA-S-1	-0.5	-0.52	-0.30	-0.30
IAEA-S-2	21.5	22.45	22.67	22.67

*Two decimal places are recorded in column 3. This does not imply that the data have a higher level of precision than the measured data in column 2. The extra decimal place is added to avoid rounding errors. Reported data should have the level of decimal places appropriate to their uncertainty.

Step 1. The accepted difference ($\Delta_{accepted}$) between IAEA-S-2 and IAEA-S-1 is (22.67 – -0.3) = 22.97‰. The measured difference ($\Delta_{measured}$) between IAEA-S-2 and IAEA-S-1 in our example is (21.5 – -0.5) = 22.0‰. The measured isotope scale is compressed relative to the accepted one by a ratio of $\Delta_{accepted}/\Delta_{measured}$ given by 22.97/22.0 = 1.0441. This is the 'stretching' factor, required to bring the scale of the measured values into agreement with the accepted one. All measurements are multiplied by the stretching factor (column 3 – Measured × stretching factor).

Step 2. The data now need to be shifted by a constant amount to bring them into agreement with the VCDT scale. The difference between the accepted and measured values 'stretched' to the IAEA scale is given by (-0.3 – -0.52) = 0.22 or (22.67 – 22.45) = 0.22. 0.22 is added to all data in column 3 to bring them into agreement with the VCDT scale (column 4 – Shifted to VCDT scale). Note that the two measured IAEA samples have been corrected so that they are identical to the accepted IAEA values.

The two steps outlined above are illustrated graphically in Fig. A2. In the top row, the measured delta values of two references and two samples are given. In step one, all delta values are multiplied by a constant to increase the difference between them, so that the measured difference between the two standards is the same as the accepted difference. (The difference between the measured values of the references could be larger than the accepted values. In such a case, step 1 involves multiplication by a constant less than 1, and the delta values are compressed). In the step 2, a constant is added to each value to bring the measured values of the two references in agreement with the accepted values. At this point, the corrected delta values of the samples will be on the IAEA scale.

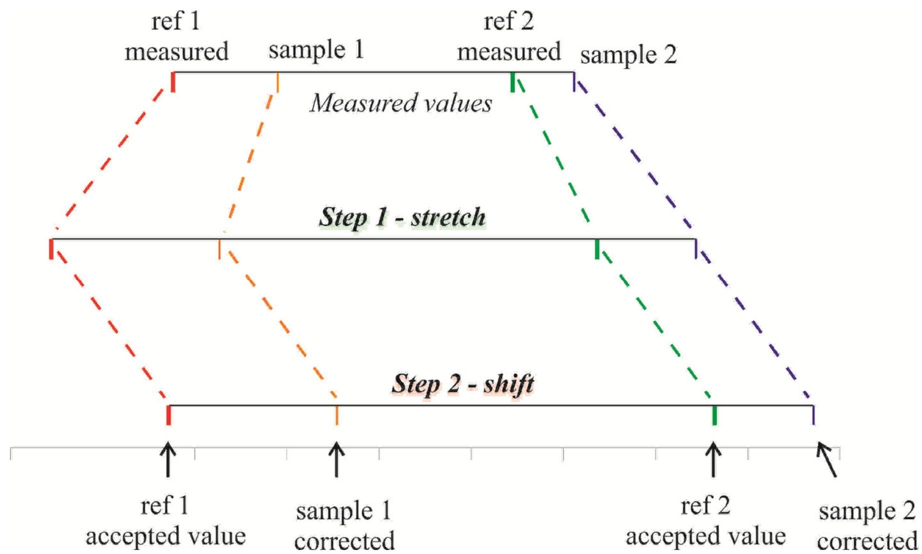

Fig. A2. Schematic of stretching