SEAFAST ICP-MS data, analysed in a snap

R script manual for the fast data analysis of trace metals extracted from seawater using a SEAFAST system and measured by ICP-MS

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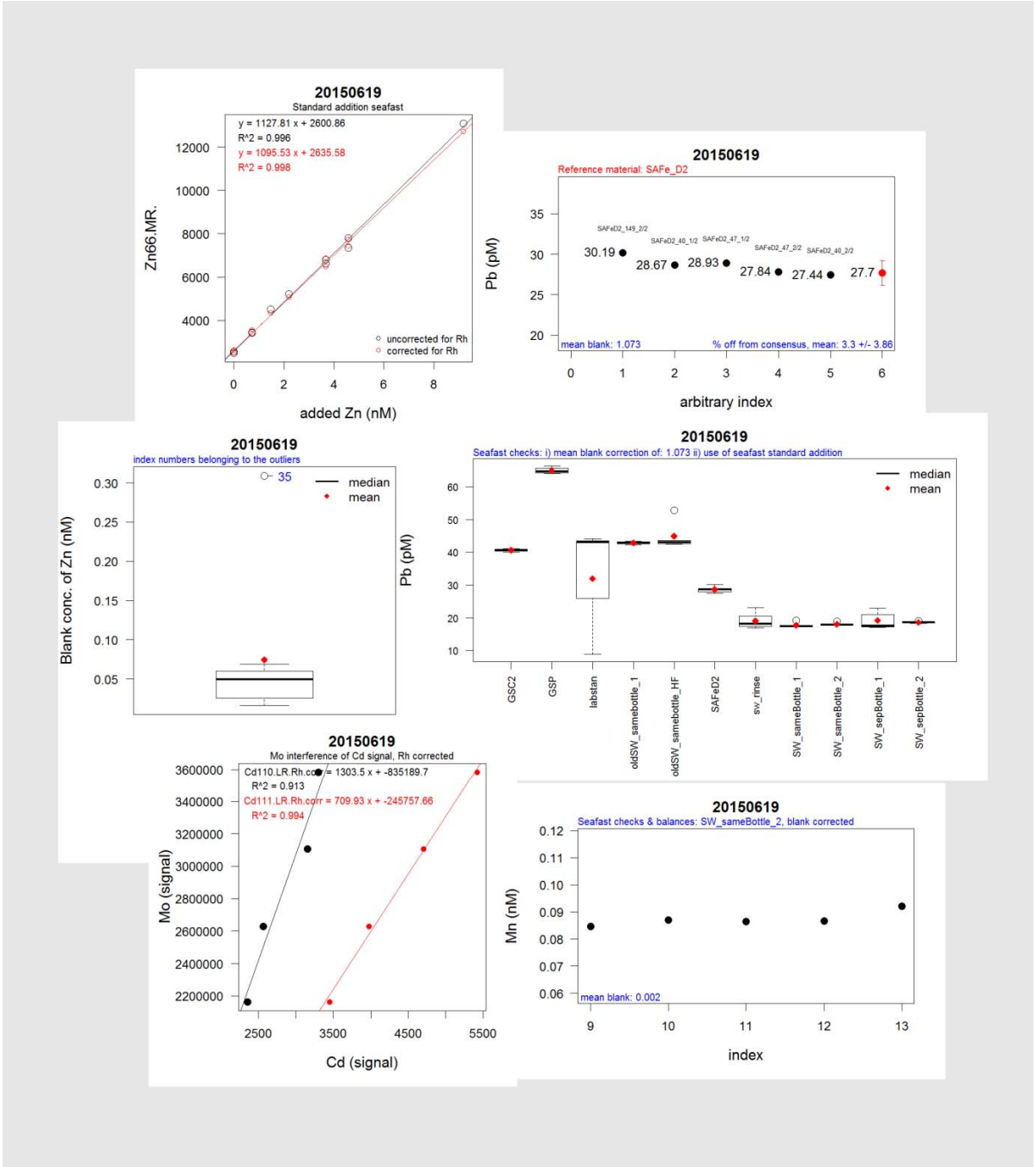


Contents

1) Summary

The complete analysis of the trace metal data extracted from seawater by a SEAFAST system and measured by ICP-MS takes a lot of time using excel. This R script was developed to speed up this process so that all checks and balances and the resulting data can be assessed before the next set of samples are measured. This prevents that problems are detected in a later stage necessitating re-measurement of large quantities of samples. This R script allows correction for changes in the ICP-MS sensitivity using measurements of Rh added to the samples. It allows for the correction of the Cd data due to the interference of Mo using the ICP-MS. It visualizes the standard additions and provides a csv file with slopes and other data. It visualizes all checks and balances (separately treating ICP-MS and SEAFAST checks). It calculates the recovery efficiency of your SEAFAST column. It graphs the consensus reference values (e.g. SAFE, GEOTRACES, and any others to be added by the user) besides the measured results of reference samples. It calculates the final concentrations of all trace metals of interest of your environmental samples. If you don't want to correct your data for changes in ICP-MS sensitivity using Rh and the interference of Mo in the measurement of Cd you can turn these options off. It will take about 30 minutes to copy past the ICP-MS data in a series of separate csv files. Using the R script it will take you not more than 15 minutes to analyse the full data resulting in a perfect overview of all your checks and balances and a final dataset of your environmental samples.

2) General information:

The R script and the functions were written in R version 3.0.1 (2013-05-16), 32-bit under Windows. Sometimes function will not work in earlier versions because the R packages that are needed don't work there. For example, "library(string)" does not work in version R2.10.0. Please, if you use this R script send me your e-mail address (to micharijkenberg@yahoo.com.au) so that I can send you updates of the script when available.

The use of this script is free but at your own risk.

The reference values provided with this script for the SAFE and GEOTRACES reference materials (version May 2013) originate from the GEOTRACES website (http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials).

3) Setting up the R working directory

a. Create a folder
b. place in here your latest R script (Script_icpmsDataAnalysis_310516.r)
c. place in here your latest R Functions (Functions_ResultsICPMS_310516.r)
d. place in here your csv file with reference values
(TraceMetalReferenceConsensusValues.csv)

The R script is the script that you open and work in. The R Functions need to be in the same folder but you don't have to do anything with it other than activate it within your R script. The TraceMetalReferenceConsensusValues.csv will also be opened from within the R script. However, if you want to change anything in this file (e.g. add or change reference materials) you can do this in excel.

4) Setting up the data files

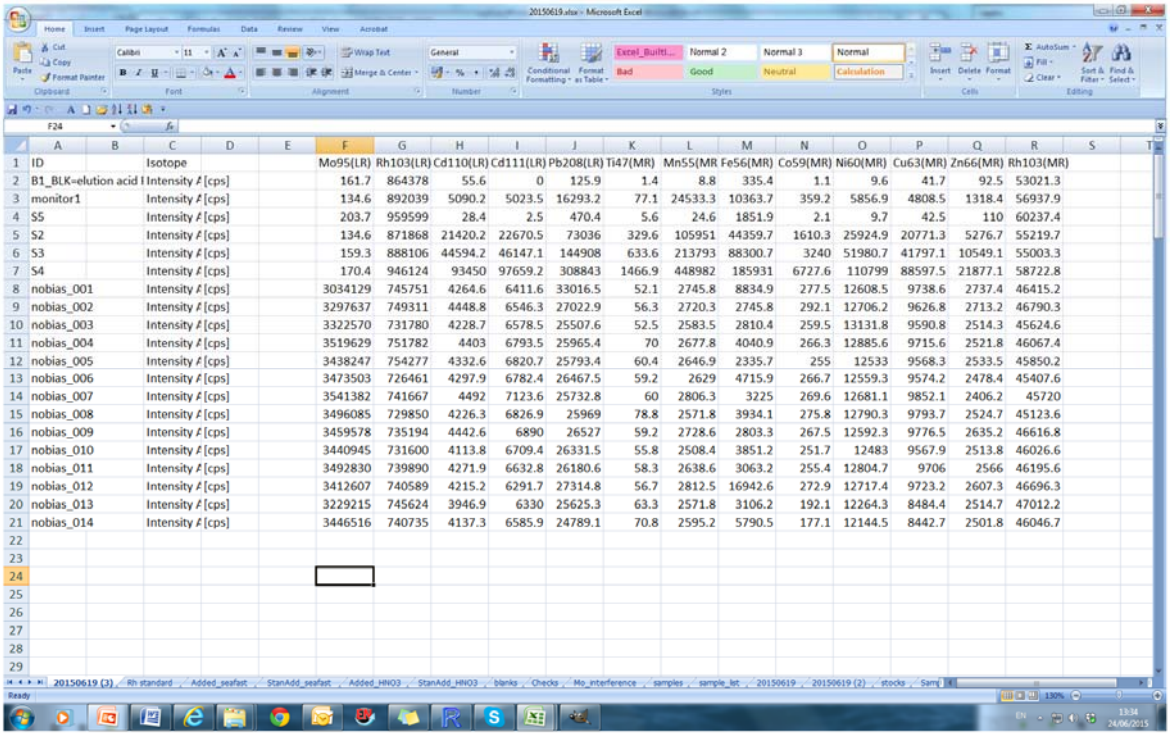
First we create a folder (other than the R work directory) where we place the excel file with the ICPMS data. In our case we name the folder after the date of the ICPMS run, e.g. 20150619. On a windows system you can use a number or a "text" to indicate the run. On an Apple system you need to use a number to indicate the run.

<u>The main-datasheet</u>

The excel file with ICPMS results (not Rh corrected) looks in our case like the example as shown in Figure 1 a. The first action is to add a column with an "index", see red arrow in Figure 1 b. This index will be copy pasted with subsets of the data so that all data stays retraceable to the original main-datasheet. This index is also necessary to allow identification of the right Rh correction for each sample data.

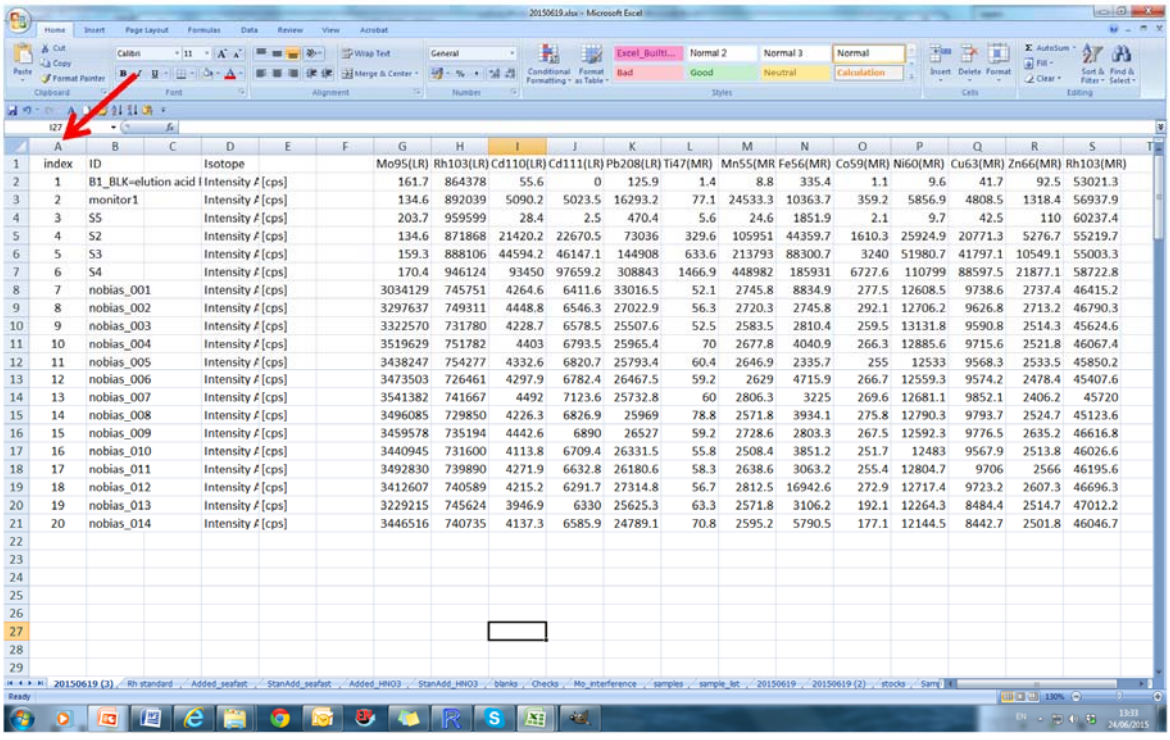
As some groups do not use Rh to correct for variation in ICPMS sensitivity and sample evaporation but for example Ga it is now possible to set the element that you use. However, throughout this manual Rh is used as example.

a.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	ID		Isotope			Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)	
2	B1_BLK=elution acid I		Intensity / [cps]			161.7	864378	55.6	0	125.9	1.4	8.8	335.4	1.1	9.6	41.7	92.5	53021.3	
3	monitor1		Intensity / [cps]			134.6	892039	5090.2	5023.5	16293.2	77.1	24533.3	10363.7	359.2	5856.9	4808.5	1318.4	56937.9	
4	S5		Intensity / [cps]			203.7	959599	28.4	2.5	470.4	5.6	24.6	1851.9	2.1	9.7	42.5	110	60237.4	
5	S2		Intensity / [cps]			134.6	871868	21420.2	22670.5	73036	329.6	105951	44359.7	1610.3	25924.9	20771.3	5276.7	55219.7	
6	S3		Intensity / [cps]			159.3	888106	44594.2	46147.1	144908	633.6	213793	88300.7	3240	51980.7	41797.1	10549.1	55003.3	
7	S4		Intensity / [cps]			170.4	946124	93450	97659.2	308843	1466.9	448982	185931	6727.6	110799	88597.5	21877.1	58722.8	
8	nobias_001		Intensity / [cps]			3034129	745751	4264.6	6411.6	33016.5	52.1	2745.8	8834.9	277.5	12608.5	9738.6	2737.4	46415.2	
9	nobias_002		Intensity / [cps]			3297637	749311	4448.8	6546.3	27022.9	56.3	2720.3	2745.8	292.1	12706.2	9626.8	2713.2	46790.3	
10	nobias_003		Intensity / [cps]			3322570	731780	4228.7	6578.5	25507.6	52.5	2583.5	2810.4	259.5	13131.8	9590.8	2514.3	45624.6	
11	nobias_004		Intensity / [cps]			3519629	751782	4403	6793.5	25965.4	70	2677.8	4040.9	266.3	12885.6	9715.6	2521.8	46067.4	
12	nobias_005		Intensity / [cps]			3438247	754277	4332.6	6820.7	25793.4	60.4	2646.9	2335.7	255	12533	9568.3	2533.5	45850.2	
13	nobias_006		Intensity / [cps]			3473503	726461	4297.9	6782.4	26467.5	59.2	2629	4715.9	266.7	12559.3	9574.2	2478.4	45407.6	
14	nobias_007		Intensity / [cps]			3541382	741667	4492	7123.6	25732.8	60	2806.3	3225	269.6	12681.1	9852.1	2406.2	45720	
15	nobias_008		Intensity / [cps]			3496085	729850	4226.3	6826.9	25969	78.8	2571.8	3934.1	275.8	12790.3	9793.7	2524.7	45123.6	
16	nobias_009		Intensity / [cps]			3459578	735194	4442.6	6890	26527	59.2	2728.6	2803.3	267.5	12592.3	9776.5	2635.2	46616.8	
17	nobias_010		Intensity / [cps]			3440945	731600	4113.8	6709.4	26331.5	55.8	2508.4	3851.2	251.7	12483	9567.9	2513.8	46026.6	
18	nobias_011		Intensity / [cps]			3492830	739890	4271.9	6632.8	26180.6	58.3	2638.6	3063.2	255.4	12804.7	9706	2566	46195.6	
19	nobias_012		Intensity / [cps]			3412607	740589	4215.2	6291.7	27314.8	56.7	2812.5	16942.6	272.9	12717.4	9723.2	2607.3	46696.3	
20	nobias_013		Intensity / [cps]			3229215	745624	3946.9	6330	25625.3	63.3	2571.8	3106.2	192.1	12264.3	8484.4	2514.7	47012.2	
21	nobias_014		Intensity / [cps]			3446516	740735	4137.3	6585.9	24789.1	70.8	2595.2	5790.5	177.1	12144.5	8442.7	2501.8	46046.7	

b.

