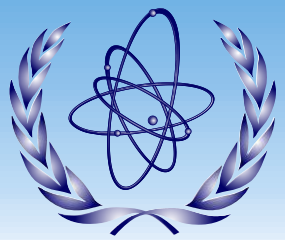

International Atomic Energy Agency

Consistent data compilation and error propagation for stable isotope data to compile meaningful reference values and uncertainties

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Abstract

Nowadays stable isotope data need to be accompanied by meaningful uncertainty statements for their full utilization, whether to evaluate their isotopic composition as evidence for origin of samples, for observation and proper evaluation of small isotopic trends due to transient effects, or to their use as laboratory standards. The Guide of Expression of Uncertainty in Measurements (GUM) provides a general framework to perform the task to calculate data with combined standard uncertainties. However, combining several such measurement data in a proper way is not straightforward without consideration of the correlation matrix and mathematical complicated elaborations. An Excel based tool provides means for any laboratory to calculate individual data with their associated combined standard uncertainties, including all major sources of uncertainty like the repeatability and long-term reproducibility of measurements, the possible bias of quality controls, the assigned uncertainty of used reference materials and their measurement data scatter. The tool further allows to calculate and correct memory effects and drifts as occurring in measurements. Standardized correction means allow the merging of data from different instruments with varying performance. This provides ultimately the means to combine such data without compromising the validity of the calculated combined standard uncertainty of the average value. This constitutes the possibility to produce a meaningful reference value with associated combined standard uncertainty from heterogeneous data, e.g. for the purpose to characterize a laboratory reference material by use of independent methods. The tool (SICalib) is available free of charge, is based on Excel macros as a standalone tool for measured rawdata files without the requirement of any particular database or other tool, and is still under further development. Its intention is complementary to available data management systems with a focus of proper uncertainty propagation.

M. Gröning, Jan 2020, for EGU-2020 session BG2.5: Quality of stable isotope data – Methods and tools for producing high quality data

Purpose of the talk

Documenting the quality of stable isotope data is needed including checking state of the art techniques to achieve quality.

Internal laboratory standards (ILS) for calibration and quality control are needed, as well as calculation of the uncertainty for their calibrated values.

A tool (SICalib) will be presented to calculate Combined Standard Uncertainties of measurements (following GUM principle “Guide to the Expresion of Uncertainty in Measurements”)

A solution with SICalib tool will be presented for the non-trivial task to properly calculate the mean from several data with a proper uncertainty propagation

Outline of the talk

Four parts:

A – General principles for stable isotope analyses

B – Existing problems in data evaluations including the non-trivial task to properly calculate the mean from several data with a proper uncertainty propagation

C – A tool (SICalib) to apply corrections, calibration and GUM compliant uncertainty evaluation

D – Detailed explanation of correction tools applied and uncertainty calculations performed

A: General principles

Repetition of what we all know already…

Basics (A)

To assure the quality of data from stable isotope laboratories, general principles are applied:

a) Use of state of the art techniques for measurements

b) Use of reference materials and internal laboratory standards for calibration and quality control

c) Reporting of Combined Standard Uncertainties of measurements as qualifiers for measurement values

d) Appropriate combination of all relevant uncertainty sources will establish combined standard uncertainty for a value (following GUM principles)

e) Tool is needed to properly calculate mean values with useful associated uncertainty values

Calibration of measurement data (A)

Calibration of measurements is key to ensure comparability of data between laboratories

a) Raw data as measured by instrument

b) External influences and corrections – temperature fluctuations, variations in used amounts, background

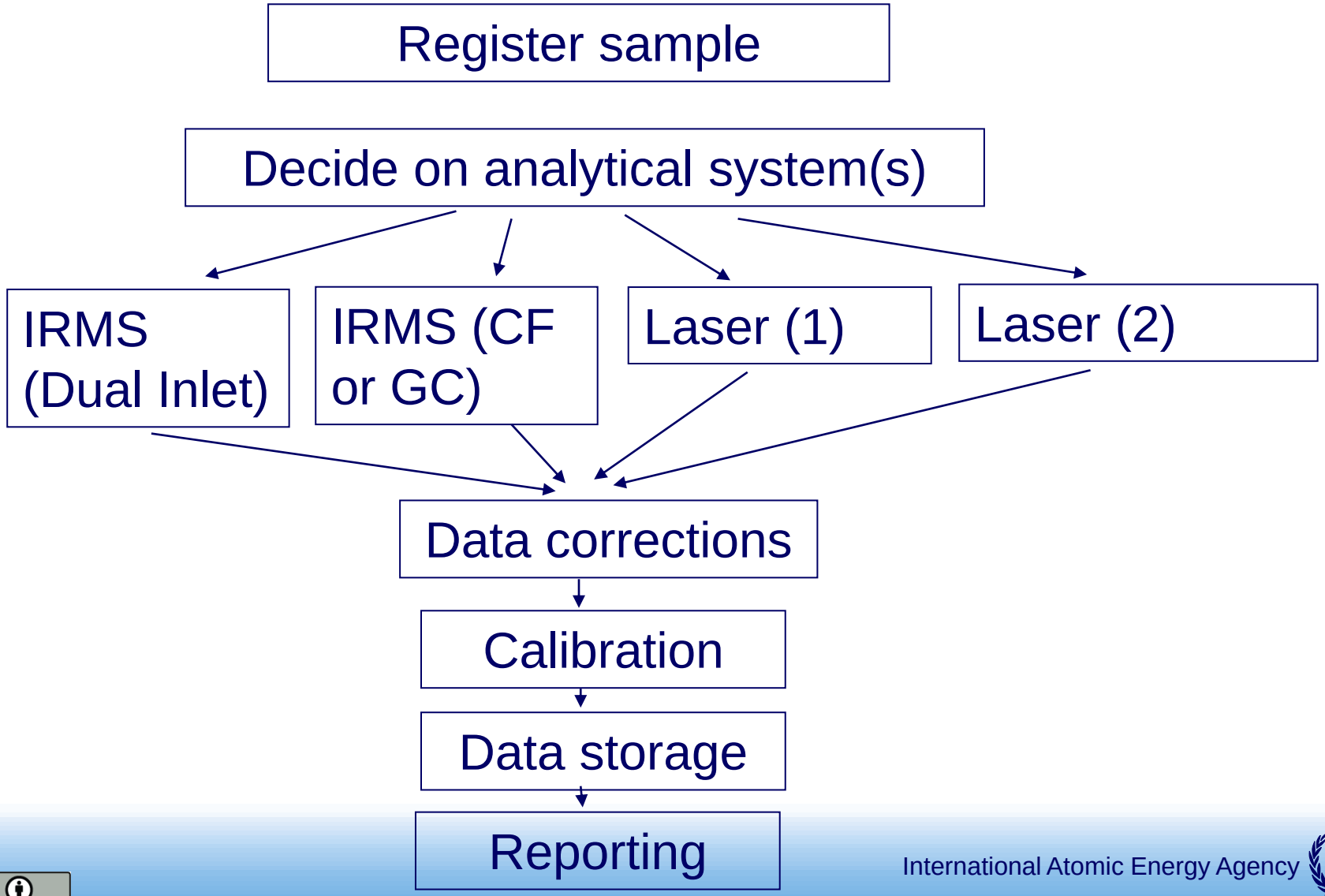
c) Memory effect correction

d) Drift of isotope data with time and correction

e) Actual calibration using ILS and

f) Uncertainty evaluation

Sample flowchart at a Laboratory (A)



Basic Concepts (A)

After installation of a new analytical instrument:

1.Decide on internal laboratory standards (ILS), obtain and test them to ensure long term performance

2.Calibrate the ILS samples versus suitable reference materials (RMs) and monitor the data (QC, ILS)

3.Establish routine reporting of data and uncertainties with appropriate quality assurance and tests

In case of several available instruments:

4.Decide which one(s) to use and how to evaluate and combine data and how to calculate its uncertainty

B: Headaches for data evaluation

Some non trivial cases…

Author's experience and data needs (B)

- In the author's former lab at IAEA, five different methods existed to analyze hydrogen $\delta^{2}H$ and four methods for oxygen $\delta^{18}O$, all with different reproducibility and individual data correction requirements
- Individual instruments used different data algorithms
- New laser-systems were tested (which had yet no evaluation software at that time)
- All individual data were fed into a central database LabData
- However, for customers only one mean value per sample was to be reported

A new unified evaluation method was needed to take into account differences in method precision and accuracy

General data handling problems I (B)

- Due to large differences in performance of instruments and number of data produced, in view of different data evaluation algorithms no straightforward method for data compilation was available
- An application of a similar data correction for all instruments was tested with positive result
- All individual instrument data were calibrated and relevant uncertainty components added into a combined standard uncertainty for each analysis
- The combination of all these data using a weighted mean approach was used (however the uncertainties of individual measurements were still highly correlated) and the combined uncertainty was still questionable

General data handling problems II (B)

- The evaluated combined standard uncertainty for each measurement was split into two components: the statistically independent “type A”-component (from individual measurements), and the fully correlated systematic “type B”-component (e.g. assigned unc. of calibration standards from certificate, exactly the same for all measurements)

- Now every user can evaluate all measurements, combine all individual data in a weighted means approach according to their type A uncertainties, and in a final step adds to the weighted mean uncertainty once the type B uncertainty which is the same for all measurements to create a combined standard uncertainty for the weighted mean

General data handling problems III (B)

- This last step has established a combined standard uncertainty for the weighted mean of all data
- This is (in case of use of the same calibration standards for all instruments) equivalent to using the correlation matrix as stated in GUM
- This is strictly applicable only in fully correlated condition (all measurements are done with calibration against the same reference materials with same assigned uncertainties)
- With this approach the calibration of internal laboratory standards is possible with a proper uncertainty statement, which then fulfills the requirements of data traceability back to the delta-scale definition

C: How to automate the process

SI-Calib as evaluation tool, especially for calibration needs of references …

SICalib as Calibration tool (C)

- Development of an Excel based tool (to facilitate use in a very IT-regulated environment) to evaluate $\delta^{2}H$ and $\delta^{18}O$ data for five different methods used interchangeably in one lab for input to a common database
- Use common features for all instruments: raw-data-corr; memory-corr; drift-corr; calibration and uncertainty evaluation
- Increase user-acceptance by use of Excel (and VBA-macros)
- Use for new laser-systems (which had no available evaluation software at that time in 2006)
- H and O isotope names are hardcoded in program, however use for other elements possible

SICalib – Basic Concepts I (C)

- SICalib: semi-automated calibration of any stable isotope measurements (H & O) using a common set of equations
- Database LabData can directly import the final data from the evaluation file. Individual data ValueID is stored back in the Excel file to ensure data consistency.
- Later re-calibrations are possible, re-import with ValueID updates properly the information stored in LabData.

SICalib – Basic Concepts II (C)

- SICalib supported the raw data formats of all instrumentation available at the IAEA laboratory:

1. IsoDat and IsoDatNT (Finnigan Delta+, DI-IRMS, water equilib with H2, CO2)
2. ASCII File format (Finnigan MAT250, DI-IRMS, Zn-reduction)
3. MassLynx (GVI Isoprime, CF-IRMS, pyrolysis)
4. LGR laser isotope ratio data
5. Picarro laser isotope ratio data
6. Generic Excel format (import of any raw data format)

Further import formats could be added with moderate effort (write macro-import routine)

SICalib – Basic Concepts III (C)

Requirements for use of SICalib:

- Necessity for use of two different calibration standards, analysed at least twice per analytical run (for drift correction)
- Knowledge on reference values of ILS standards (to be stored once in SICalib)
- Knowledge on typical reproducibility for used analytical method (at least its estimation)
- For initial memory correction: apply the same number of injections for each sample is a requirement for computation

SICalib – Status (C)

Published version 2.14 (2011): Gröning, M.: Improved water δ2H and δ18O calibration and calculation of measurement uncertainty using a simple software tool. Rapid Comm Mass Spec 2011, 25, 2711-2720 doi: 10.1002/rcm.5074

Available version 2.16f (2016) download at IAEA Reference Products website (expected again from June 2020 onwards):

https://nucleus.iaea.org/sites/ReferenceMaterials/SitePages/Home.aspx

Most recent version 2.16k (2020): available from author (M.Groening@iaea.org)

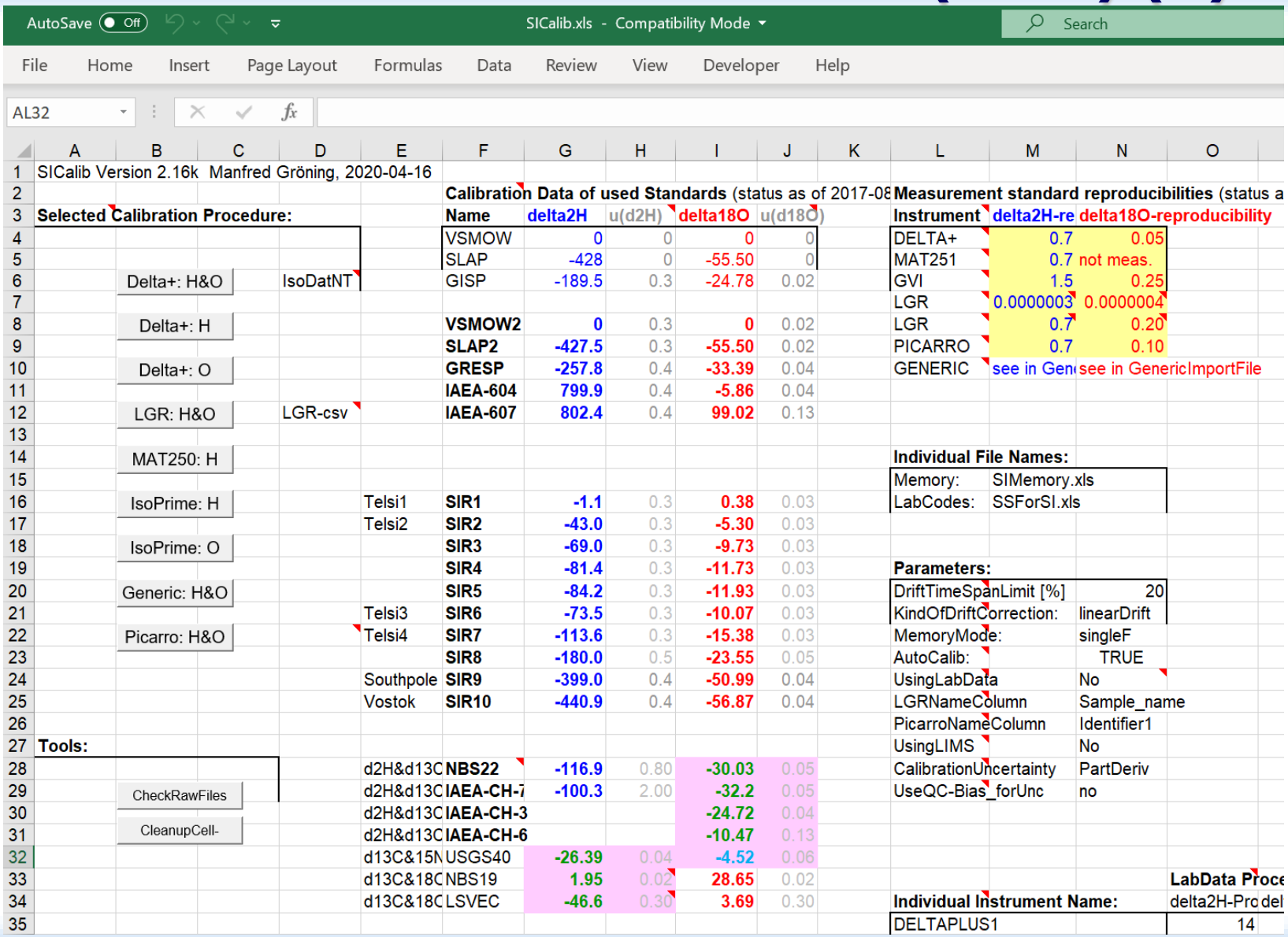
In development: new version 2.20 (major revision supporting major isotope systems H C N O S; import script for conceptually most data files; versatile user-lab adjustment)

SI-Calib for sample calibration (C)

Procedure in steps:

- Select the analytical system
- Import the raw data file
- Eventual corrections to raw data for external effects are possible later e.g. amount effects, temperature changes
- Memory correction (simple automatic algorithm)
- Drift correction
- Calibration using two standards
- Calculation of combined standard uncertainties

SICalib Main Screen 2.16k (2020) (C)



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SICalib Version 2.16k Manfred Gröning, 2020-04-16

Selected Calibration Procedure:

Delta+: H&O | IsoDatNT
Delta+: H
Delta+: O
LGR: H&O | LGR-csv
MAT250: H
IsoPrime: H
IsoPrime: O
Generic: H&O
Picarro: H&O

Tools:

CheckRawFiles
CleanupCell-

Calibration Data of used Standards (status as of 2017-08)

Name	delta2H	u(d2H)	delta18O	u(d18O)	
VSMOW	0	0	0	0	
SLAP	-428	0	-55.50	0	
GISP	-189.5	0.3	-24.78	0.02	
VSMOW2	**0**	0.3	**0**	0.02	
SLAP2	**-427.5**	0.3	**-55.50**	0.02	
GRESP	**-257.8**	0.4	**-33.39**	0.04	
IAEA-604	**799.9**	0.4	**-5.86**	0.04	
IAEA-607	**802.4**	0.4	**99.02**	0.13	
Telsi1	**SIR1**	**-1.1**	0.3	**0.38**	0.03
Telsi2	**SIR2**	**-43.0**	0.3	**-5.30**	0.03
	SIR3	**-69.0**	0.3	**-9.73**	0.03
	SIR4	**-81.4**	0.3	**-11.73**	0.03
	SIR5	**-84.2**	0.3	**-11.93**	0.03
Telsi3	**SIR6**	**-73.5**	0.3	**-10.07**	0.03
Telsi4	**SIR7**	**-113.6**	0.3	**-15.38**	0.03
	SIR8	**-180.0**	0.5	**-23.55**	0.05
Southpole	**SIR9**	**-399.0**	0.4	**-50.99**	0.04
Vostok	**SIR10**	**-440.9**	0.4	**-56.87**	0.04
d2H&d13C	**NBS22**	**-116.9**	0.80	**-30.03**	0.05
d2H&d13C	**IAEA-CH-7**	**-100.3**	2.00	**-32.2**	0.05
d2H&d13C	**IAEA-CH-3**			**-24.72**	0.04
d2H&d13C	**IAEA-CH-6**			**-10.47**	0.13
d13C&15N	USGS40	-26.39	0.04	-4.52	0.06
d13C&18C	NBS19	1.95	0.02	28.65	0.02
d13C&18C	LSVEC	-46.6	0.30	3.69	0.30

Measurement standard reproducibilities (status a

Instrument	delta2H-re	delta18O-reproducibility
DELTA+	0.7	0.05
MAT251	0.7	not meas.
GVI	1.5	0.25
LGR	0.0000003	0.0000004
LGR	0.7	0.20
PICARRO	0.7	0.10
GENERIC	see in Gen	see in GenericImportFile