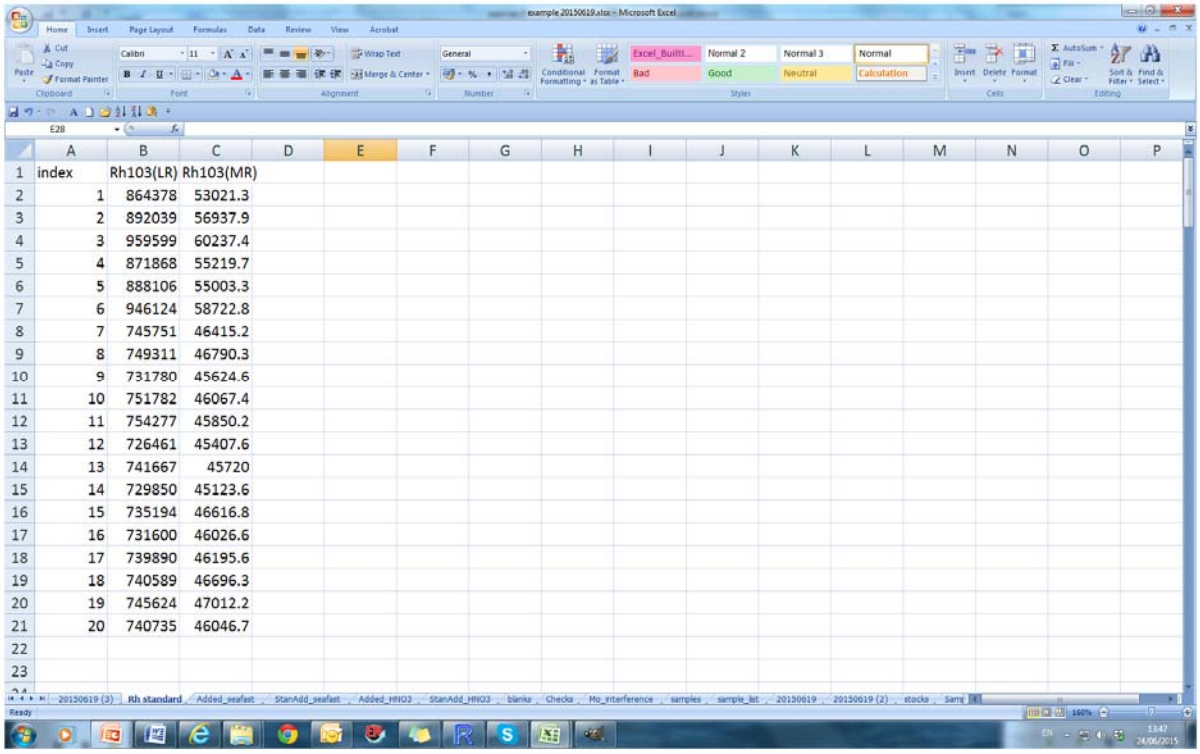


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	index	ID		Isotope			Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)
2	1	B1_BLK=elution acid I		Intensity / [cps]			161.7	864378	55.6	0	125.9	1.4	8.8	335.4	1.1	9.6	41.7	92.5	53021.3
3	2	monitor1		Intensity / [cps]			134.6	892039	5090.2	5023.5	16293.2	77.1	24533.3	10363.7	359.2	5856.9	4808.5	1318.4	56937.9
4	3	S5		Intensity / [cps]			203.7	959599	28.4	2.5	470.4	5.6	24.6	1851.9	2.1	9.7	42.5	110	60237.4
5	4	S2		Intensity / [cps]			134.6	871868	21420.2	22670.5	73036	329.6	105951	44359.7	1610.3	25924.9	20771.3	5276.7	55219.7
6	5	S3		Intensity / [cps]			159.3	888106	44594.2	46147.1	144908	633.6	213793	88300.7	3240	51980.7	41797.1	10549.1	55003.3
7	6	S4		Intensity / [cps]			170.4	946124	93450	97659.2	308843	1466.9	448982	185931	6727.6	110799	88597.5	21877.1	58722.8
8	7	nobias_001		Intensity / [cps]			3034129	745751	4264.6	6411.6	33016.5	52.1	2745.8	8834.9	277.5	12608.5	9738.6	2737.4	46415.2
9	8	nobias_002		Intensity / [cps]			3297637	749311	4448.8	6546.3	27022.9	56.3	2720.3	2745.8	292.1	12706.2	9626.8	2713.2	46790.3
10	9	nobias_003		Intensity / [cps]			3322570	731780	4228.7	6578.5	25507.6	52.5	2583.5	2810.4	259.5	13131.8	9590.8	2514.3	45624.6
11	10	nobias_004		Intensity / [cps]			3519629	751782	4403	6793.5	25965.4	70	2677.8	4040.9	266.3	12885.6	9715.6	2521.8	46067.4
12	11	nobias_005		Intensity / [cps]			3438247	754277	4332.6	6820.7	25793.4	60.4	2646.9	2335.7	255	12533	9568.3	2533.5	45850.2
13	12	nobias_006		Intensity / [cps]			3473503	726461	4297.9	6782.4	26467.5	59.2	2629	4715.9	266.7	12559.3	9574.2	2478.4	45407.6
14	13	nobias_007		Intensity / [cps]			3541382	741667	4492	7123.6	25732.8	60	2806.3	3225	269.6	12681.1	9852.1	2406.2	45720
15	14	nobias_008		Intensity / [cps]			3496085	729850	4226.3	6826.9	25969	78.8	2571.8	3934.1	275.8	12790.3	9793.7	2524.7	45123.6
16	15	nobias_009		Intensity / [cps]			3459578	735194	4442.6	6890	26527	59.2	2728.6	2803.3	267.5	12592.3	9776.5	2635.2	46616.8
17	16	nobias_010		Intensity / [cps]			3440945	731600	4113.8	6709.4	26331.5	55.8	2508.4	3851.2	251.7	12483	9567.9	2513.8	46026.6
18	17	nobias_011		Intensity / [cps]			3492830	739890	4271.9	6632.8	26180.6	58.3	2638.6	3063.2	255.4	12804.7	9706	2566	46195.6
19	18	nobias_012		Intensity / [cps]			3412607	740589	4215.2	6291.7	27314.8	56.7	2812.5	16942.6	272.9	12717.4	9723.2	2607.3	46696.3
20	19	nobias_013		Intensity / [cps]			3229215	745624	3946.9	6330	25625.3	63.3	2571.8	3106.2	192.1	12264.3	8484.4	2514.7	47012.2
21	20	nobias_014		Intensity / [cps]			3446516	740735	4137.3	6585.9	24789.1	70.8	2595.2	5790.5	177.1	12144.5	8442.7	2501.8	46046.7

Figure 1. a) The main-datasheet in excel with data as it originates from the ICPMS. Please, note that shown is a truncated example used for illustration purposes and not a full run. B) First add a column “index” with numbers. This index will be copy pasted with subsets of the data so that all data stays retraceable in the original main data sheet.

“StandardElement” sub-datasheet (Rh, Ga or other element used)

We now construct a number of sub-datasheets with data from the main-datasheet. The first sub-datasheet is the “StandardElement” sub-datasheet. Rh is used as an example throughout this manual. This sub-datasheet contains three columns: i) the “index”, ii) the Rh103(LR), and iii) the Rh103(MR), see Figure 2. The “index” column contains the index numbers as created in the first column of the main-datasheet and is a necessary column. Make sure that the header names of the necessary columns remain the same as in this manual. This sub-datasheet needs to be saved as “StandardElement.csv” in the same example folder “20150615”.

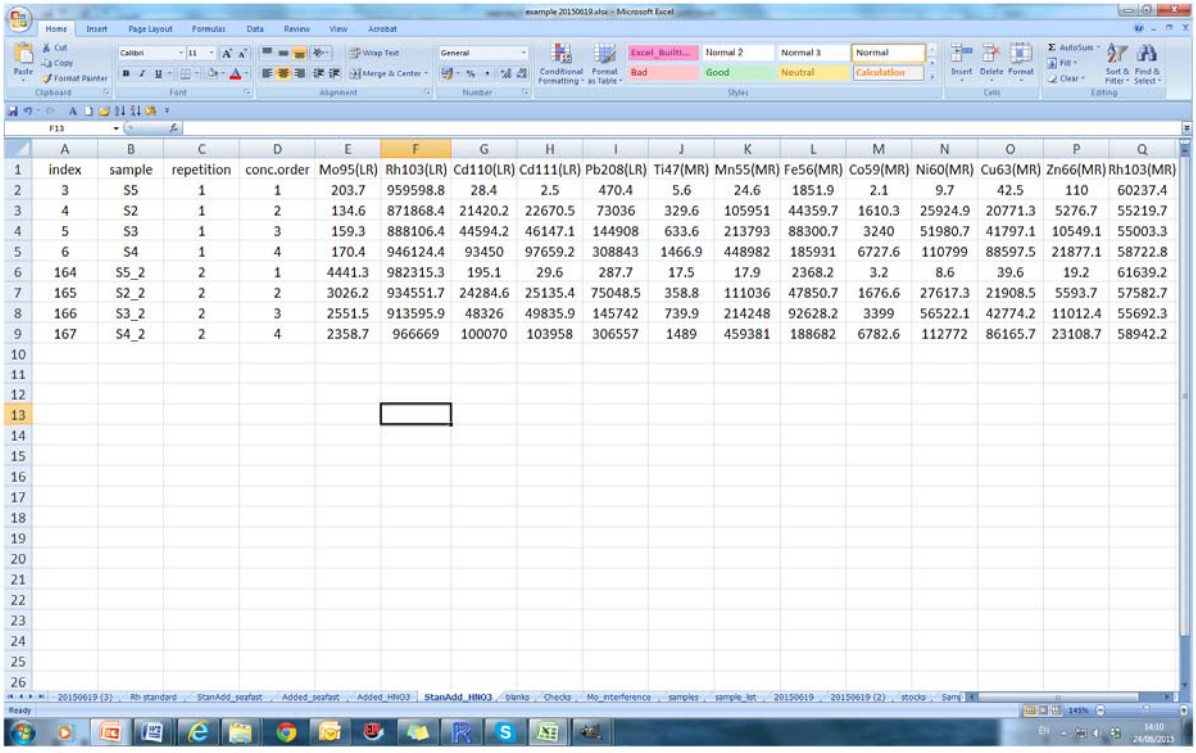


index	Rh103(LR)	Rh103(MR)
1	864378	53021.3
2	892039	56937.9
3	959599	60237.4
4	871868	55219.7
5	888106	55003.3
6	946124	58722.8
7	745751	46415.2
8	749311	46790.3
9	731780	45624.6
10	751782	46067.4
11	754277	45850.2
12	726461	45407.6
13	741667	45720
14	729850	45123.6
15	735194	46616.8
16	731600	46026.6
17	739890	46195.6
18	740589	46696.3
19	745624	47012.2
20	740735	46046.7

Figure 2. The StandardElement sub-datasheet.

“StanAdd_HNO3” sub-datasheet

The “StanAdd_HNO3” sub-datasheet contains the data of a standard addition to the HNO3 eluent. This data are only useful to relate the metal concentrations in the eluent blank to. This data is also used to calculate the percent recovery of the Seafast extracted metals. The necessary columns are: i) the “index”, ii) “sample”, iii) “repetition”, and iv) “conc.order”, see Figure 3. Make sure that the header names of the necessary columns remain the same as in this manual. The remaining columns contain the metal ICPMS data including the original header names (as long as they don’t contain spaces or exotic symbols). The ICPMS trace metal data can be copy pasted from the main-datasheet into this sub-datasheet in any order after the first four columns, with any metal identity (header needs to start with an element code e.g. Fe and end with LR or MR mode between brackets, e.g. (LR), so at a minimum Cd(LR)) or in any number. The “index” column contains the index numbers as created in the first column of the main-datasheet. The “sample” column contains the sample names as given in the main-datasheet, the “repetition” column shows the repeated standard additions. In this case we did a standard addition in the beginning of the run and at the end. The “conc.order” column gives the order and the identity of the standard additions. A sub-datasheet with the standard addition concentrations will also be created (next). The sub-datasheet StanAdd_HNO3 needs to be saved as “StanAdd_HNO3.csv” in the same example folder “20150615”.

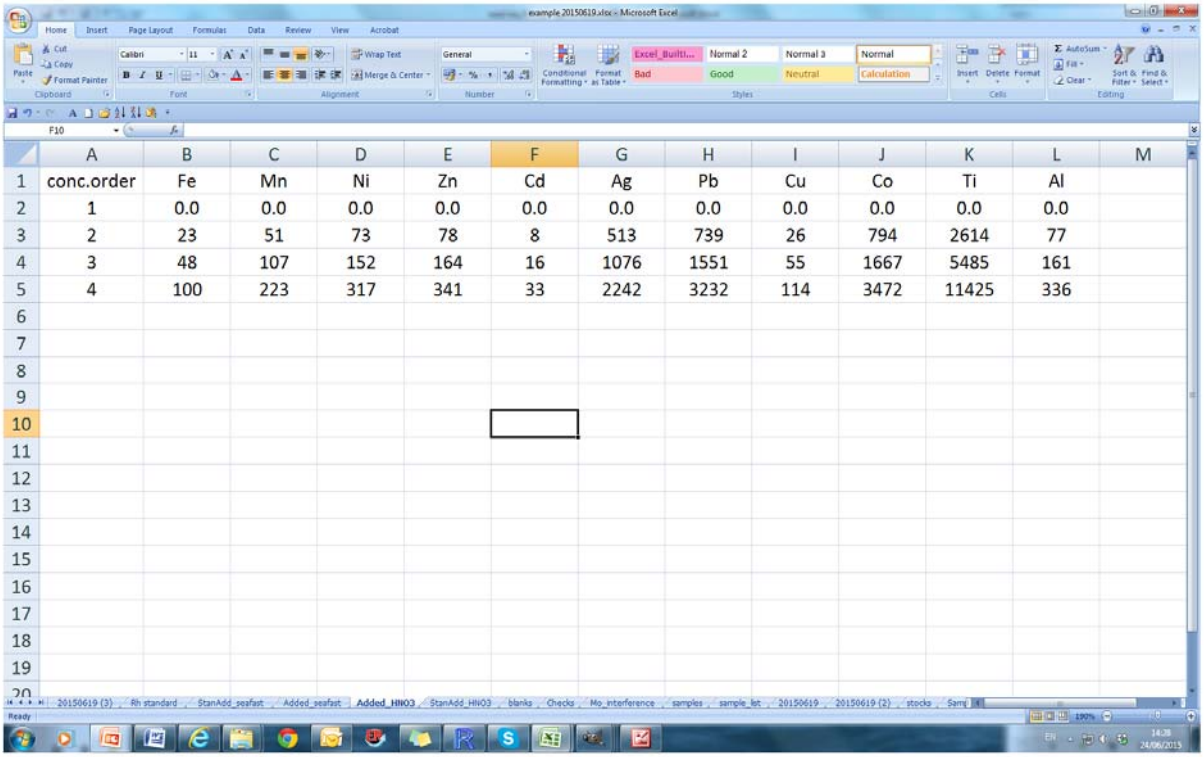


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	index	sample	repetition	conc.order	Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR)	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)
2	3	S5	1	1	203.7	959598.8	28.4	2.5	470.4	5.6	24.6	1851.9	2.1	9.7	42.5	110	60237.4
3	4	S2	1	2	134.6	871868.4	21420.2	22670.5	73036	329.6	105951	44359.7	1610.3	25924.9	20771.3	5276.7	55219.7
4	5	S3	1	3	159.3	888106.4	44594.2	46147.1	144908	633.6	213793	88300.7	3240	51980.7	41797.1	10549.1	55003.3
5	6	S4	1	4	170.4	946124.4	93450	97659.2	308843	1466.9	448982	185931	6727.6	110799	88597.5	21877.1	58722.8
6	164	S5_2	2	1	4441.3	982315.3	195.1	29.6	287.7	17.5	17.9	2368.2	3.2	8.6	39.6	19.2	61639.2
7	165	S2_2	2	2	3026.2	934551.7	24284.6	25135.4	75048.5	358.8	111036	47850.7	1676.6	27617.3	21908.5	5593.7	57582.7
8	166	S3_2	2	3	2551.5	913595.9	48326	49835.9	145742	739.9	214248	92628.2	3399	56522.1	42774.2	11012.4	55692.3
9	167	S4_2	2	4	2358.7	966669	100070	103958	306557	1489	459381	188682	6782.6	112772	86165.7	23108.7	58942.2

Figure 3. The StanAdd_HNO3 sub-datasheet.

“Added_HNO3” sub-datasheet

The “Added_HNO3” sub-datasheet contains the final concentrations of the standard additions to the HNO3 eluent for each metal, see Figure 4. The necessary column is: i) the “conc.order”, it contains the order and identity of the standard additions. The numbers in this columns need to match the numbers in the “conc.order” column of the “StanAdd_HNO3” sub-datasheet. Make sure that the header names of the necessary columns remain the same as in this manual. The headers for the metals need to be their element name, e.g. “Fe”. You can bring as many metal columns in as wished (no double though). It does not form a problem if it contains metals that you did not measure by IPMS or if it did not contain the metals that you did measure by ICPMS (however, these data will not be further used) in the seafast percent recovery calculations. The sub-datasheet Added_HNO3 needs to be saved as “Added_HNO3.csv” in the same example folder “20150615”.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	conc.order	Fe	Mn	Ni	Zn	Cd	Ag	Pb	Cu	Co	Ti	Al	
2	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
3	2	23	51	73	78	8	513	739	26	794	2614	77	
4	3	48	107	152	164	16	1076	1551	55	1667	5485	161	
5	4	100	223	317	341	33	2242	3232	114	3472	11425	336	
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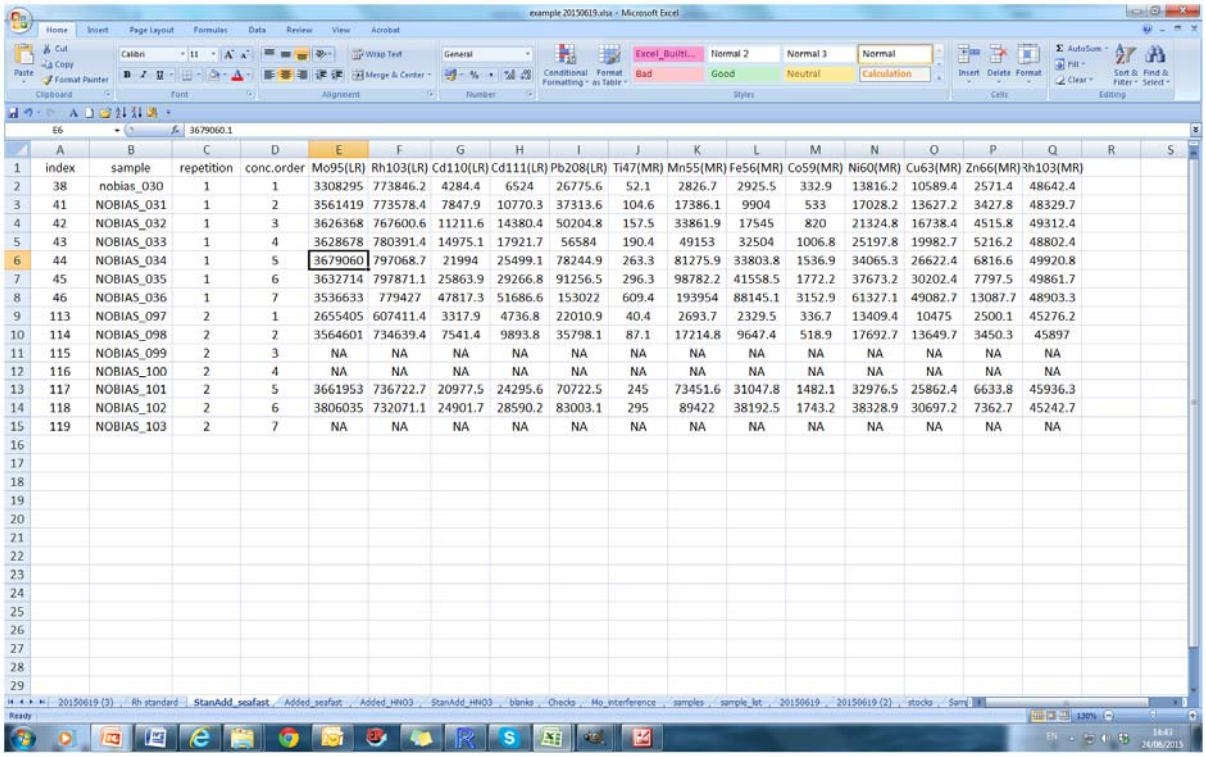
Figure 4. The Added_HNO3 sub-datasheet.

“StanAdd_seafast” sub-datasheet

The “StanAdd_seafast” sub-datasheet contains the data of a standard addition to seawater samples to be used with the seafast, see Figure 5. This data will be used to calculate the concentration metals in the original seawater samples.The necessary columns are: i) the “index”, ii) “sample”, iii) “repetition”, and iv) “conc.order”, see Figure 5. Make sure that the header names of the necessary columns remain the same as in this manual. The remaining columns contain the metal ICPMS data including the original header names (as long as they don’t contain spaces or exotic symbols). The ICPMS trace metal data can be copy pasted from the main-datasheet into this sub-datasheet in any order after the first four columns, with any metal identity (header needs to start with an element code e.g. Fe and end with LR or MR mode between brackets, e.g. (LR), so at a minimum Cd(LR)) or in any number. The “index” column contains the index numbers as created in the first column of the main-datasheet. The “sample” column contains the sample names as given in the main-datasheet, the “repetition” column shows the repeated standard additions. In this case we did a standard addition in the beginning of the run and at the end. The “conc.order” column gives the order and the identity of the standard additions. A sub-datasheet with the standard addition concentrations will also be created (next). The sub-datasheet StanAdd_seafast needs to be saved as “StanAdd_seafast.csv” in the same example folder “20150615”.

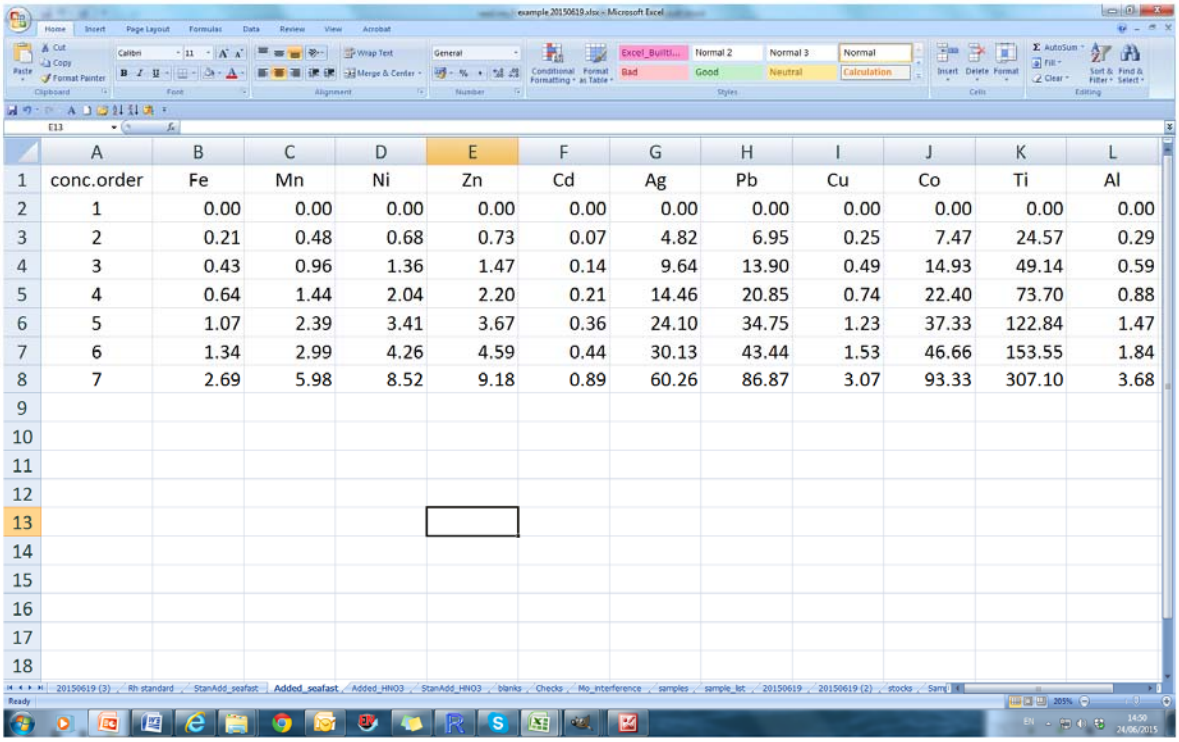


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	index	sample	repetition	conc.order	Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR)	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)		
2	38	nobias_030	1	1	3308295	773846.2	4284.4	6524	26775.6	52.1	2826.7	2925.5	332.9	13816.2	10589.4	2571.4	48642.4		
3	41	NOBIAS_031	1	2	3561419	773578.4	7847.9	10770.3	37313.6	104.6	17386.1	9904	533	17028.2	13627.2	3427.8	48329.7		
4	42	NOBIAS_032	1	3	3626368	767600.6	11211.6	14380.4	50204.8	157.5	33861.9	17545	820	21324.8	16738.4	4515.8	49312.4		
5	43	NOBIAS_033	1	4	3628678	780391.4	14975.1	17921.7	56584	190.4	49153	32504	1006.8	25197.8	19982.7	5216.2	48802.4		
6	44	NOBIAS_034	1	5	3679060	797068.7	21994	25499.1	78244.9	263.3	81275.9	33803.8	1536.9	34065.3	26622.4	6816.6	49920.8		
7	45	NOBIAS_035	1	6	3632714	797871.1	25863.9	29266.8	91256.5	296.3	98782.2	41558.5	1772.2	37673.2	30202.4	7797.5	49861.7		
8	46	NOBIAS_036	1	7	3536633	779427	47817.3	51686.6	153022	609.4	193954	88145.1	3152.9	61327.1	49082.7	13087.7	48903.3		
9	113	NOBIAS_097	2	1	2655405	607411.4	3317.9	4736.8	22010.9	40.4	2693.7	2329.5	336.7	13409.4	10475	2500.1	45276.2		
10	114	NOBIAS_098	2	2	3564601	734639.4	7541.4	9893.8	35798.1	87.1	17214.8	9647.4	518.9	17692.7	13649.7	3450.3	45897		
11	115	NOBIAS_099	2	3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
12	116	NOBIAS_100	2	4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
13	117	NOBIAS_101	2	5	3661953	736722.7	20977.5	24295.6	70722.5	245	73451.6	31047.8	1482.1	32976.5	25862.4	6633.8	45936.3		
14	118	NOBIAS_102	2	6	3806035	732071.1	24901.7	28590.2	83003.1	295	89422	38192.5	1743.2	38328.9	30697.2	7362.7	45242.7		
15	119	NOBIAS_103	2	7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		

Figure 5. The StanAdd_seafast sub-datasheet.

“Added_seafast” sub-datasheet

The “Added_seafast” sub-datasheet contains the final concentrations of the standard additions for each metal to the seawater samples used with the seafast, see Figure 6. The necessary column is: i) the “conc.order”, it contains the order and identity of the standard additions. The numbers in this columns need to match the numbers in the “conc.order” column of the “StanAdd_seafast” sub-datasheet. Make sure that the header names of the necessary columns remain the same as in this manual. The headers for the metals need to be their element name, e.g. “Fe”. You can bring as many metal columns in as wished (no double though). It does not form a problem if it contains metals that you did not measure by IPMS or if it did not contain the metals that you did measure by ICPMS (however, these data will not be further used). The sub-datasheet Added_seafast needs to be saved as “Added_seafast.csv” in the same example folder “20150615”.

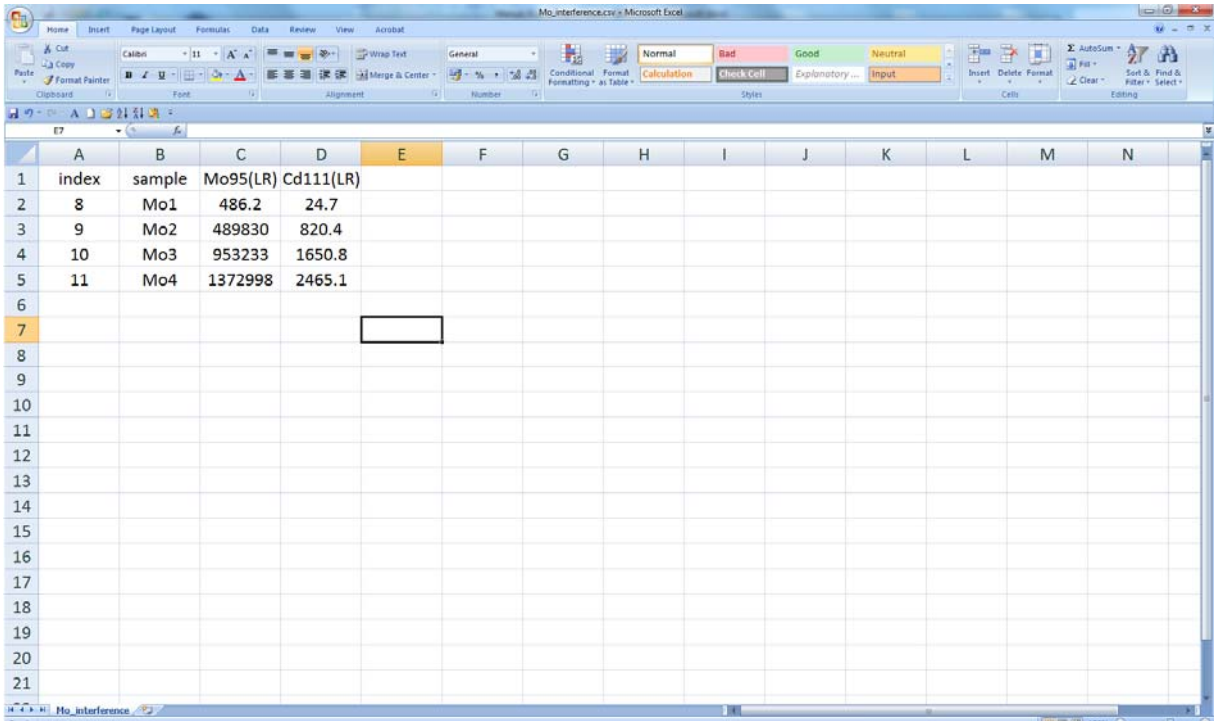


	A	B	C	D	E	F	G	H	I	J	K	L
1	conc.order	Fe	Mn	Ni	Zn	Cd	Ag	Pb	Cu	Co	Ti	Al
2	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	2	0.21	0.48	0.68	0.73	0.07	4.82	6.95	0.25	7.47	24.57	0.29
4	3	0.43	0.96	1.36	1.47	0.14	9.64	13.90	0.49	14.93	49.14	0.59
5	4	0.64	1.44	2.04	2.20	0.21	14.46	20.85	0.74	22.40	73.70	0.88
6	5	1.07	2.39	3.41	3.67	0.36	24.10	34.75	1.23	37.33	122.84	1.47
7	6	1.34	2.99	4.26	4.59	0.44	30.13	43.44	1.53	46.66	153.55	1.84
8	7	2.69	5.98	8.52	9.18	0.89	60.26	86.87	3.07	93.33	307.10	3.68
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												

Figure 6. The Added_seafast sub-datasheet.