Individual File Names:

Memory:	SIMemory.xls
LabCodes:	SSForSI.xls

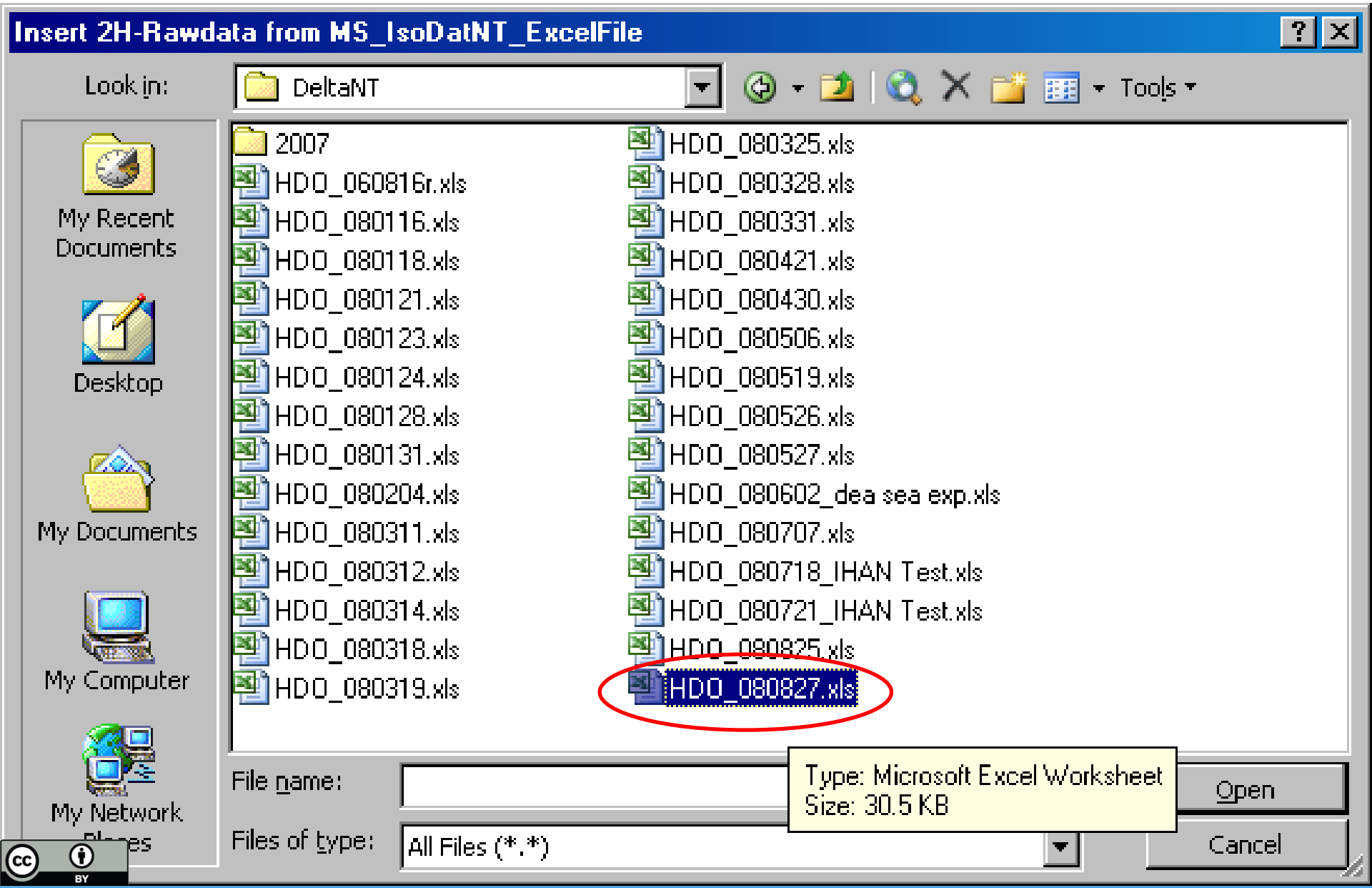
Parameters:

DriftTimeSpanLimit [%]	20
KindOfDriftCorrection:	linearDrift
MemoryMode:	singleF
AutoCalib:	TRUE
UsingLabData	No
LGRNameColumn	Sample_name
PicarroNameColumn	Identifier1
UsingLIMS	No
CalibrationUncertainty	PartDeriv
UseQC-Bias_forUnc	no

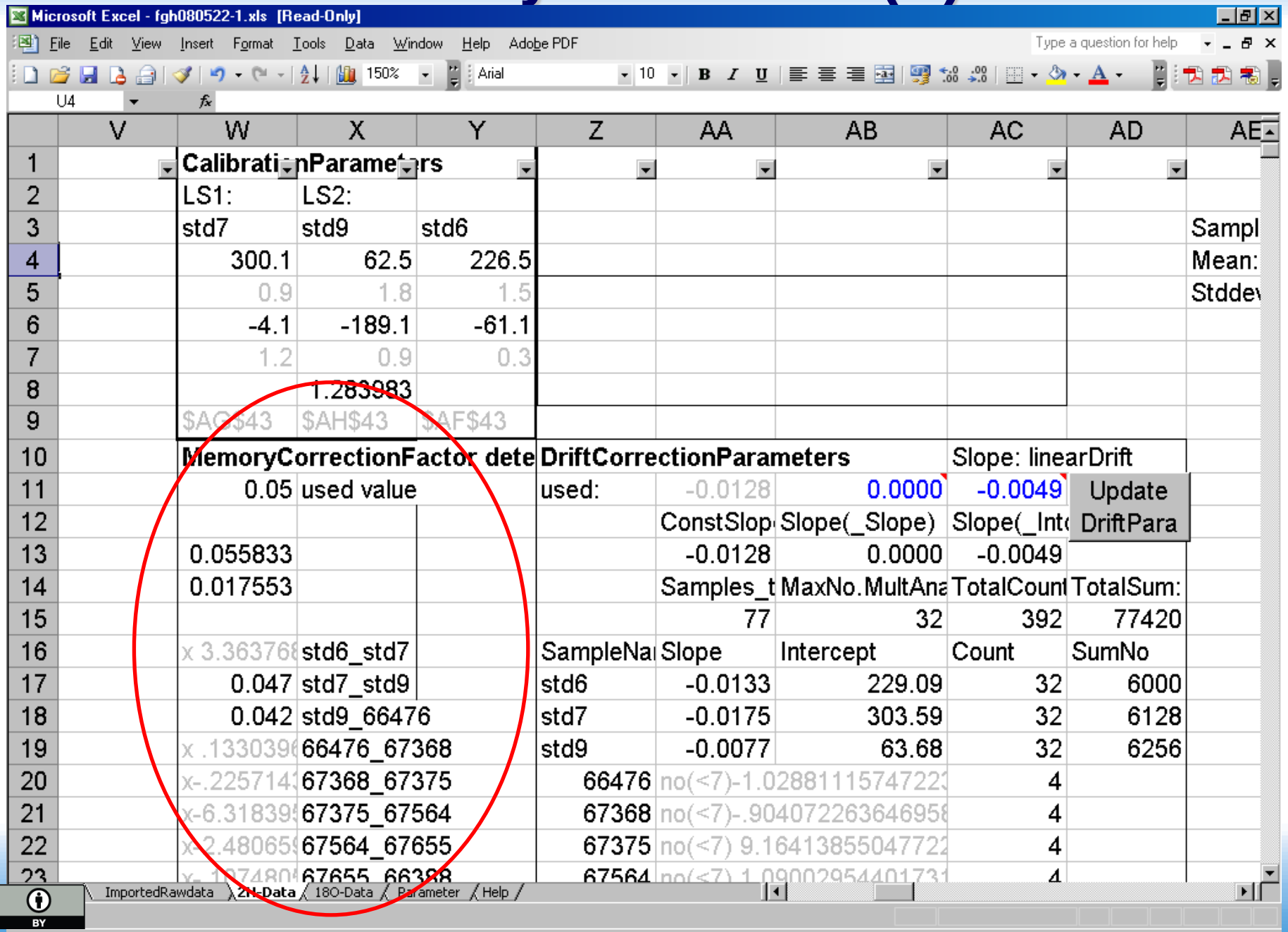
Individual Instrument Name: | LabData Proce