“Mo_interference” sub-datasheet

The “Mo_interference” sub-datasheet contains the data of a standard addition of Mo to seawater samples to be used to correct for Mo interference of the Cd measurement on the ICPMS, see Figure 7. This data will be used to determine the Mo interference of Cd and correct the Cd concentrations for it. If you are not interested in Cd you don’t need this sub_datasheet. Also if you have Cd data you can chose not to correct for Mo interference. The necessary columns are: i) the “index”, ii) “sample”, iii) “Mo95(LR)”, and iv) one of both Cd110(LR) or Cd111(LR), see Figure 7. Make sure that the header names of the necessary columns remain the same as in this manual. Make sure that the Cd isotope that you use is the same as the Cd isotope in your dataset. The “index” column contains the index numbers as created in the first column of the main-datasheet. The “sample” column contains the sample names as given in the main-datasheet. The sub-datasheet Mo_interference needs to be saved as “Mo_interference.csv” in the same example folder “20150615”.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	index	sample	Mo95(LR)	Cd111(LR)										
2	8	Mo1	486.2	24.7										
3	9	Mo2	489830	820.4										
4	10	Mo3	953233	1650.8										
5	11	Mo4	1372998	2465.1										
6														
7														
8														
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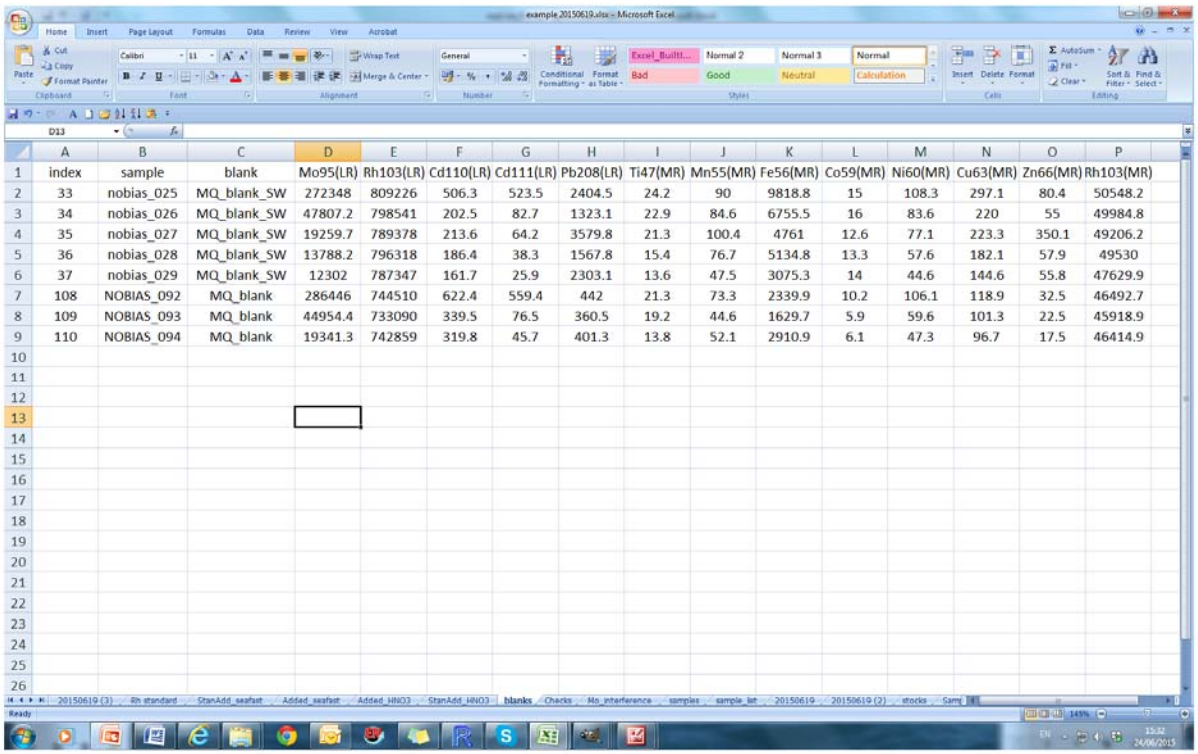
Figure 7. The Mo_interference sub-datasheet.

“blanks” sub-datasheet

The “blanks” sub-datasheet contains the data to determine the seafast blank, see Figure 8. This data will be used to correct all seawater trace metal data for the seafast blank. The necessary columns are: i) the “index”, ii) “sample”, and iii) “blank”, see Figure 7. Make sure that the header names of the necessary columns remain the same as in this manual. The ICPMS trace metal data can be copy pasted from the main-datasheet into this sub-datasheet in any order after the first four columns, with any metal identity (header needs to start with an element code e.g. Fe and end with LR or MR mode between brackets, e.g. (LR), so at a minimum Cd(LR)) or in any number. The “index” column contains the index numbers as created in the first column of the main-datasheet. The “sample” column contains the sample names as given in the main-datasheet. The “blank” column gets and identifier for the type of blank you use. So you can do different blanks and group them by a common identifier in the “blank” column, see e.g. MQ_blank_SW and MQ_blank in Figure 8. Later you can chose which blank you will use to correct your data. The sub-datasheet blanks needs to be saved as “blanks.csv” in the same example folder “20150615”.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	index	sample	blank	Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR)	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)
2	33	nobias_025	MQ_blank_SW	272348	809226	506.3	523.5	2404.5	24.2	90	9818.8	15	108.3	297.1	80.4	50548.2
3	34	nobias_026	MQ_blank_SW	47807.2	798541	202.5	82.7	1323.1	22.9	84.6	6755.5	16	83.6	220	55	49984.8
4	35	nobias_027	MQ_blank_SW	19259.7	789378	213.6	64.2	3579.8	21.3	100.4	4761	12.6	77.1	223.3	350.1	49206.2
5	36	nobias_028	MQ_blank_SW	13788.2	796318	186.4	38.3	1567.8	15.4	76.7	5134.8	13.3	57.6	182.1	57.9	49530
6	37	nobias_029	MQ_blank_SW	12302	787347	161.7	25.9	2303.1	13.6	47.5	3075.3	14	44.6	144.6	55.8	47629.9
7	108	NOBIAS_092	MQ_blank	286446	744510	622.4	559.4	442	21.3	73.3	2339.9	10.2	106.1	118.9	32.5	46492.7
8	109	NOBIAS_093	MQ_blank	44954.4	733090	339.5	76.5	360.5	19.2	44.6	1629.7	5.9	59.6	101.3	22.5	45918.9
9	110	NOBIAS_094	MQ_blank	19341.3	742859	319.8	45.7	401.3	13.8	52.1	2910.9	6.1	47.3	96.7	17.5	46414.9

Figure 8. The blanks sub-datasheet.

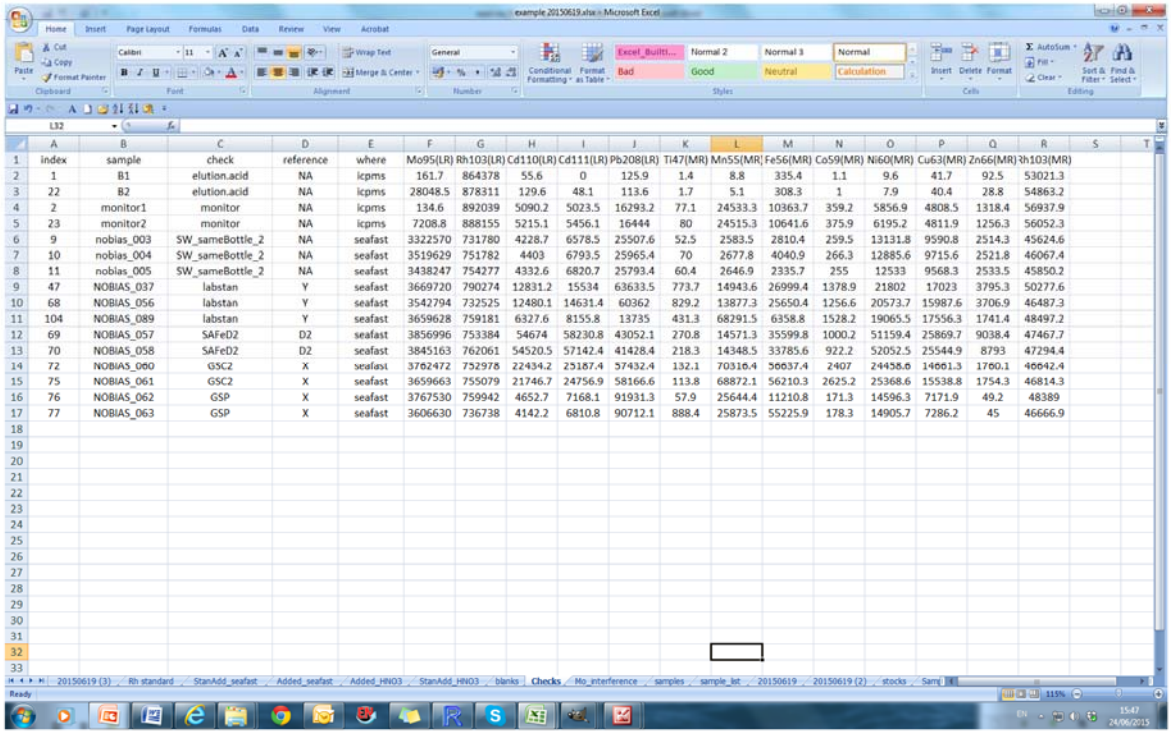
"checks" sub-datasheet

The "checks" sub-datasheet contains the data used to check different aspects, see Figure 9a. Figure 9a shows a checks sub-dataset checking the elution acid, a monitor to check the ICPMS, a check of reproducibility, a labstandard and several reference materials like SAFE. The necessary columns are: i) the "index", ii) "sample", iii) "check", iv) "reference", and v) "where", see Figure 9a. Make sure that the header names of the necessary columns remain the same as in this manual. The ICPMS trace metal data can be copy pasted from the main-datasheet into this sub-datasheet in any order after the first four columns, with any metal identity (header needs to start with an element code e.g. Fe and end with LR or MR mode between brackets, e.g. (LR), so at a minimum Cd(LR)) or in any number. The "index" column contains the index numbers as created in the first column of the main-datasheet. The "sample" column contains the sample names as given in the main-datasheet. The "check" column contains an identifier for the type of check and to group them. So you can do different checks and group them by a common identifier in the "check" column, see e.g. elution.acid and SafeD2 in Figure 9a. The "reference" column identifies the reference materials used. There is a code for the several SAFE and GEOTRACES reference samples that have consensus values attached (e.g. D2 for the SafeD2 sample see Figure 9a, other codes can be found and/or changed in the csv file with reference materials in the column "code", see Figure 9b). You can use a code like X, Y or Z or any other not used yet to indicate reference samples without consensus values like the lab standards or some of the newer official reference samples. The "where" column contains only the identifiers "seafast" and "icpms" to identify what is being checked. These identifiers are important as it determines which standard addition is used and which blanks or if blanks are used. The sub-datasheet checks needs to be saved as "checks.csv" in the same example folder "20150615".

The "TraceMetalReferenceConsensusValues.csv" file

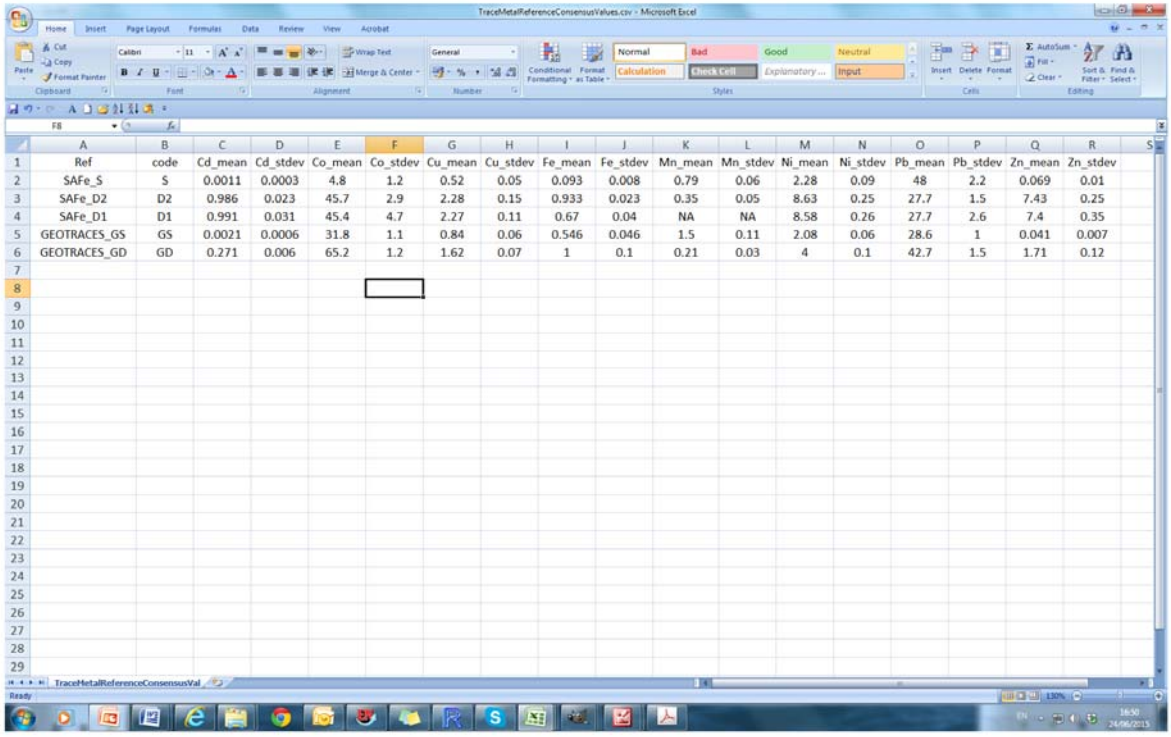
The "TraceMetalReferenceConsensusValues.csv" file contains any know consensus values, see Figure 9b. The necessary columns are: i) the "Ref", and ii) "code". The "Ref" column identifies the reference material used. The "code" column provides an identifier that is also used in the "reference" column of the "check" sub-datasheet. You can change these codes if you want or you can add reference materials to it and add a new code. The "TraceMetalReferenceConsensusValues.csv" needs to be saved in the same folder as the R script and the Functions script as this file will not change between different ICPMS runs.

a.



index	sample	check	reference	where	Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR)	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)
1	B1	elution.acid	NA	icpms	161.7	864378	55.6	0	125.9	1.4	8.8	335.4	1.1	9.6	41.7	92.5	53021.3
22	B2	elution.acid	NA	icpms	28048.5	878311	129.6	48.1	113.6	1.7	5.1	308.3	1	7.9	40.4	28.8	54863.2
2	monitor1	monitor	NA	icpms	134.6	892039	5090.2	5023.5	16293.2	77.1	24533.3	10363.7	359.2	5856.9	4808.5	1318.4	56937.9
23	monitor2	monitor	NA	icpms	7208.8	888155	5215.1	5456.1	16444	80	24515.3	10641.6	375.9	6195.2	4811.9	1256.3	56052.3
9	nobias_003	SW_sameBottle_2	NA	seafast	3322570	731780	4228.7	6578.5	25507.6	52.5	2583.5	2810.4	259.5	13131.8	9590.8	2514.3	45624.6
10	nobias_004	SW_sameBottle_2	NA	seafast	3519629	751782	4403	6793.5	25965.4	70	2677.8	4040.9	266.3	12885.6	9715.6	2521.8	46067.4
11	nobias_005	SW_sameBottle_2	NA	seafast	3438247	754277	4332.6	6820.7	25793.4	60.4	2646.9	2335.7	255	12533	9568.3	2533.5	45850.2
47	NOBIAS_037	labstan	Y	seafast	3669720	790274	12831.2	15534	63633.5	773.7	14943.6	26999.4	1378.9	21802	17023	3795.3	50277.6
68	NOBIAS_056	labstan	Y	seafast	3542794	732525	12480.1	14631.4	60362	829.2	13877.3	25650.4	1256.6	20573.7	15987.6	3706.9	46487.3
104	NOBIAS_089	labstan	Y	seafast	3659628	759181	6327.6	8155.8	13735	431.3	68291.5	6358.8	1528.2	19065.5	17556.3	1741.4	48497.2
69	NOBIAS_057	SAFeD2	D2	seafast	3856996	753384	54674	58230.8	43052.1	270.8	14571.3	35599.8	1000.2	51159.4	25869.7	9038.4	47467.7
70	NOBIAS_058	SAFeD2	D2	seafast	3845163	762061	54520.5	57142.4	41428.4	218.3	14348.5	33785.6	922.2	52052.5	25544.9	8793	47294.4
72	NOBIAS_060	GSC2	X	seafast	3762472	752978	22434.2	25187.4	57432.4	132.1	70316.4	56637.4	2407	24458.6	14661.3	1760.1	46642.4
75	NOBIAS_061	GSC2	X	seafast	3659663	755079	21746.7	24756.9	58166.6	113.8	68872.1	56210.3	2625.2	25368.6	15538.8	1754.3	46814.3
76	NOBIAS_062	GSP	X	seafast	3767530	759942	4652.7	7168.1	91931.3	57.9	25644.4	11210.8	171.3	14596.3	7171.9	49.2	48389
77	NOBIAS_063	GSP	X	seafast	3606630	736738	4142.2	6810.8	90712.1	888.4	25873.5	55225.9	178.3	14905.7	7286.2	45	46666.9

b.

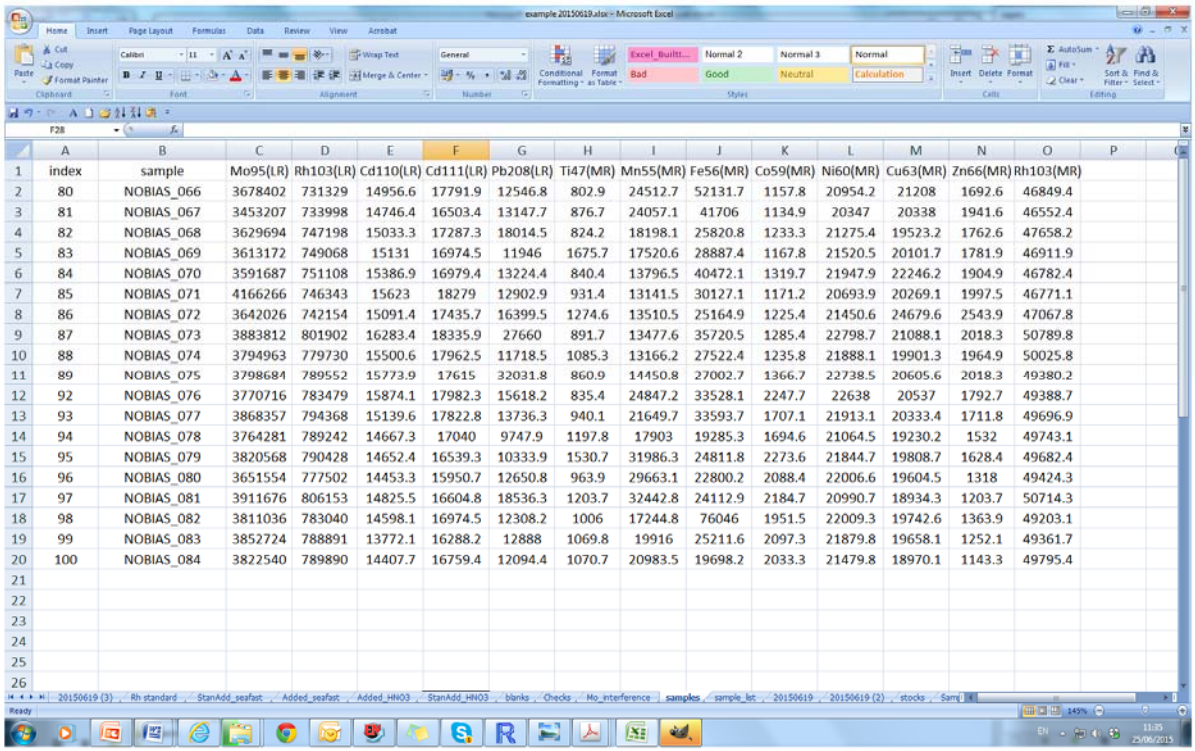


Ref	code	Cd_mean	Cd_stdev	Co_mean	Co_stdev	Cu_mean	Cu_stdev	Fe_mean	Fe_stdev	Mn_mean	Mn_stdev	Ni_mean	Ni_stdev	Pb_mean	Pb_stdev	Zn_mean	Zn_stdev
SAFe_S	S	0.0011	0.0003	4.8	1.2	0.52	0.05	0.093	0.008	0.79	0.06	2.28	0.09	48	2.2	0.069	0.01
SAFe_D2	D2	0.986	0.023	45.7	2.9	2.28	0.15	0.933	0.023	0.35	0.05	8.63	0.25	27.7	1.5	7.43	0.25
SAFe_D1	D1	0.991	0.031	45.4	4.7	2.27	0.11	0.67	0.04	NA	NA	8.58	0.26	27.7	2.6	7.4	0.35
GEOTRACES_GS	GS	0.0021	0.0006	31.8	1.1	0.84	0.06	0.546	0.046	1.5	0.11	2.08	0.06	28.6	1	0.041	0.007
GEOTRACES_GD	GD	0.271	0.006	65.2	1.2	1.62	0.07	1	0.1	0.21	0.03	4	0.1	42.7	1.5	1.71	0.12

Figure 9. a) The checks sub-datasheet, and b) the “TraceMetalReferenceConsensusValues.csv” data file.

“samples” sub-datasheet

The “samples” sub-datasheet contains the sample data, see Figure 10. This are the icpms data of the samples in which we wanted to measure the concentrations of the metals. The necessary columns are: i) the “index” and ii) “sample”. Make sure that the header names of the necessary columns remain the same as in this manual. The ICPMS trace metal data can be copy pasted from the main-datasheet into this sub-datasheet in any order after the first four columns, with any metal identity (header needs to start with an element code e.g. Fe and end with LR or MR mode between brackets, e.g. (LR), so at a minimum Cd(LR)) or in any number. The “index” column contains the index numbers as created in the first column of the main-datasheet. The “sample” column contains the sample names as given in the main-datasheet. The sub-datasheet samples needs to be saved as “samples.csv” in the same example folder “20150615”.

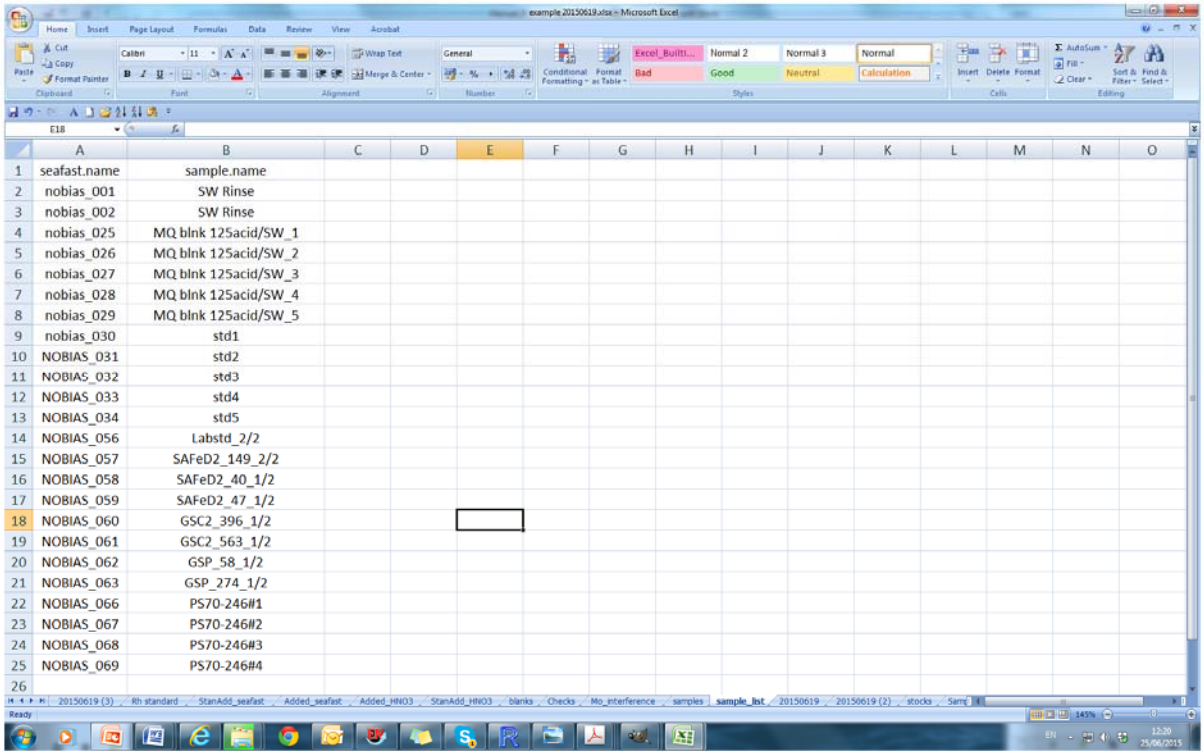


index	sample	Mo95(LR)	Rh103(LR)	Cd110(LR)	Cd111(LR)	Pb208(LR)	Ti47(MR)	Mn55(MR)	Fe56(MR)	Co59(MR)	Ni60(MR)	Cu63(MR)	Zn66(MR)	Rh103(MR)
80	NOBIAS_066	3678402	731329	14956.6	17791.9	12546.8	802.9	24512.7	52131.7	1157.8	20954.2	21208	1692.6	46849.4
81	NOBIAS_067	3453207	733998	14746.4	16503.4	13147.7	876.7	24057.1	41706	1134.9	20347	20338	1941.6	46552.4
82	NOBIAS_068	3629694	747198	15033.3	17287.3	18014.5	824.2	18198.1	25820.8	1233.3	21275.4	19523.2	1762.6	47658.2
83	NOBIAS_069	3613172	749068	15131	16974.5	11946	1675.7	17520.6	28887.4	1167.8	21520.5	20101.7	1781.9	46911.9
84	NOBIAS_070	3591687	751108	15386.9	16979.4	13224.4	840.4	13796.5	40472.1	1319.7	21947.9	22246.2	1904.9	46782.4
85	NOBIAS_071	4166266	746343	15623	18279	12902.9	931.4	13141.5	30127.1	1171.2	20693.9	20269.1	1997.5	46771.1
86	NOBIAS_072	3642026	742154	15091.4	17435.7	16399.5	1274.6	13510.5	25164.9	1225.4	21450.6	24679.6	2543.9	47067.8
87	NOBIAS_073	3883812	801902	16283.4	18335.9	27660	891.7	13477.6	35720.5	1285.4	22798.7	21088.1	2018.3	50789.8
88	NOBIAS_074	3794963	779730	15500.6	17962.5	11718.5	1085.3	13166.2	27522.4	1235.8	21888.1	19901.3	1964.9	50025.8
89	NOBIAS_075	3798684	789552	15773.9	17615	32031.8	860.9	14450.8	27002.7	1366.7	22738.5	20605.6	2018.3	49380.2
92	NOBIAS_076	3770716	783479	15874.1	17982.3	15618.2	835.4	24847.2	33528.1	2247.7	22638	20537	1792.7	49388.7
93	NOBIAS_077	3868357	794368	15139.6	17822.8	13736.3	940.1	21649.7	33593.7	1707.1	21913.1	20333.4	1711.8	49696.9
94	NOBIAS_078	3764281	789242	14667.3	17040	9747.9	1197.8	17903	19285.3	1694.6	21064.5	19230.2	1532	49743.1
95	NOBIAS_079	3820568	790428	14652.4	16539.3	10333.9	1530.7	31986.3	24811.8	2273.6	21844.7	19808.7	1628.4	49682.4
96	NOBIAS_080	3651554	777502	14453.3	15950.7	12650.8	963.9	29663.1	22800.2	2088.4	22006.6	19604.5	1318	49424.3
97	NOBIAS_081	3911676	806153	14825.5	16604.8	18536.3	1203.7	32442.8	24112.9	2184.7	20990.7	18934.3	1203.7	50714.3
98	NOBIAS_082	3811036	783040	14598.1	16974.5	12308.2	1006	17244.8	76046	1951.5	22009.3	19742.6	1363.9	49203.1
99	NOBIAS_083	3852724	788891	13772.1	16288.2	12888	1069.8	19916	25211.6	2097.3	21879.8	19658.1	1252.1	49361.7
100	NOBIAS_084	3822540	789890	14407.7	16759.4	12094.4	1070.7	20983.5	19698.2	2033.3	21479.8	18970.1	1143.3	49795.4

Figure 10. The samples sub-datasheet.

“sample_list” sub-datasheet

The “sample_list” sub-datasheet connects the sample name given to the seafast with the sample names, see Figure 11. This list will be used to implement the original sample names to the final results file. It is also used to implement the individual sample names into the figures with the reference material. This feature can be turned off by setting: sample.naming <- "no" in the script. So you ca use the script without this sub-datasheet. The necessary columns are: i) the “seafast.name” and ii) “sample.name”. The “seafast.name” column contains the sample names as given in the main-datasheet. The “sample.name” column contains the original sample names. Make sure that the header names of the necessary columns remain the same as in this manual. The sub-datasheet sample_list needs to be saved as “sample_list.csv” in the same example folder “20150615”.



	A	B
1	seafast.name	sample.name
2	nobias_001	SW Rinse
3	nobias_002	SW Rinse
4	nobias_025	MQ blnk 125acid/SW_1
5	nobias_026	MQ blnk 125acid/SW_2
6	nobias_027	MQ blnk 125acid/SW_3
7	nobias_028	MQ blnk 125acid/SW_4
8	nobias_029	MQ blnk 125acid/SW_5
9	nobias_030	std1
10	NOBIAS_031	std2
11	NOBIAS_032	std3
12	NOBIAS_033	std4
13	NOBIAS_034	std5
14	NOBIAS_056	Labstd_2/2
15	NOBIAS_057	SAFeD2_149_2/2
16	NOBIAS_058	SAFeD2_40_1/2
17	NOBIAS_059	SAFeD2_47_1/2
18	NOBIAS_060	GSC2_396_1/2
19	NOBIAS_061	GSC2_563_1/2
20	NOBIAS_062	GSP_58_1/2
21	NOBIAS_063	GSP_274_1/2
22	NOBIAS_066	PS70-246#1
23	NOBIAS_067	PS70-246#2
24	NOBIAS_068	PS70-246#3
25	NOBIAS_069	PS70-246#4
26		

Figure 11. The sample_list sub-datasheet.

5) Using the R script

Here below I will explain how to use the R script using a number of computer screen shots. I will also show how the results look like. The red number refer to numbers in the figures. Please, note that don't have to change any coding to upload the different data files as long as you positioned them in your main directory (see explanation below). All results will be automatically located in this folder and re-opened from this folder. So do not change their locations.