DELTAPLUS1 | delta2H-Pro del 14

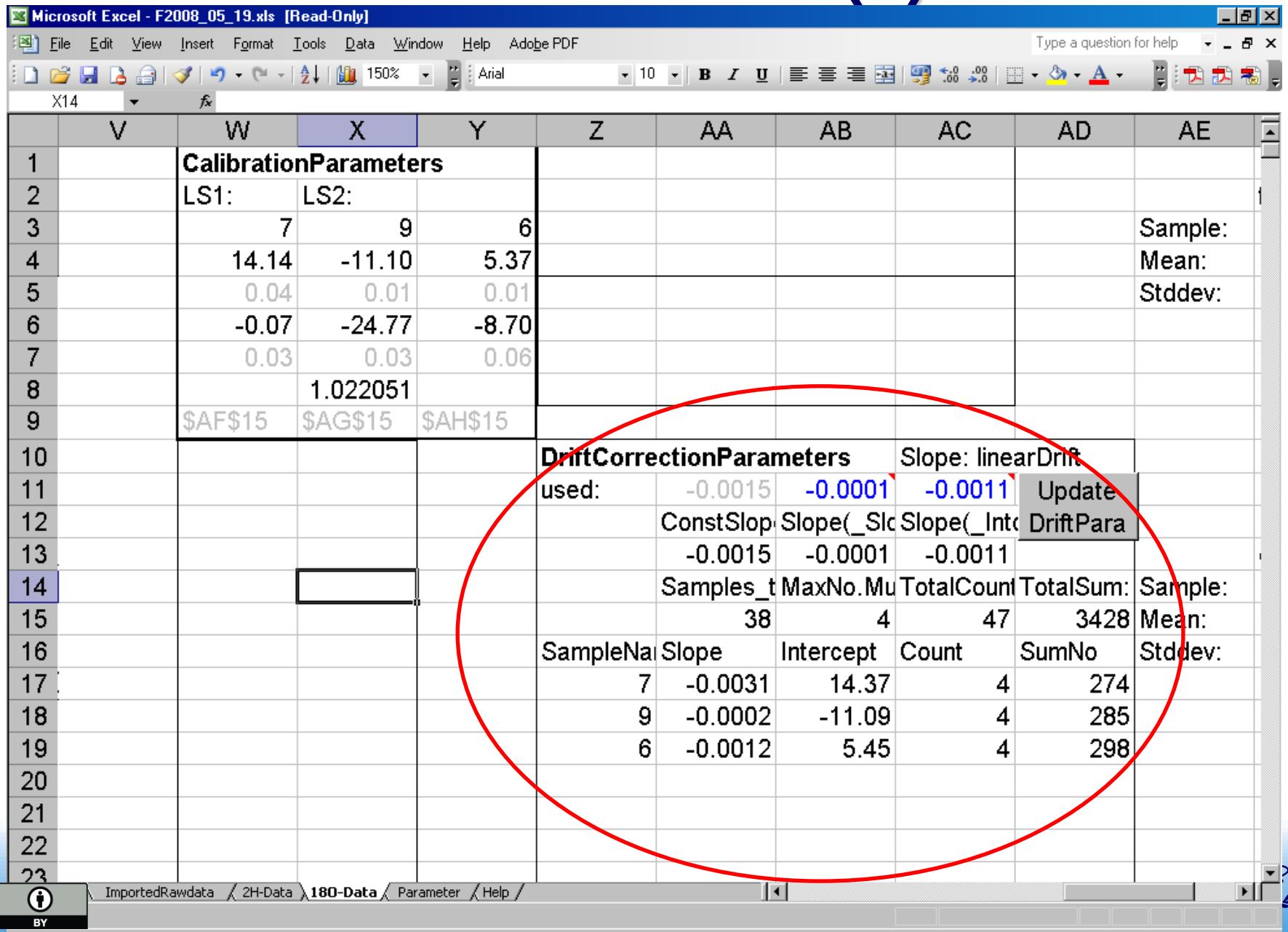
Import the raw data file (C)



Memory correction (C)



Drift correction (C)



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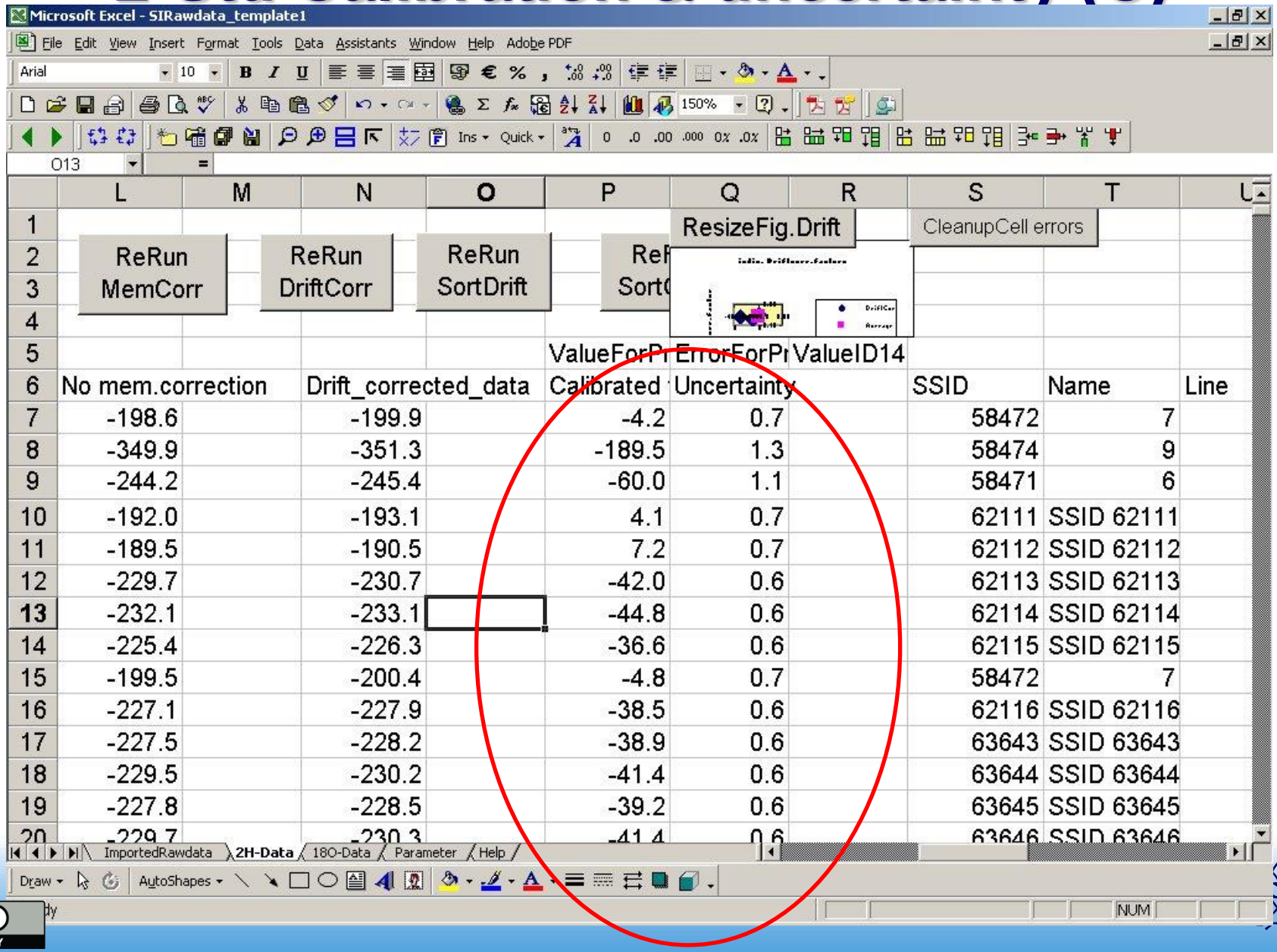
	W	X	Y
1	**CalibrationParameters**		
2	LS1:	LS2:	
3	7	9	6
4	14.14	-11.10	5.37
5	0.04	0.01	0.01
6	-0.07	-24.77	-8.70
7	0.03	0.03	0.06
8		1.022051	
9	AF15	AG15	AH15

	Z	AA	AB	AC	AD	AE
3						Sample:
4						Mean:
5						Stddev:
10	**DriftCorrectionParameters**			Slope: linearDrift		
11	used:	-0.0015	-0.0001	-0.0011	Update DriftPara	
12		ConstSlop	Slope(_Slc	Slope(_Intc		
13		-0.0015	-0.0001	-0.0011		
14		Samples_t	MaxNo.Mu	TotalCount	TotalSum:	Sample:
15		38	4	47	3428	Mean:
16	SampleNa	Slope	Intercept	Count	SumNo	Stddev:
17	7	-0.0031	14.37	4	274	
18	9	-0.0002	-11.09	4	285	
19	6	-0.0012	5.45	4	298	

ImportedRawdata | 2H-Data | 18O-Data | Parameter | Help

2-Std Calibration & uncertainty (C)



Microsoft Excel - SIRawdata_template1

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O13 =

ReRun MemCorr | ReRun DriftCorr | ReRun SortDrift | ReRun SortC | ResizeFig.Drift | CleanupCell errors

	L	M	N	O	P	Q	R	S	T	U
1										
2										
3										
4										
5					ValueForPr	ErrorForPr	ValueID14			
6	No mem.correction		Drift_corrected_data		Calibrated	Uncertainty		SSID	Name	Line
7	-198.6		-199.9		-4.2	0.7		58472	7	
8	-349.9		-351.3		-189.5	1.3		58474	9	
9	-244.2		-245.4		-60.0	1.1		58471	6	
10	-192.0		-193.1		4.1	0.7		62111	SSID 62111	
11	-189.5		-190.5		7.2	0.7		62112	SSID 62112	
12	-229.7		-230.7		-42.0	0.6		62113	SSID 62113	
13	-232.1		-233.1		-44.8	0.6		62114	SSID 62114	
14	-225.4		-226.3		-36.6	0.6		62115	SSID 62115	
15	-199.5		-200.4		-4.8	0.7		58472	7	
16	-227.1		-227.9		-38.5	0.6		62116	SSID 62116	
17	-227.5		-228.2		-38.9	0.6		63643	SSID 63643	
18	-229.5		-230.2		-41.4	0.6		63644	SSID 63644	
19	-227.8		-228.5		-39.2	0.6		63645	SSID 63645	
20	-229.7		-230.3		-41.4	0.6		63646	SSID 63646	

ImportedRawdata | 2H-Data | 18O-Data | Parameter | Help

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Combined std uncertainty & type A and B (C)

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G26

Uncertainty calculation based on: (PartDeriv)
Sample:
WeightedMean/CombinedUnc:
WeightedESE/uncTypeB:
Mean/ESE:
ESE:
Stddev:
AverageSingleUnc:
Count:

Final summary data for all measured samples

Name	WeightedM	CombinedU	UncTypeA	UncTypeB	Mean	Stddev	ESE	count	SSID
dummy	-0.74	0.73	0.67	0.30	-0.74	0.92	0.33	8	
VSMOW2	-0.01	0.41	0.28	0.30	0.00	1.66	0.20	72	25
GISP 2_T2425	-257.26	0.26	0.14	0.22	-257.26	0.77	0.09	72	
SLAP 2	-427.50	0.34	0.17	0.30	-427.50	1.00	0.12	72	
GISP2_F1025	-256.74	0.25	0.12	0.22	-256.74	0.42	0.05	64	
GISP2_F1362	-256.91	0.26	0.14	0.22	-256.91	0.64	0.08	64	
GISP2_F1512	-256.99	0.26	0.14	0.22	-256.99	0.62	0.08	63	
GISP 2_F1913	-256.84	0.25	0.13	0.22	-256.84	0.53	0.07	64	
DI	-68.11	0.61	0.55	0.20	-68.10	0.66	0.23	8	

final calibrated data (sorted by sample)

	dummy			VSMOW2			GISP 2_T2425			SLAP 2
dummy	-0.74	0.73	VSMOW2	-0.01	0.41	GISP 2_T2	-257.26	0.26	SLAP 2	-427.50
	0.67	0.30		0.28	0.30		0.14	0.22		0.17
	-0.74	0.33		0.00	0.20		-257.26	0.09		-427.50
	0.33			0.20			0.09			0.12
	0.92			1.66			0.77			1.00
	1.90			2.35			1.18			1.42
	8			72			72			72
	-0.2	1.9		0.1	2.3		-257.8	1.2		-426.7
	-2.8	1.9		0.6	2.4		-258.7	1.2		-427.4
	-1.6	1.9		0.2	2.3		-258.4	1.2		-427.5
	-0.9	1.9		0.6	2.4		-258.3	1.2		-426.6
	-0.4	1.9		0.6	2.4		-258.5	1.2		-426.6
	-0.2	1.9		0.7	2.4		-258.5	1.2		-427.5
	-0.1	1.9		0.8	2.4		-258.1	1.2		-427.8
	0.1	1.9		1.1	2.4		-258.3	1.2		-428.1
				0.9	2.4		-258.2	1.2		-428.6
				1.1	2.4		-258.3	1.2		-427.7
				0.7	2.4		-258.4	1.2		-427.3
				0.9	2.4		-258.2	1.2		-426.9
				1.5	2.4		-257.6	1.2		-429.2
				1.5	2.4		-257.1	1.2		-430.2
				1.4	2.4		-257.2	1.2		-430.2
				1.7	2.4		-257.0	1.2		-427.7
				1.6	2.4		-257.2	1.2		-426.6
				1.8	2.4		-257.3	1.2		-427.2
				1.4	2.4		-257.2	1.2		-428.4
				1.3	2.4		-256.9	1.2		-429.5
				1.0	2.4		-256.9	1.2		-429.3
				1.3	2.4		-257.1	1.2		-428.9
				1.1	2.4		-256.6	1.2		-427.9
				1.1	2.4		-256.3	1.2		-427.7
				-1.7	2.3		-258.7	1.2		-426.8
				-2.5	2.3		-258.1	1.2		-426.4
				-2.7	2.3		-258.0	1.2		-426.2
				-2.4	2.3		-258.0	1.2		-426.6
				-2.1	2.3		-258.0	1.2		-426.6

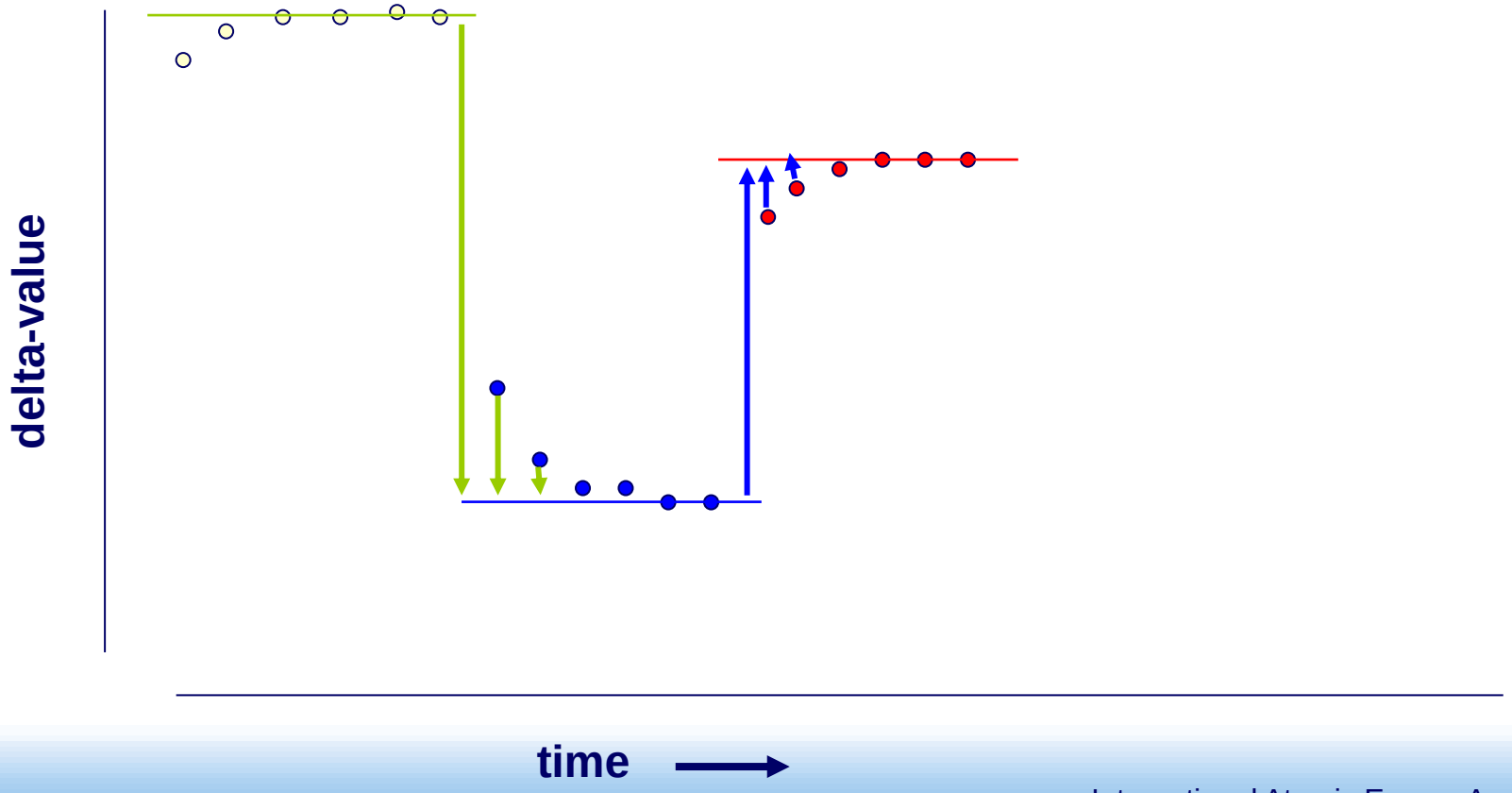
The combined standard uncertainty of each sample is listed together with its components of type A and B; it allows calculation of combined uncertainty for mean of different samples (e.g. for mean of all listed GISP2 samples)

D: Concepts for corrections

Here finally some details on correction methods as applied in SICalib …

Memory – Calculation (D)

Relative offset of isotopic value of injection *i* from true difference to previous sample



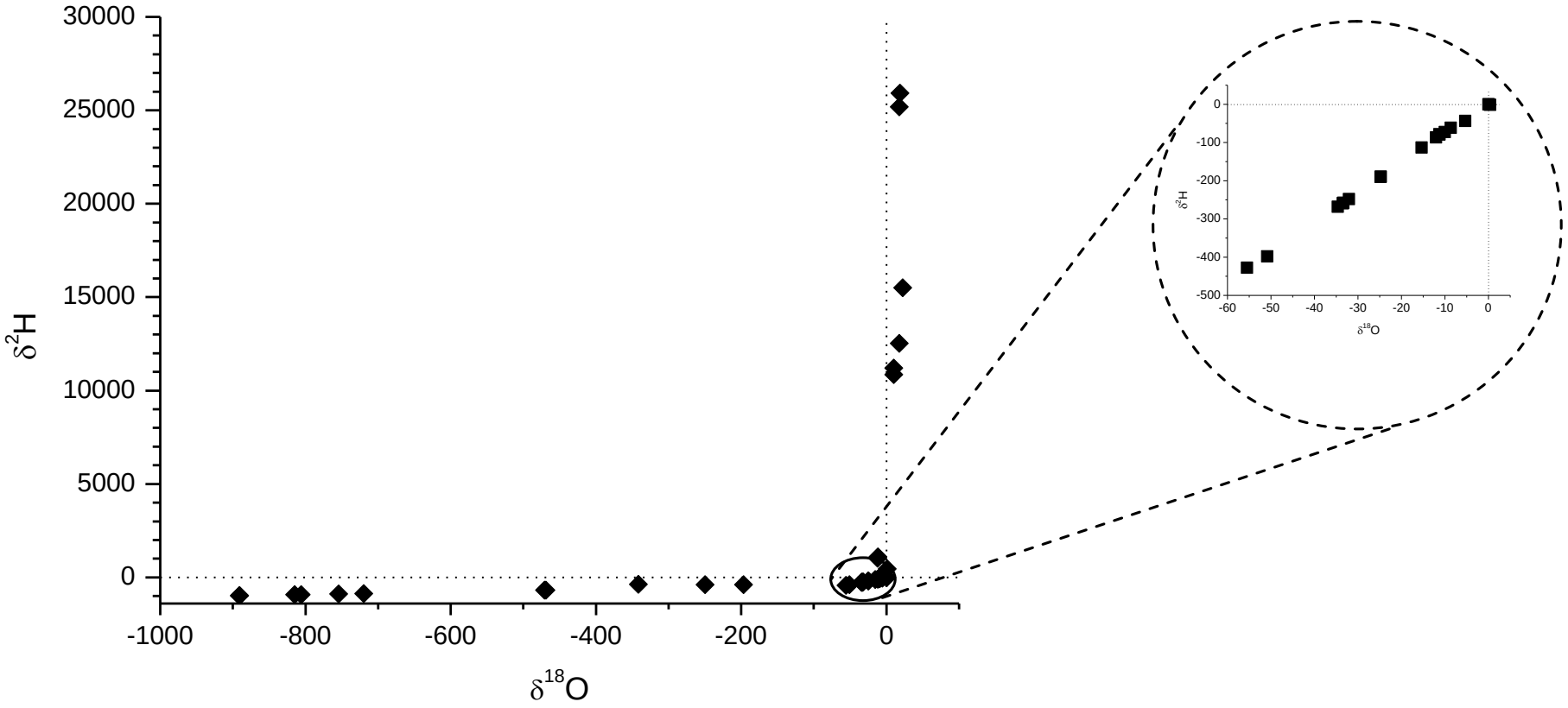
Necessary minimum number of injections (D)