Starting

(1) If you use this script for the first time you will have to download a number of R packages. You only have to do this ones. Just remove the # and activate the line (run or cntrl R) and follow the instructions. After this you can replace the # (which prevents the line from being activated) because you do not need this line of code anymore.
(2) This line just cleans the memory from anything that R has put in there. You don't need to re-run this all the time.
(3) Part of the code depends on code written by others. To be able to use this script the libraries need to be activated when you start.
(4) When you work in the basic R environment (not R studio or such) it is easiest to turn of the buffer so that you see the messages displayed in the R console that shows you how far you are with your analysis. It also provides extra information.
(5) Some R code is different between Windows and Apple computers. Here you can indicate which system you use to run your script on. Basically the only difference in this script is that to create a figure a windows computer uses windows( ) and an Apple computer uses quartz ( ) instead.
(6) This line sets the working directory where your R script, your R Functions and your TraceMetalReferenceConsensusValues.csv file are located. You need to adapt this to your situation. Note, the example included and to use "/" instead of "\".
(7) This line opens the R Functions script with the functions needed to analyse your data for use in your R script.

The general parameters are a number of parameters that you need to adapt if necessary and which stay the same throughout the remainder of the R script. So adapt them and you activate them once after you started. If you start working with a new data set you may have to change part of it again.

(8) This vector shows the units used for each metal. You may have to change the location of the metals with respect to the vectors from nM (units.nM) to pM (units.pM) or visa versa depending on your own preferences.
(9) Generally an element like Rh or Ga is used to correct for variations in the sensitivity of the ICPMS. If you add this element to the bulk eluting HNO3 solution before extracting the metals from the column it also corrects for solution evaporation between extraction and measurement on the ICPMS. At this line you can include the element that you use for this.
(10) The **mainDir** directs the script to the folder with your data (the main-datasheet) and the sub-datasheet csv files. With this line the R script knows where to load the data from and where to save the results. The **name.run** is the name of your icpms run. It will appear in all file names (graphs and data) and as title in your figures.
(11) The fAcces.prev.files function allows loading data that has been produced during a previous use of this script with a certain data set when the procedure was not completed. It

prevents you to have to rerun the part of the script that you used in a previous session with a certain data set.

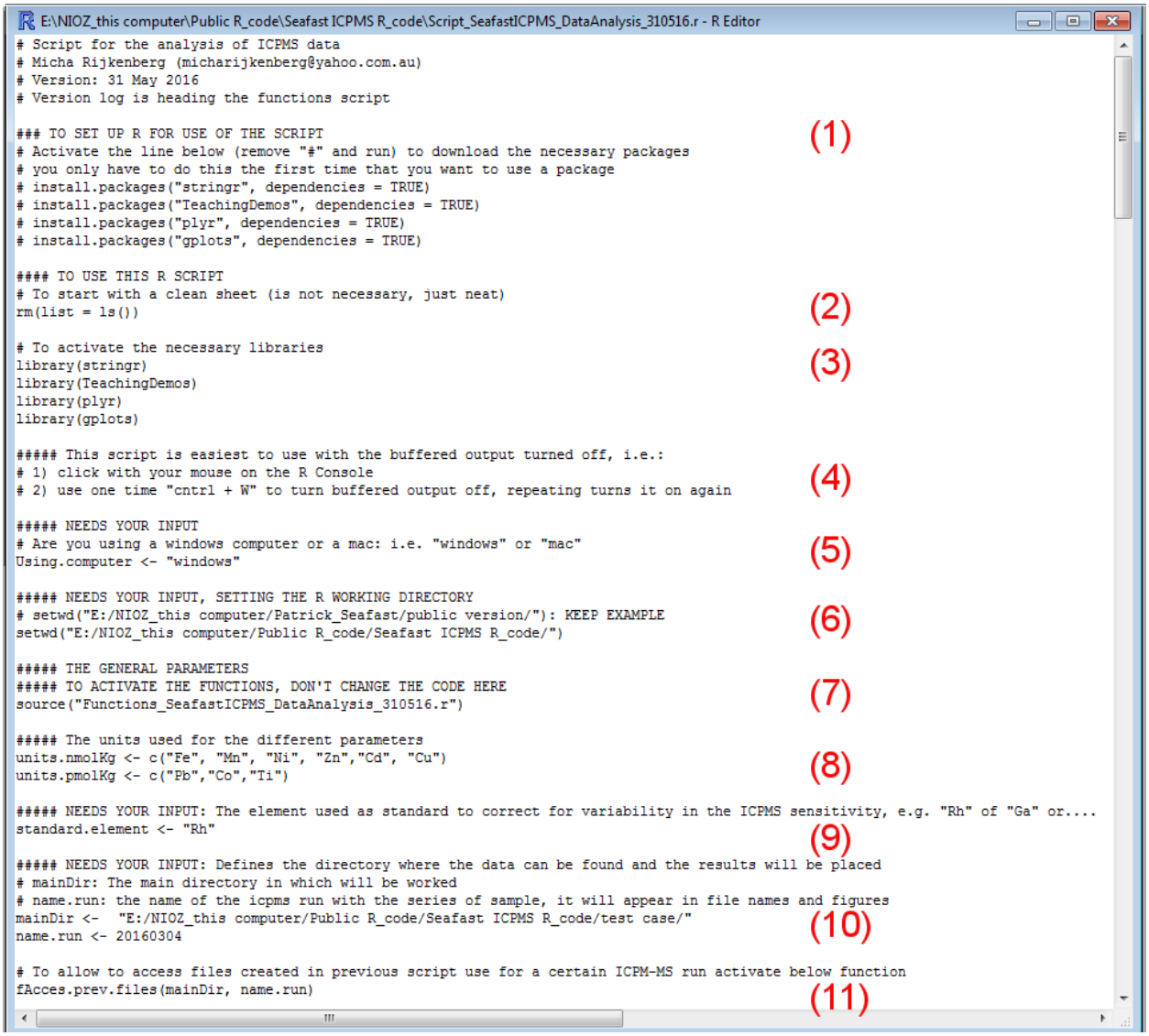


Figure 12. Start of the R script.

The fStElement.stand function

This function takes the standard.element like for example Rh or Ga etc data and normalizes your metal data to the mean standard element concentration. Variation due to changes in ICPMS sensitivity or evaporation of the sample extract are than corrected for, see Figure 13. Rh is used as an example throughout this manual.

(1) This line codes read in the data from the StandardElement.csv file that you created and shows you the headers and first five data points.

(2) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols

(3) In our case we find sometimes different levels of Rh concentrations depending on the additions to the samples. You cannot just all normalize them to one Rh value. You have to do that for each group separate. Using the "line.high.lr", "line.low.lr", "line.high.mr", "line.low.mr" you can separate a maximum of three different Rh concentration groups for both the LR and the MR resolution. By changing the numbers behind them and re-running the function below you can fine tune the groups, see Figure 14. If you have only two Rh concentration groups you can put the "line.low" at 0 and if all samples had the same Rh concentration you can change "line.low" and "line.high" to 0 for both LR and MR. Sometimes it is impossible to neatly separate the groups. Try to do it as good as possible and adapt the final resulting csv file by hand for the samples that you were unable to place in the Rh concentration group where they belonged. After manual adaption of the csv file don't rerun the fRh.stand function anymore as it will change your adapted csv file again.

(4) This line runs the function. It results in a tif file of the graph shown in Figure 14 and in a csv file with the mean Rh concentration for the different Rh groups and the two different resolutions LR and MR. The csv file needs to stay at the location where it was saved to as it will be used from there further on in the script.

```
################ Standard Element ###################################################################
# With Standard Element the elment like Rh or Ga is meant which is used
# among others to correct for variation in the ICPMS sensitivity.

# To read in the results of the StandardElement.csv, DON'T CHANGE THE CODE HERE                    (1)
st.el <- read.csv(paste(mainDir,"StandardElement.csv",sep=""),header=TRUE)
head(st.el)

# Graphing parameters, CAN BE CHANGED                                                              (2)
resolution.figures <- 150
cex=1.5
cex.lab=1.5
cex.axis = 1.5

# NEEDS YOUR INPUT, These lines separate the different Standard Element concentrations used.
# With the line.high and line.low you can divide the Standard.Element in a maximum of three distinct groups.   (3)
# You can fill in any number for the lines as long line.high > line.low and as long there is a number, at least a 0.
# LR
line.high.lr <- 0.78e5
line.low.lr <- 0.45e5

# MR
line.high.mr <- 4e4
line.low.mr <- 1e4

# Function, DON'T CHANGE THE CODE HERE                                                             (4)
fStElement.stand(st.el, name.run, mainDir, resolution.figures, cex, cex.lab, cex.axis)
```

Figure 13. The function needed to correct the data for changes in ICPMS sensitivity using Rh.

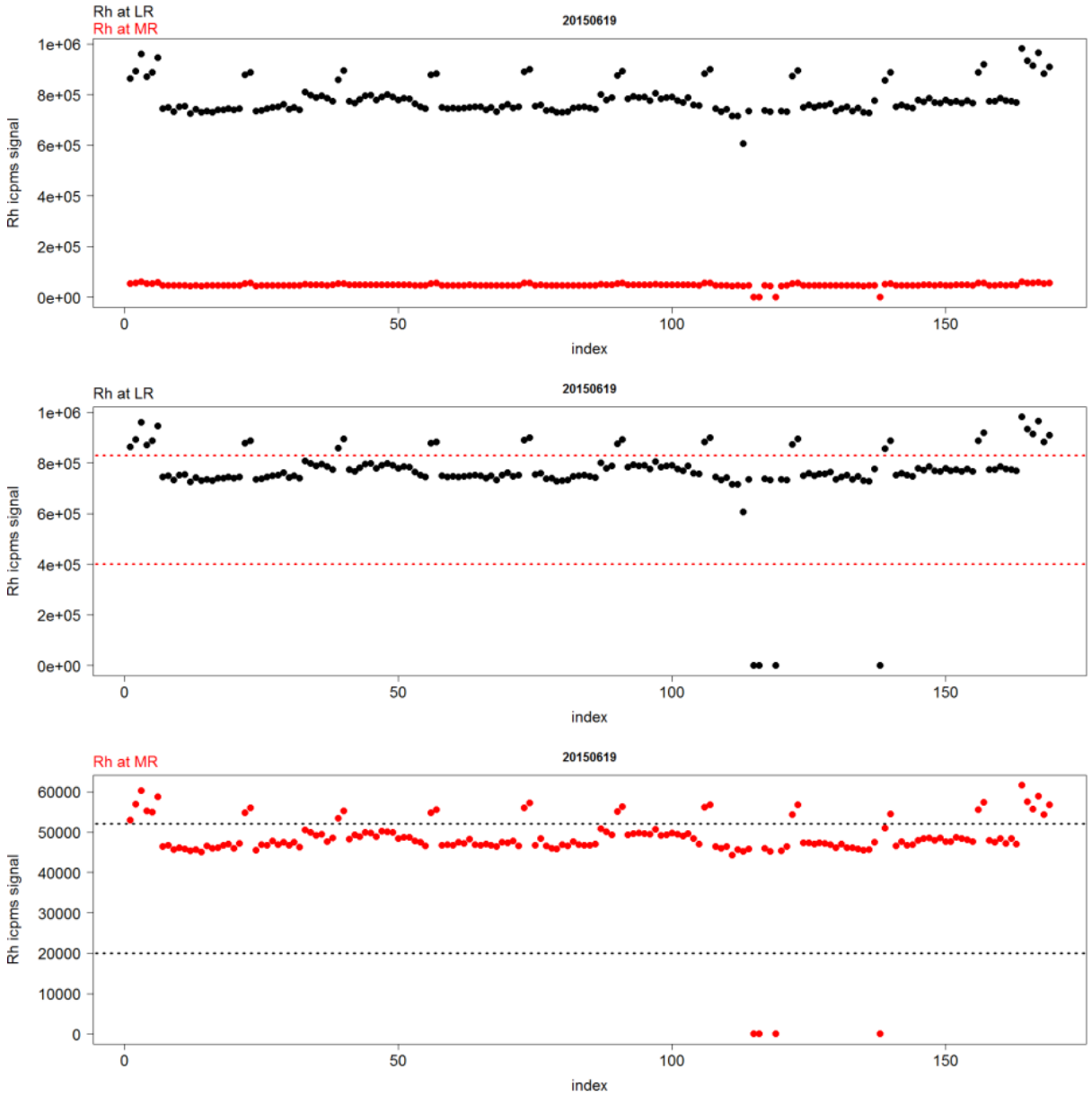


Figure 14. The fStElement.stand_function results (among others) in this graph. The lines in the lower two graphs visualize how you divided the groups with different Rh concentrations. You can manipulate this lines within the R script. The data will be normalized to the mean Rh concentration of the Rh concentration group that they belong to.

The fStandAdd.HNO3 and fStandAdd.seafast functions

These functions uses the "StanAdd_HNO3.csv", "StanAdd_seafast.csv", "Add_HNO3.csv" and "Add_seafast.csv" files for the standard additions in the HNO3 eluent and in seawater used with the seafast and provides the slopes for each metal of each standard addition and visualizes the results in graphs saved as tif files, see Figure 15 a,b. Variation due to changes in ICPMS sensitivity are corrected for using the Rh data.

(1, 2 and 3) These lines read in the data from the files "StanAdd_HNO3.csv", "StanAdd_seafast.csv", "Add_HNO3.csv" and "Add_seafast.csv" and the results from the fRh.stand function to correct the data for changes in ICPMS sensitivity. In each case the header and five of the data rows will be shown.

(4) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols

(5) This line determines if you want to have the data corrected for changes in ICPMS sensitivity (Standard.element.correction <- "yes") or not (Standard.element.correction <- "no").

(6) These are the functions fStandAdd.HNO3 and fStandAdd.seafast that you need to run. It will result in graphs visualizing the standard additions and in a .csv file with the slope etc that will be used later to calculate the metal concentrations in your samples, see Figure 16. The HNO3 standard addition is only used for sample that are directly (without using the seafast) measured on the ICPMS and to calculate the recovery efficiency of each metal by the seafast system.

a.

```
######### Standard addition in HNO3 ###################################################################

# To read in the results of the ICPMS, DON'T CHANGE THE CODE HERE                                    (1)
ic <- read.csv(paste(mainDir,"StanAdd_HNO3.csv",sep=""),header=TRUE)
head(ic)

# To read in the added metal concentrations for the standard addition, DON'T CHANGE THE CODE HERE   (2)
ad <- read.csv(paste(mainDir,"Added_HNO3.csv",sep=""),header=TRUE)
head(ad)

# To read in the results of the standard.element, DON'T CHANGE THE CODE HERE                         (3)
st.el <- read.csv(paste(folder.rh,standard.element," standard data_",name.run,".csv",sep=""),header=TRUE)
head(st.el)

# Graphing parameters, CAN BE CHANGED                                                                (4)
resolution.figures <- 150
cex=1.3
cex.lab=1.2
cex.axis = 1

# Other parameters, CAN BE CHANGED                                                                   (5)
# Standard.element correction
Standard.element.correction <- "yes"

# Function, DON'T CHANGE THE CODE HERE                                                               (6)
fStandAdd.HNO3(ic, ad, st.el, name.run, mainDir, resolution.figures, cex, cex.lab, cex.axis, Standard.element.correction)
```

b.

```
######### Standard addition in seawater over the seafast ##################################

# To read in the results of the ICPMS, DON'T CHANGE THE CODE HERE                                    (1)
sf <- read.csv(paste(mainDir,"StanAdd_seafast.csv",sep=""),header=TRUE)
head(sf)

# To read in the added metal concentrations for the standard addition, DON'T CHANGE THE CODE HERE   (2)
ad.sf <- read.csv(paste(mainDir,"Added_seafast.csv",sep=""),header=TRUE)
head(ad.sf)

# To read in the results of the standard.element, DON'T CHANGE THE CODE HERE                         (3)
st.el <- read.csv(paste(folder.rh,standard.element," standard data_",name.run,".csv",sep=""),header=TRUE)
head(st.el)

# Graphing parameters, CAN BE CHANGED                                                                (4)
resolution.figures <- 150
cex=1.3
cex.lab=1.2
cex.axis = 1

# Other parameters, CAN BE CHANGED                                                                   (5)
# Rh correction
Standard.element.correction <- "yes"

# Function, DON'T CHANGE THE CODE HERE                                                               (6)
fStandAdd.seafast(sf, ad.sf, st.el, name.run, mainDir, resolution.figures, cex, cex.lab, cex.axis, Standard.element.correction)
```

Figure 15 a,b. The functions fStandAdd.HNO3 and fStandAdd.seafast for the standard additions.

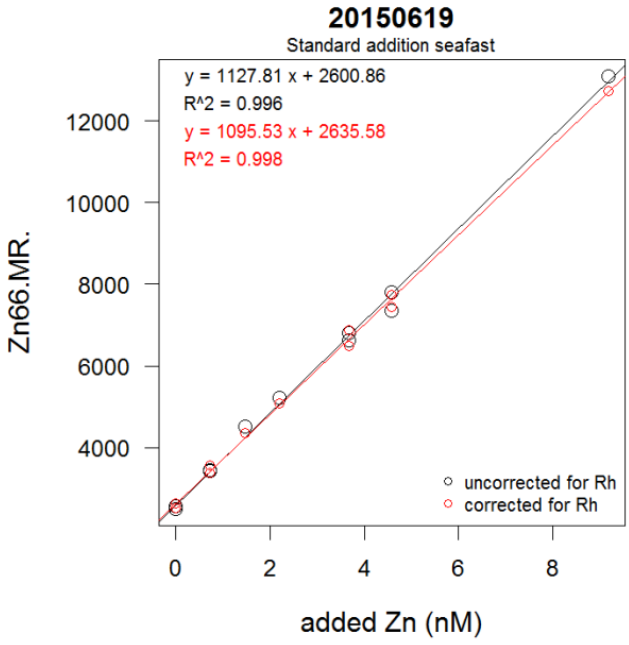


Figure 16. Example of a figure with the seafast standard addition of Zn.

The fMo.interference function

This function takes the data of a Mo standard addition to HNO3 eluent to determine the Mo interference on the Cd signal. This can be used to correct the Cd data for this interference, see Figure 17.

(1, 2) These lines read in the data from the Mo_interference.csv file and the Rh results to correct the data for changes in the ICPMS sensitivity.

(3) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols

(4) This line determines if you want to have the data corrected for changes in ICPMS sensitivity (Standard.element.correction <- "yes") or not (Standard.element.correction <- "no").

(5) This line activates the fMo.interference function. It results in a csv file with the slope between changes in Mo and Cd used to correct the Cd data further on in the script. It also creates a graph as a tif file visualizing the relationship between Mo and Cd, see Figure 18.

```
### Correct Cd concentrations for Mo interference ########################################

# To read in the results of the ICPMS for the checks and balances, DON'T CHANGE THE CODE HERE
mo <- read.csv(paste(mainDir,"Mo_interference.csv",sep=""),header=TRUE)
head(mo)

# To read in the results of the standard.element, DON'T CHANGE THE CODE HERE
st.el <- read.csv(paste(folder.rh,standard.element," standard data_",name.run,".csv",sep=""),header=TRUE)
head(st.el)

# Graphing parameters, CAN BE CHANGED
resolution.figures <- 150
cex=1.3
cex.lab=1.2
cex.axis = 1

# Other parameters, CAN BE CHANGED
Standard.element.correction <- "yes"

# Function, DON'T CHANGE THE CODE HERE
fMo.interference.Cd(mo, st.el, resolution.figures, cex, cex.lab, cex.axis, Standard.element.correction)
```

(1)
(2)
(3)
(4)
(5)

Figure 17. The function fMo.interference for the correction of the Cd signal by Mo interference.

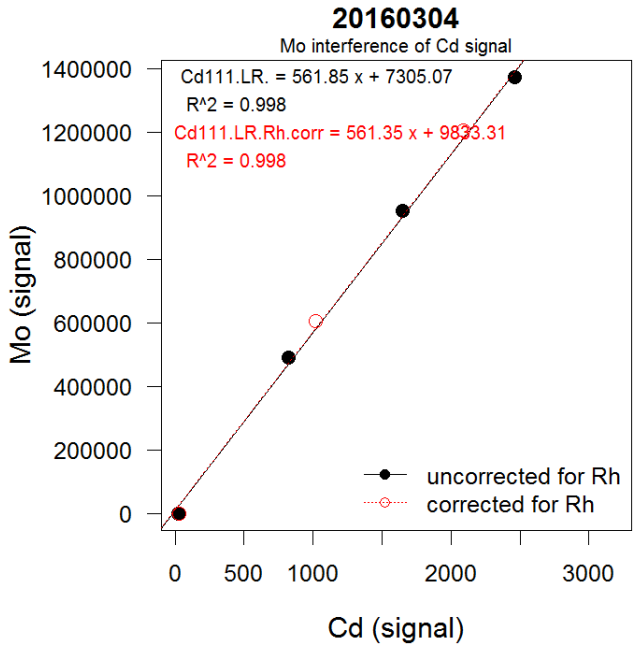


Figure 18. Example of the graph visualizing the Mo interference of the Cd signal.

The fBlank.Conc.Stats function

This function calculates the mean and median blanks for the different metals and visualizes them as boxplots saved as tif files where outliers are indicated by the index numbers as defined in the main-datasheet, see Figure 19. This so you can delete (replace by NA) these outliers from the blanks.csv file and re-run the function. In the remainder of the script the possibility is left open to either use the mean or the median to correct the metal data for the blank.

(1, 2, 3, 4) These code lines open the "blanks.csv" file with the blank data, the file with the results of the seafast standard addition, the results of the Rh correction, and the results to correct the Cd data for Mo interference and it shows the headers and first five rows of each of these files.

(5) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols

(6) This line determines if you want to have the data corrected for changes in ICPMS sensitivity (Standard.element.correction <- "yes") or not (Standard.element.correction <- "no"). You can also chose if you correct your Cd data for Mo interference (Mo.correction.Cd <- "yes") or not (Mo.correction.Cd <- "no").

(7) This line activates the fBlank.Conc.Stats function. It results in a csv file with the with among others the mean and median blanks of the metals of interest. It also creates for each metal a graph as a tif file with a boxplot visualizing the data spread and any outliers. Outliers are identified in blue numbers by their index number, see Figure 20. This is the index number that has been added to the main-datasheet.

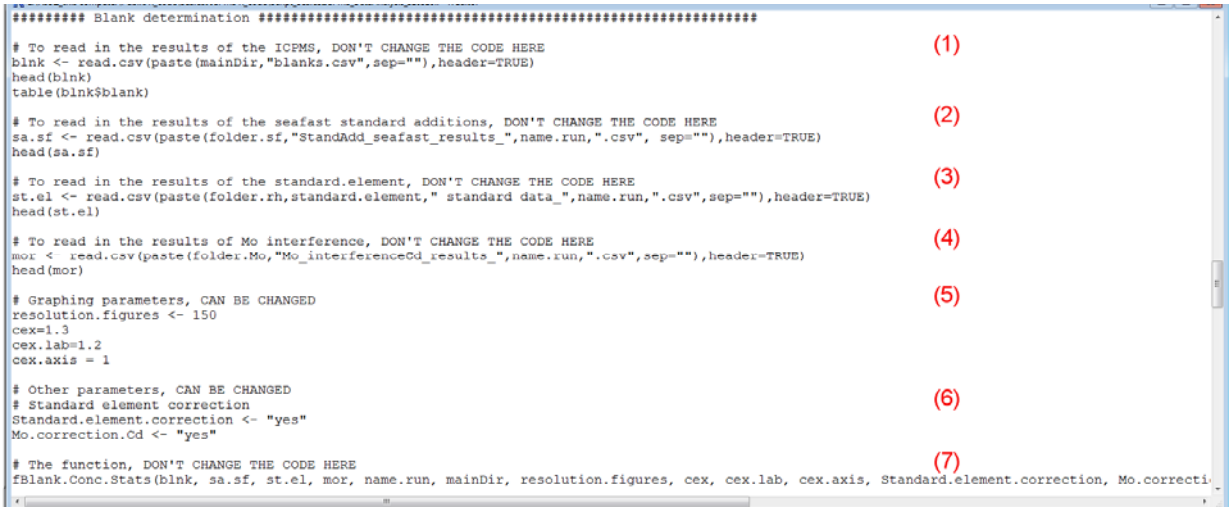


Figure 19. The function fBlank.Conc.Stats for calculation of mean and median blank values.

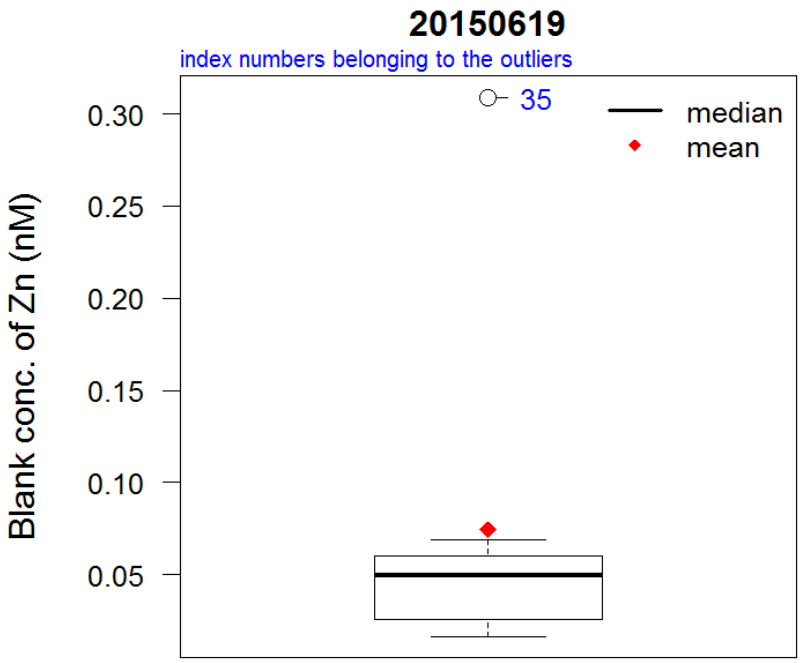


Figure 20. Example of the graph visualizing the spread in the Zn blank data with one outlier with index number 35 (you see how it increases the mean).

The fChecks.balances function

This function dela with the checks and balances for the seafast and the ICPMS, see Figure 21. It has several outputs:

1) Two csv files with metal concentrations of the seafast and icpms checks, respectively.
2) Boxplots as tif files summarizing all checks for each metal seperately, see Figure 22.
3) Dot plots as tif files for each metal and each check separate in separate folders for each check, see Figure 23
4) Dot plots with the reference samples including the consensus values when known or given, see Figure 24
5) csv file with the metal concentration of the reference samples
6) csv file with the percentage recovery efficiencies of the seafast. The percentage recovery efficiencies were calculated from the slope of the standard addition in the HNO3 elution acid and the standard addition of the seafast corrected for the preconcentration factor.

(1) This line opens the data file with the data of the checks ("checks.csv")
(2) This line opens the data file with the results of the seafast standard addition
(3) This line opens the data file with the results of the standard addition in the HNO3 elution acid
(4) This line opens the data file with the Rh results needed to correct the data for changes in ICPMS sensitivity (it also corrects for the evaporation of eluent).
(5) This line opens the data file with results of the metal blanks. By defining:
blank.type.name <- "MQ_blank_SW" (or another code from the column "blank" in "blanks.csv" that represents the blank data that you want to use to correct your metal data.
(6) This line opens the file with reference sample consensus values "TraceMetalReferenceConsensusValues.csv". You can add new reference samples to this file yourself.
(7) This line opens the data file with the results needed to correct the Cd data for Mo interference.
(8) This line opens the data file with the original sample names connected to the seafast sample names "sample_list.csv". This allows the individual reference samples to be indicated in the graphs when multiple reference samples are used.
(9) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols
(10) This set of lines provides you with some choices:
Standard.element.correction <- "yes" (or "no") determines if you want to have the data corrected for changes in ICPMS sensitivity using Rh. It also corrects for evaporation of the elution acid.
Mo.correction.Cd <- "yes" (or "no") determines if you want your Cd data to be corrected for Mo interference.
use.Blank <- "mean" (or "median") indicates if you want to use the mean or median of the blanks to correct your metal data.
Seafast.conc.factor <- 10/0.65 indicates the seafast concentration factor (10 ml seawater into 650 µl HNO3 eluent). This factor is needed to calculate the seafast percentage recovery efficiency for each metal.
outliers.boxplot <- "yes" (or "no") The boxplots comparing all the checks and balances in one plot can be graphed with the outliers included. However, sometime this would affect the scale of the boxplot such that the boxplots become unreadable/useless. In this case you can choose for "no" and choose to not graph the outliers.

(11) sample.naming <- “yes” (or “no”) indicates if you want to have the original sample naming of your reference material in the graphs with results of the reference samples. It makes it easier to identify the results of individual reference samples, see Figure 24.
(12) This line activates the function.

```
######### Checks & balances ##################################################################

# To read in the results of the ICPMS for the checks and balances, DON'T CHANGE THE CODE HERE                                                    (1)
ck <- read.csv(paste(mainDir,"checks.csv",sep=""),header=TRUE)
head(ck)
table(ck$check)

# To read in the results of the seafast standard additions, DON'T CHANGE THE CODE HERE                                                           (2)
sa.sf <- read.csv(paste(folder.sf,"StandAdd_seafast_results_",name.run,".csv", sep=""),header=TRUE)
head(sa.sf)

# To read in the results of the HNO3 standard additions, DON'T CHANGE THE CODE HERE                                                              (3)
sa.HNO3 <- read.csv(paste(folder.HNO3,"StandAdd_HNO3_results_",name.run,".csv", sep=""),header=TRUE)
head(sa.HNO3)

# To read in the results of the standard.element, DON'T CHANGE THE CODE HERE                                                                     (4)
st.el <- read.csv(paste(folder.rh,standard.element," standard data_",name.run,".csv",sep=""),header=TRUE)
head(st.el)

# To read in the results of the seafast blank, ONLY CHANGE "blank.type.name" to the name that you gave to the blank that you will use           (5)
blank.type.name <- "MQ_blank"
blank <- read.csv(paste(folder.blank,"StatsData_blank_",blank.type.name,"_",name.run,".csv",sep=""),header=TRUE)
head(blank)

# To read in the reference material consensus values, DON'T CHANGE THE CODE HERE                                                                 (6)
ref.mat <- read.csv("TraceMetalReferenceConsensusValues.csv",header=TRUE)
head(ref.mat)

# To read in the results of Mo interference, DON'T CHANGE THE CODE HERE                                                                          (7)
mor <- read.csv(paste(folder.Mo,"Mo_interferenceCd_results_",name.run,".csv",sep=""),header=TRUE)
head(mor)

# To read the sample coding, DON'T CHANGE THE CODE HERE                                                                                          (8)
coding <- read.csv(paste(mainDir,"sample_list.csv",sep=""),header=TRUE)
head(coding)

# Graphing parameters, CAN BE CHANGED                                                                                                            (9)
resolution.figures <- 150
cex=1.3
cex.lab=1.2
cex.axis = 1

# Other parameters, CAN BE CHANGED                                                                                                               (10)
Standard.element.correction <- "yes"
Mo.correction.Cd <- "yes"
use.Blank <- "median"         # either use "mean" or "median"
Seafast.conc.factor <- 10/0.65
outliers.boxplot <- "no"

# includes sample names in the graphs of the reference values, if you don't have a sample_list say "no"                                         (11)
sample.naming <- "yes"

# the function, DON'T CHANGE THE CODE HERE                                                                                                       (12)
fChecks.balances(ck, sa.sf, st.el, blank, ref.mat, mor, coding, sample.naming, name.run, mainDir, use.Blank, Seafast.conc.factor, outliers.boxp
```

Figure 21. The function fChecks.balances to deal with all seafast and ICPMS checks.