		Injection		1	2	3	4	5	6	7	8	9	10	11	12
Picarro	delta2H	Memory	(%)	6.1	2.8	1.6	1.0	0.7	0.6	0.5	0.4	0.3	0.3	0.2	0.2
LGR	delta2H	Memory	(%)	6.9	1.7	0.8	0.5	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.0
	Sample-Sample difference:														
Picarro	bias for	400	(‰)	24.2	11.3	6.2	4.1	3.0	2.3	1.9	1.6	1.3	1.1	0.9	0.7
	bias for	200	(‰)	12.1	5.6	3.1	2.0	1.5	1.2	0.9	0.8	0.6	0.5	0.4	0.4
	bias for	100	(‰)	6.1	2.8	1.6	1.0	0.7	0.6	0.5	0.4	0.3	0.3	0.2	0.2
LGR	bias for	400	(‰)	27.8	6.9	3.2	2.1	1.5	1.1	0.8	0.6	0.5	0.3	0.3	0.2
	bias for	200	(‰)	13.9	3.4	1.6	1.1	0.8	0.6	0.4	0.3	0.2	0.2	0.1	0.1
	bias for	100	(‰)	6.9	1.7	0.8	0.5	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.0

Result for 6 injections: Remaining δ^2H bias of 1-3 per mill
- even when first three injections are rejected.
Solution: more injections or memory correction of all results.
Deletion of first 3 injections does not solve the problem !!!

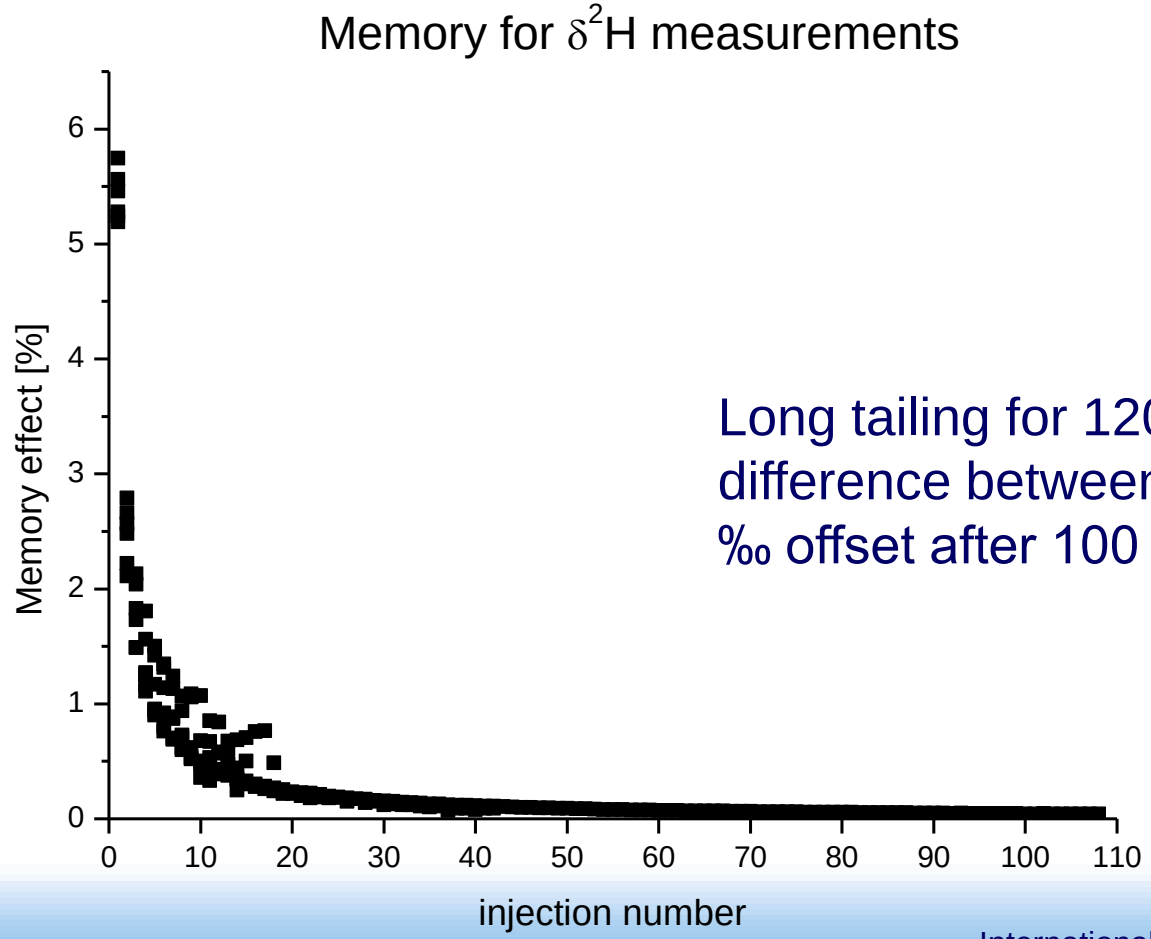
Memory – Isotopic range of samples (D)

Large (!) isotopic ranges studied to fully assess memory effects in routine use



Memory: consistent corrections (D)

Same relative memory correction factor for given injection for all δ-ranges regardless of span and isotopic direction



Long tailing for 12000 ‰ δ^2H isotopic difference between samples (still 6 ‰ offset after 100 injections)

Memory correction methods (D)

Several alternatives exist for correction/approximation of memory effects of repeated measurements:

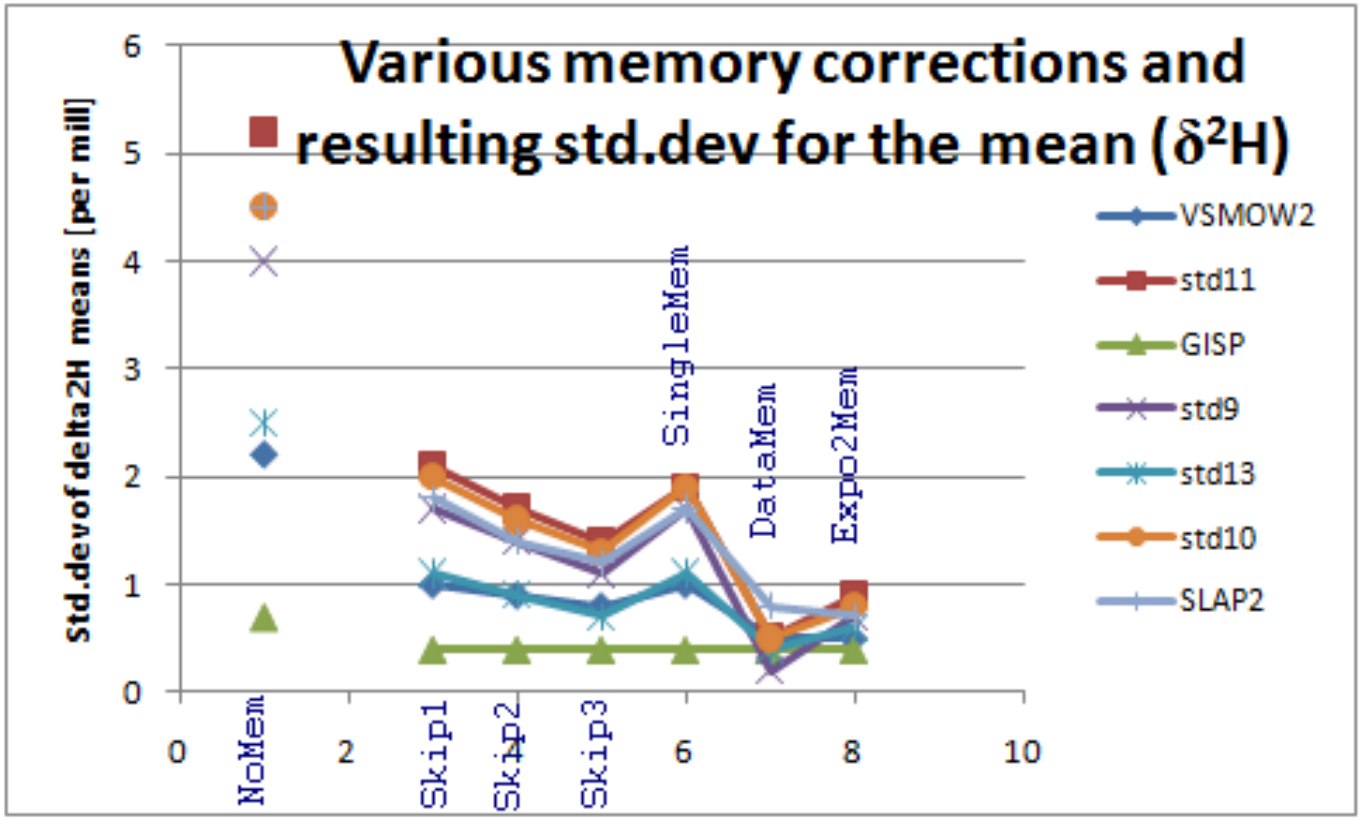
1. Power x^{-n}: memory decreases fast with certain fixed percentage per step n: e.g. 10%, 1 %, 0.1%