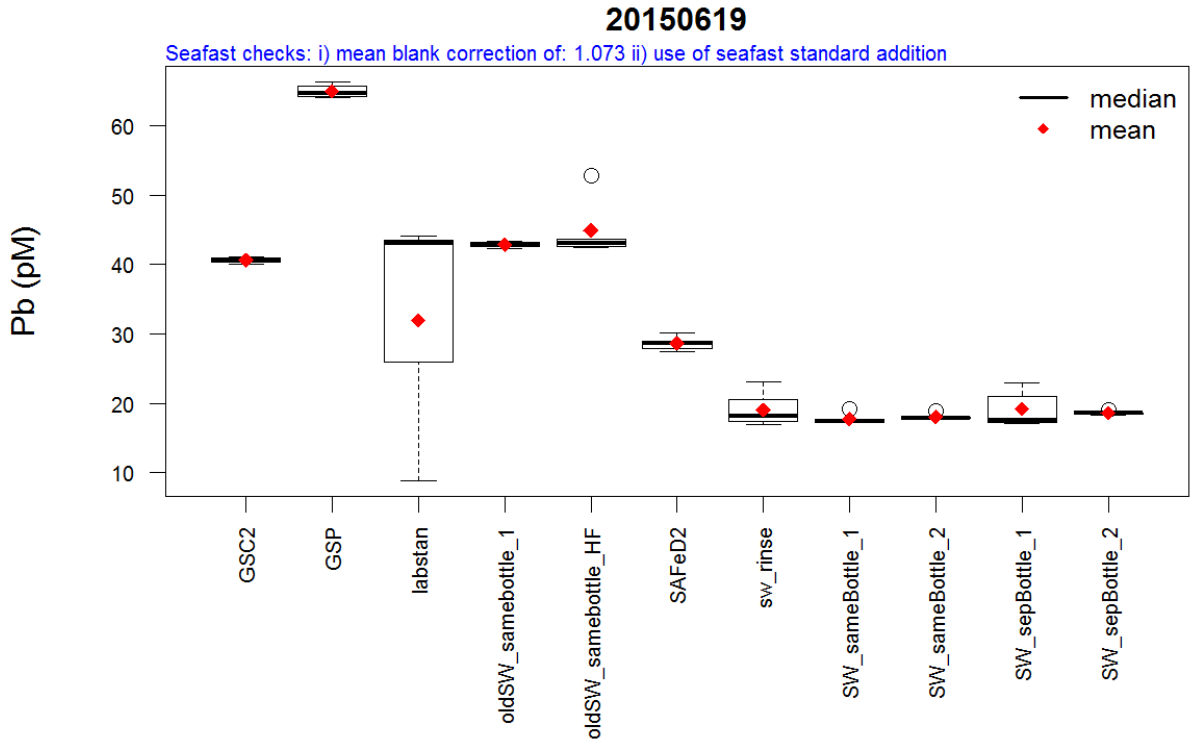


Figure 22. Example of a boxplot summarizing all seafast checks for Pb.

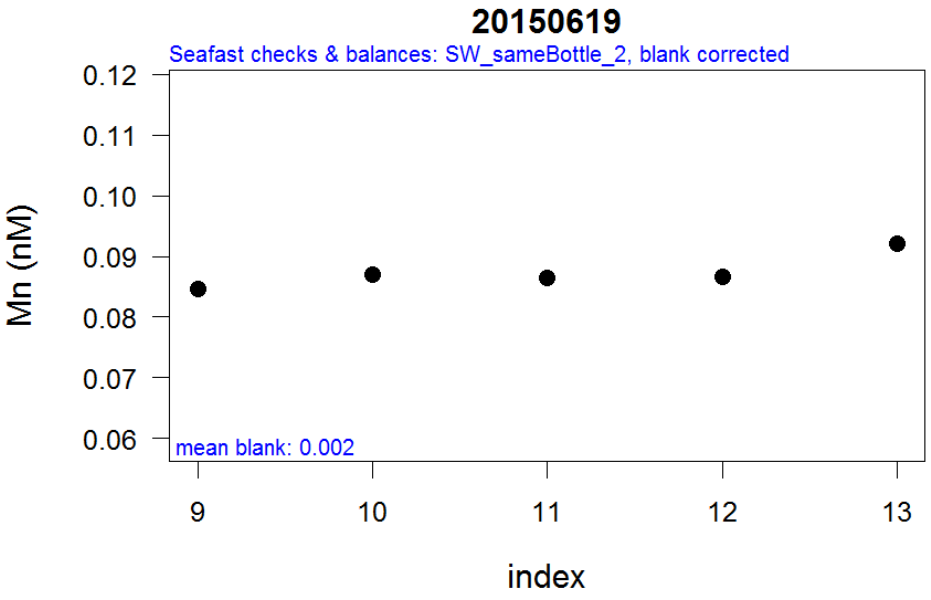


Figure 23. Example of a dotplot showing the check where repeated samples from the same bottle were extracted on the seafast for Mn.

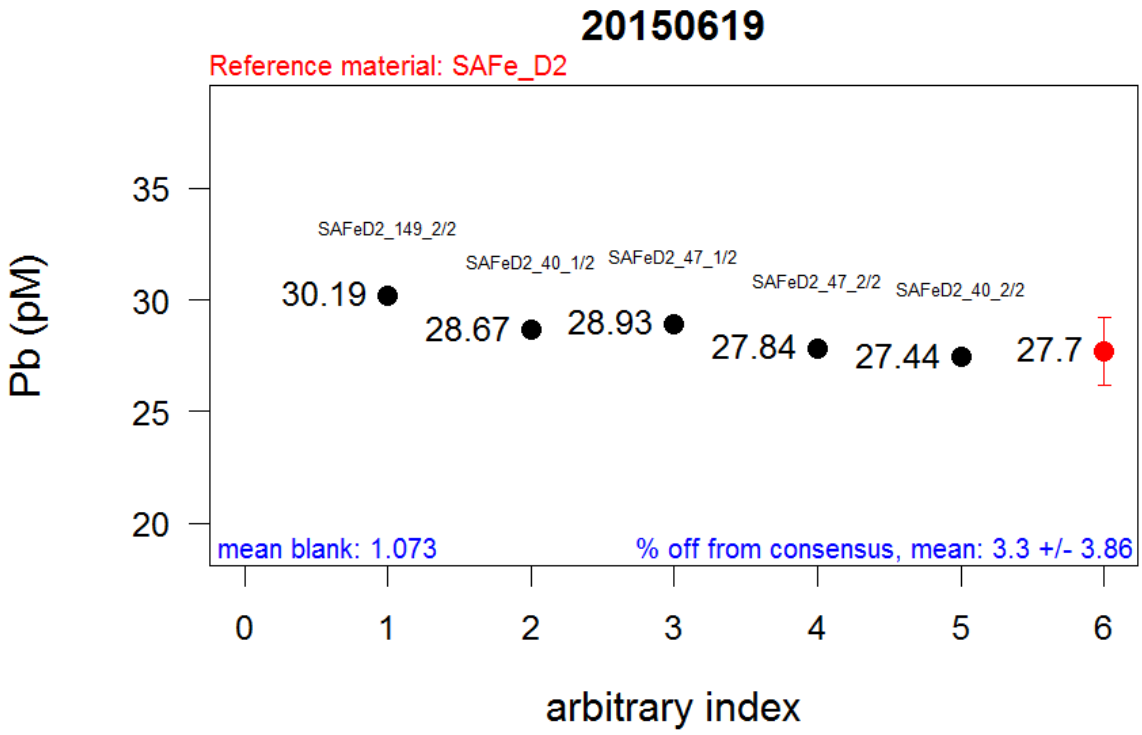


Figure 24. Example of a dotplot showing the results of the reference samples for Pb including the consensus value.

The fSample.concentrations and fSample.codes functions

The function fSample.concentrations calculates the final metal concentrations from the data in "samples.csv", see Figure 25. The output is a csv file with the concentrations and a series of dot plots as tif files showing the metal concentrations of the samples for each metal. The function fSample.codes does nothing else then to include the original the original sample names using input from "sample_list.cvs", see Figure 25.

(1) This line opens the file with sample data "samples.csv"

(2) This line opens the result of the seafast standard addition.

(3) This line opens the results for the Rh correction to correct for sensitivity changes in the ICPMS and evaporation of elution acid.

(4) This line opens the data file with results of the metal blanks. By defining:
blank.type.name <- "MQ_blank_SW" (or another code from the column "blank" in "blanks.csv" that represents the blank data that you want to use to correct your metal data.

(5) This line opens the data file with the results needed to correct the Cd data for Mo interference.

(6) The codes save the graph as a tif file and shows the graph in your window. The:
resolution.figures determines the resolution of the tif file
cex determines the size of the symbols
cex.lab determines the size of your axis titles
cex.axis determines the size of the axis symbols

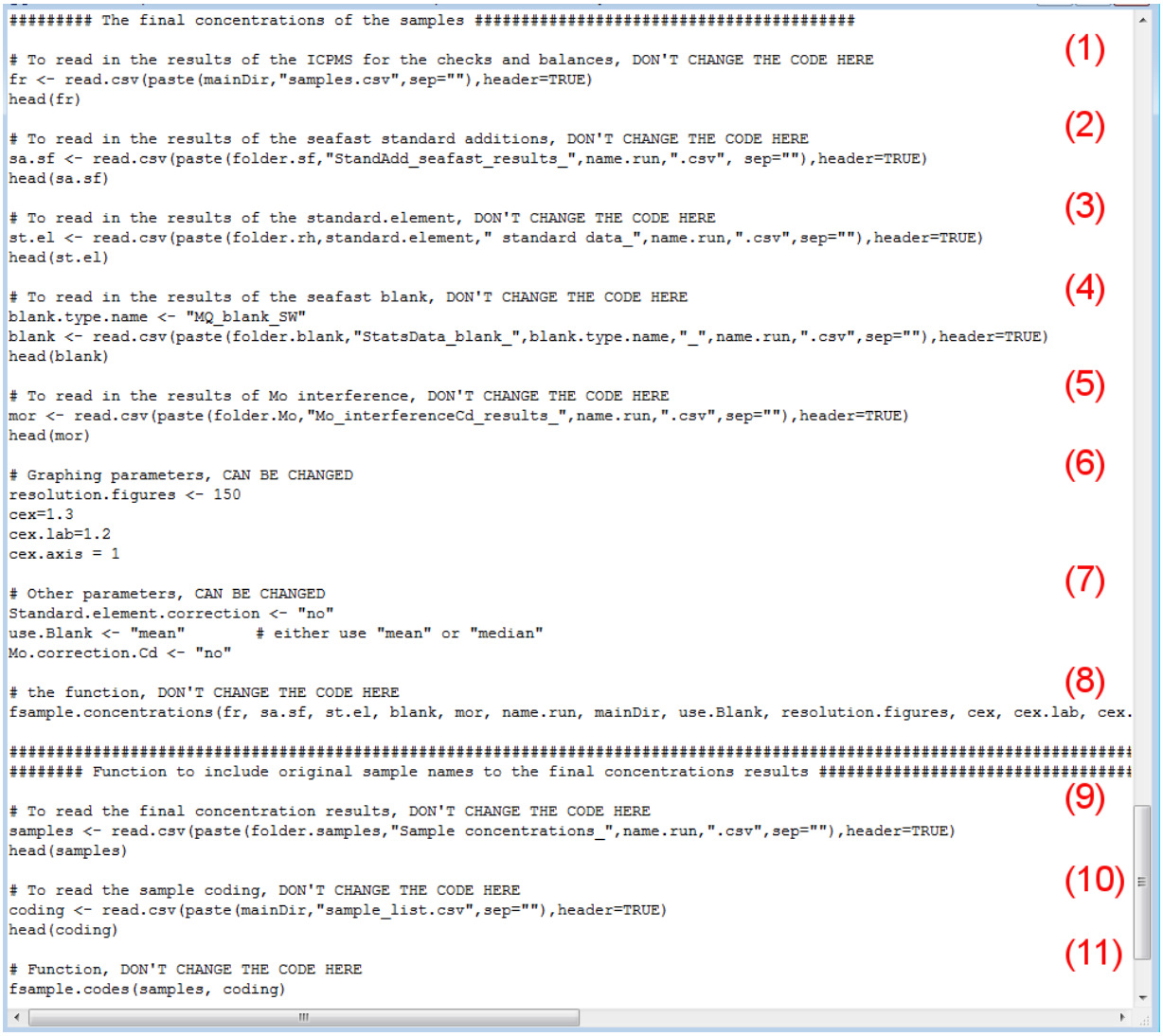
(7) This set of lines provides you with some choices:
Standard.element.correction <- "yes" (or "no") determines if you want to have the data corrected for changes in ICPMS sensitivity using Rh. It also corrects for evaporation of the elution acid.
Mo.correction.Cd <- "yes" (or "no") determines if you want your Cd data to be corrected for Mo interference.
use.Blank <- "mean" (or "median") indicates if you want to use the mean or median of the blanks to correct your metal data.

(8) This line activates the function.

(9) This line opens the file with the concentrations of the trace metals as calculated using the previous function.

(10) This line opens the data file with the original sample names connected to the seafast sample names "sample_list.csv". This allows the individual reference samples to be indicated in the graphs when multiple reference samples are used.

(11) This line activates the function.



```
######### The final concentrations of the samples ########################################

# To read in the results of the ICPMS for the checks and balances, DON'T CHANGE THE CODE HERE
fr <- read.csv(paste(mainDir,"samples.csv",sep=""),header=TRUE)
head(fr)

# To read in the results of the seafast standard additions, DON'T CHANGE THE CODE HERE
sa.sf <- read.csv(paste(folder.sf,"StandAdd_seafast_results_",name.run,".csv", sep=""),header=TRUE)
head(sa.sf)

# To read in the results of the standard.element, DON'T CHANGE THE CODE HERE
st.el <- read.csv(paste(folder.rh,standard.element," standard data_",name.run,".csv",sep=""),header=TRUE)
head(st.el)

# To read in the results of the seafast blank, DON'T CHANGE THE CODE HERE
blank.type.name <- "MQ_blank_SW"
blank <- read.csv(paste(folder.blank,"StatsData_blank_",blank.type.name,"_",name.run,".csv",sep=""),header=TRUE)
head(blank)

# To read in the results of Mo interference, DON'T CHANGE THE CODE HERE
mor <- read.csv(paste(folder.Mo,"Mo_interferenceCd_results_",name.run,".csv",sep=""),header=TRUE)
head(mor)

# Graphing parameters, CAN BE CHANGED
resolution.figures <- 150
cex=1.3
cex.lab=1.2
cex.axis = 1

# Other parameters, CAN BE CHANGED
Standard.element.correction <- "no"
use.Blank <- "mean"        # either use "mean" or "median"
Mo.correction.Cd <- "no"

# the function, DON'T CHANGE THE CODE HERE
fsample.concentrations(fr, sa.sf, st.el, blank, mor, name.run, mainDir, use.Blank, resolution.figures, cex, cex.lab, cex.

#########################################################################################################################
######## Function to include original sample names to the final concentrations results ##################################

# To read the final concentration results, DON'T CHANGE THE CODE HERE
samples <- read.csv(paste(folder.samples,"Sample concentrations_",name.run,".csv",sep=""),header=TRUE)
head(samples)

# To read the sample coding, DON'T CHANGE THE CODE HERE
coding <- read.csv(paste(mainDir,"sample_list.csv",sep=""),header=TRUE)
head(coding)

# Function, DON'T CHANGE THE CODE HERE
fsample.codes(samples, coding)
```

(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11)

Figure 25. The function fSample.concentrations and fSample.codes to calculate the metal concentrations of the environmental samples and to add the original sample coding.