2. Expo2 $c \times e^{-ax} + (1-c) \times e^{-bx}$: memory decreases according to two coupled exponential terms (two memory reservoirs with different relaxation times; c=0 is normal exponential function)

3. Data Fitting: Numerical fitting to measured data

4. 3Res: interaction of three reservoirs (variable size & exchange & isotopic composition) with each sample

Comparing memory corrections (D)



Y-Axis: Resulting std.dev for different samples after Mem.corr.
Horizontal numbers: different memory corrections applied:
1-no correction; 3-skipFirst; 4-skipTwo; 5-skipThree;
6-SingleMemory; 7-DataMemory; 8-TwoExpoFunctions

Memory approach: Power (D)

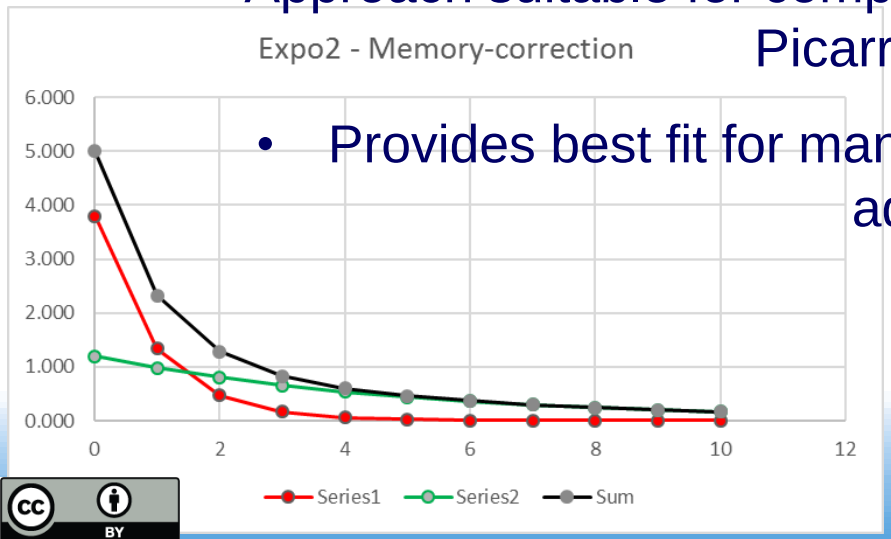
Power x^{-n}:

- calculate one correction factor f for first injection
- Method implies that memory decreases with same factor all the time. E.g. when f=0.2 (20%), next step is f*f=0.04 (4%), then f*f*f=0.008 (0.8%)
- Due to contribution from earlier injections, effective f has to be corrected accordingly
- Approach suitable for single reservoir memory effects, like for LGR or HT-EA

Memory approach: Expo2 (D)

Expo2 bi-exponential correction:
$x=x_0 \times (c \times \exp(-a \times i) + (1-c) \times \exp(-b \times i))$:

- Input of three parameters is needed: a and b for the decrease of the two exponential functions and c as fraction.
- Setting c=0 converts to normal exponential equation.
- Method allows to fit behaviour of two memory reservoirs (red and green, resulting in blue memory curve).
- Approach suitable for complex reservoir memory effects, like for Picarro laser system
- Provides best fit for many applications, but needs careful adjustments



Memory approach: Data fitting (D)

1. Data fitting according to measured data:

- In principle the most appropriate method as it really fits the real effects
- However, due to random fluctuations in analyses, it often suffers from higher degree of variations and is therefore not very satisfactory for minor corrections of long series of injections

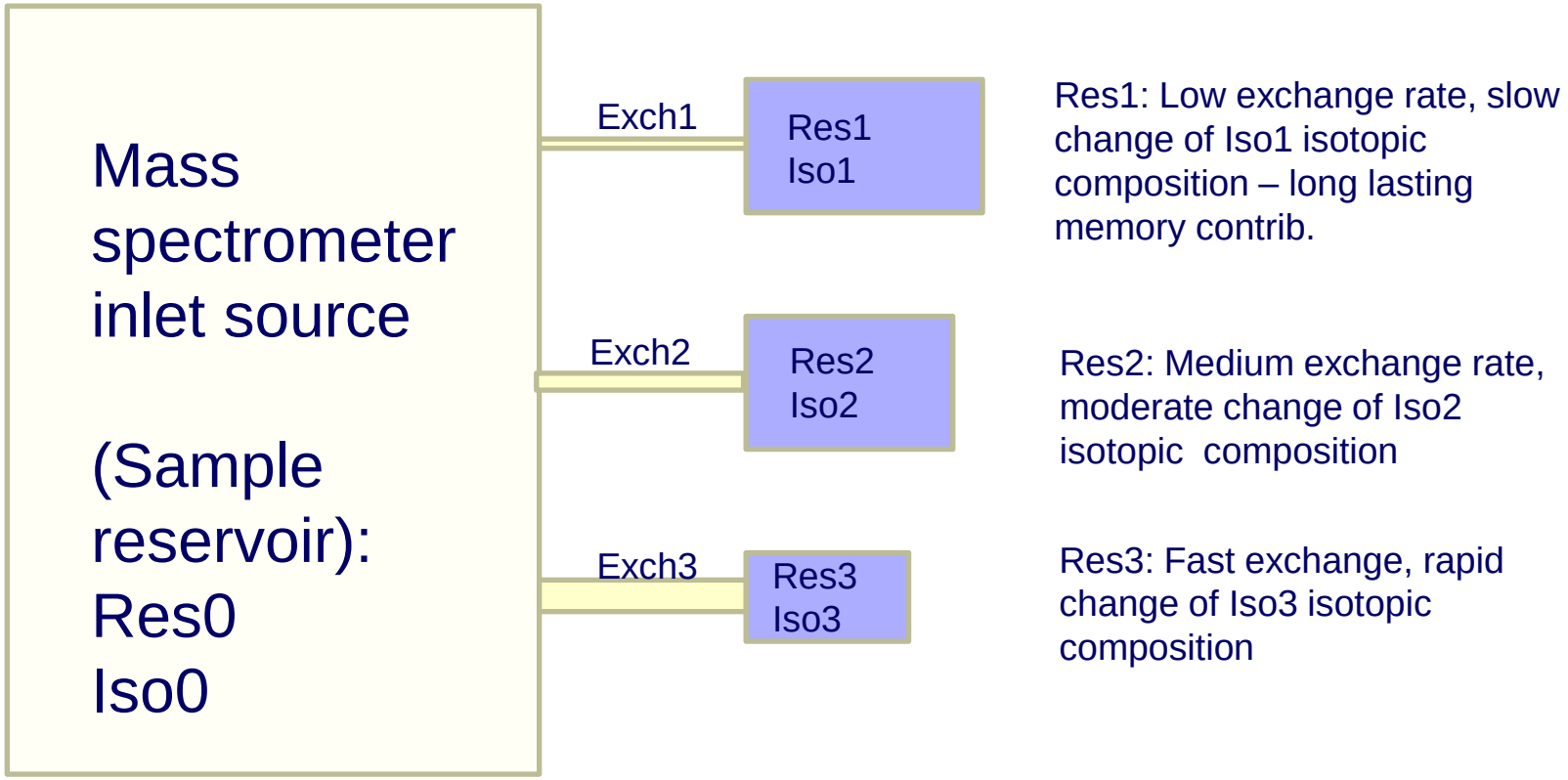
Memory approach: 3Res (D)

Three isotopically exchanging reservoirs:

- Input of six parameters: three reservoir sizes and three respective exchange rates with sample gas resulting in gradual isotopic change of reservoirs.
- Approach suitable for complex reservoir memory effects in enrichment studies, simulating long persisting memory effects.
- Evaluation by fitting and minimizing only one evaluation parameter (like least square)

Memory approach: 3Res (D)

Principle of Exchange between Sample and three Reservoirs (different reservoir sizes and exchange rates) – continuous change of isotopic compositions with time in sample and in all reservoirs



Res1: Low exchange rate, slow change of Iso1 isotopic composition – long lasting memory contrib.

Res2: Medium exchange rate, moderate change of Iso2 isotopic composition

Res3: Fast exchange, rapid change of Iso3 isotopic composition

Drift correction I (D)

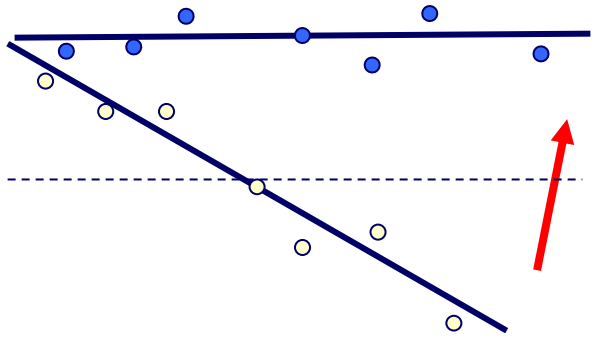
- Time drift – uses actual measurement time or individual measurement number taken as proxy for time.
- Calculated for each sample which is measured more than once over a reasonable time span.
- All data are averaged and therefore improve reliability.
- Drift correction factor can be chosen to be constant for all samples or to be dependent on the isotopic composition of samples (e.g. for H^{3+} effects).

Drift correction II (D)

- Drift corrections are adjusted for same time of measurements (equals a time median for equidistant analyses). This improves data consistency.

$$\delta^2\mathrm{H}_{\mathrm{drift}} = \delta^2\mathrm{H}_{\mathrm{memory}} - \left(\mathrm{Position} - \frac{\mathrm{TotalSum}}{\mathrm{TotalCount}} \right) \times \left(\mathrm{SlopeOfSlope} \times \delta^2\mathrm{H}_{\mathrm{memory}} + \mathrm{InterceptOfSlope} \right)$$

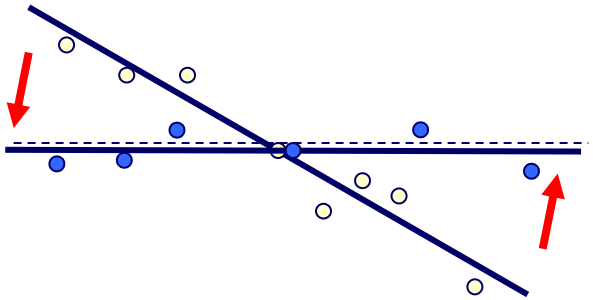
Drift correction III (D)



Drift corrected mean

Incorrect !!!

Mean



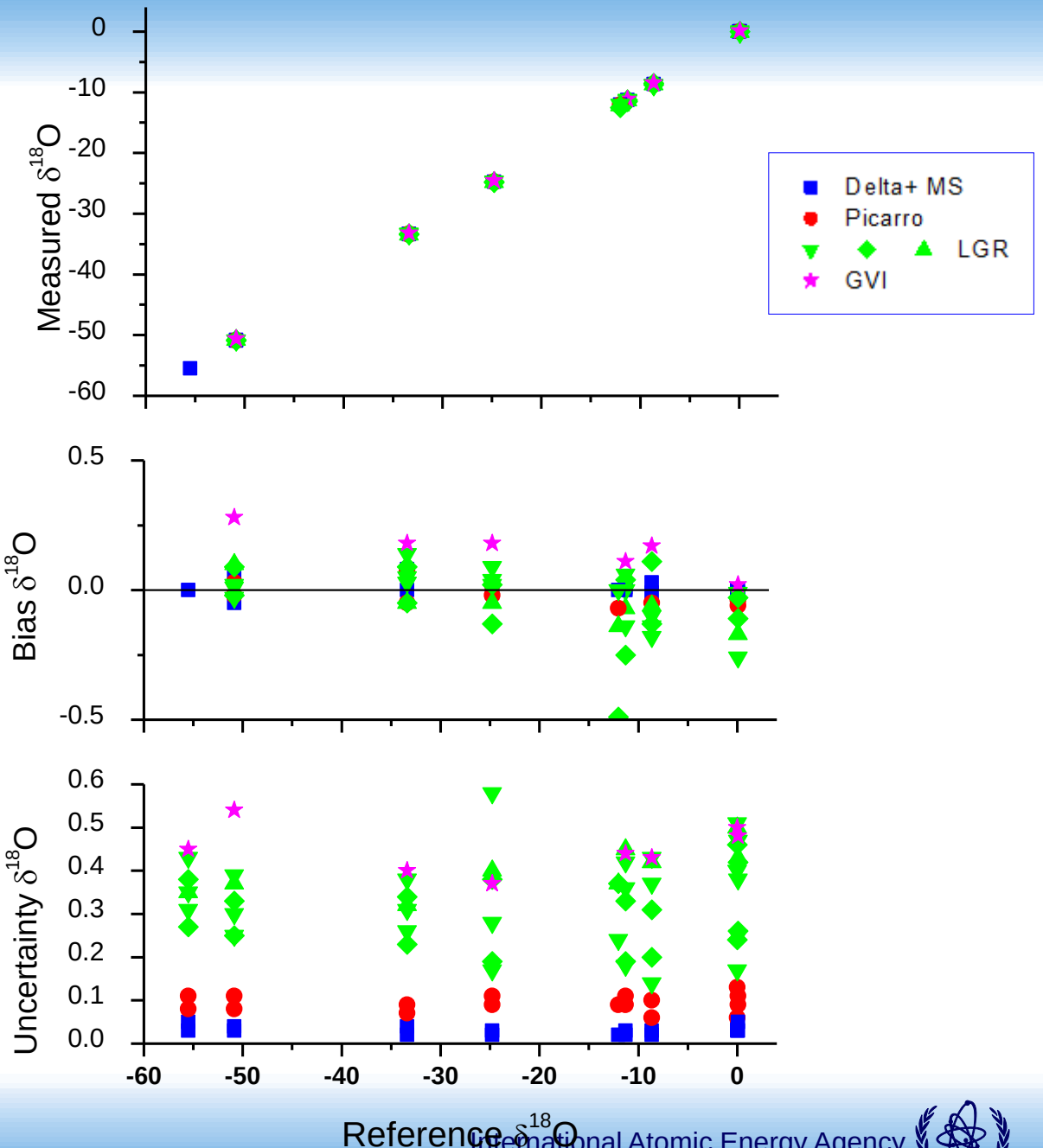
Correct

Mean & Weighted mean

For further details of the drift correction and used formula see

Manual of SICalib

Uncertainty and bias for $\delta^{18}O$ measurements (D)



Stable isotope measurements and their associated uncertainty (D)

Main uncertainty components for measurement (e.g. water):

	$\delta^{18}O$	$\delta^{2}H$
Sample measurement repeatability:	± 0.01 ‰	± 0.1 ‰
Sample measurement reproducibility:	± 0.048 ‰	± 0.76 ‰
Daily lab standard measurement:	± 0.03 ‰	± 0.6 ‰
Daily control sample measurement:	± 0.018 ‰	± 0.3 ‰
Bias offset (via QC sample)	± ?? ‰	± ?? ‰
Uncertainty of internat. standards:	± 0.02 ‰	± 0.3 ‰
Combined standard uncertainty:	**0.07 ‰**	**1.2 ‰**

Uncertainty evaluation (D)

- Calibration formula f:

$$\delta^2\mathrm{H}_{\mathrm{sample}} = \delta^2\mathrm{H}_{\mathrm{cal1}} + \left(\delta_{\mathrm{W}}{}^2\mathrm{H}_{\mathrm{sample}} - \delta_{\mathrm{W}}{}^2\mathrm{H}_{\mathrm{cal1}}\right) \cdot \left(\delta^2\mathrm{H}_{\mathrm{cal2}} - \delta^2\mathrm{H}_{\mathrm{cal1}}\right) / \left(\delta_{\mathrm{W}}{}^2\mathrm{H}_{\mathrm{cal2}} - \delta_{\mathrm{W}}{}^2\mathrm{H}_{\mathrm{cal1}}\right)$$

- Uncertainty components can be assessed according to the general law of uncertainty propagation
- Partial derivatives of the calibration formula
- Sensitivity factors
- GUM Workbench program as tool to facilitate calculations
- Components: δ^2H_{cal1}, δ^2H_{cal2}, $\delta^2H_{cal1\text{-}W}$, $\delta^2H_{cal2\text{-}W}$, $\delta^2H_{sample\text{-}W}$

Combined Uncertainty (D)

Combined uncertainty of formula f:

$$u(\delta_{\text{sample}}) = \sqrt{\left(\frac{\partial f}{\partial \delta_{\text{cal1}}}\right)^2 \cdot u(\delta_{\text{cal1}})^2 + \left(\frac{\partial f}{\partial \delta_{\text{cal2}}}\right)^2 \cdot u(\delta_{\text{cal2}})^2 + \left(\frac{\partial f}{\partial \delta_{w\ \text{cal1}}}\right)^2 \cdot u(\delta_{w\ \text{cal1}})^2 + \left(\frac{\partial f}{\partial \delta_{w\ \text{cal2}}}\right)^2 \cdot u(\delta_{w\ \text{cal2}})^2 + \left(\frac{\partial f}{\partial \delta_{w\ \text{sample}}}\right)^2 \cdot u(\delta_{w\ \text{sample}})^2}$$

For further details on the uncertainty evaluation algorithm see

Manual of SICalib

Proxy for unknown sample uncertainty (D)

Proxy needs to represent the standard deviation for a hypothetical repeated determination for each sample. It can be approximated in different manner and various approaches exist. One useful proxy (in my opinion) is the long term reproducibility of analyses:

- Long term evaluation of QC data
- Repetition of a representative fraction of samples at different days and evaluation of range in terms of standard deviation

Comparison of both methods at IHL in 2004 resulted in identical results:

±0.046‰ for QC data (n=77)

±0.047‰ for duplicate measurements (n=596)

Last calculation (D)

Reproducibility and repeatability:

$$u(\delta_{\text{w sample}}) = \sqrt{(\text{reproducibility})^2 + (\text{repeatability})^2}$$

Now the resulting sample uncertainty can be used for evaluation of the last uncertainty component.

Then the combined uncertainty of the sample $u(\delta_{sample})$ can be calculated using the combined uncertainty formula.

Information / Downloads

- Further information can be obtained from the author:

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