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Smart consideration of actual ladle status monitored by novel sensors for secondary metallurgy process parameters and ladle maintenance strategies

SmartLadle

Public

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Deliverable 2.2 – Evaluation of fast slag analysis as new process parameter

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Lead beneficiary: SWG

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Project summary

What is the effect of the actual ladle status -new to worn- on steel bath properties? How do e.g. temperature or fluid flow vary with ladle conditions? When is the optimal moment for relining?

SmartLadle will provide a solution for online monitoring and dynamic incorporation of actual ladle status for process control. A soft sensor for ladle status shall be developed, supported by a smart sensor for detecting refractory wear and thermal status. Measurement data, models and advisory tools shall provide information for decision making to operators to adapt ladle metallurgy process parameters to actual ladle status and decide about maintenance actions.

Definition of terms used in the project

Soft sensor: Mathematical calculation of value of a process parameter that is difficult or so far impossible to measure directly and online, based on other process values, measurements, models and smart sensor data.

Smart sensor: Combination of a pure sensor for the acquisition of a measured value, e.g. refractory temperature, and a small computing unit with implemented simplified models, e.g. for refractory wear.

ML model: Data-driven model that analysis data and detects relationships (linear or non-linear) among variables based on real-world data using Machine Learning (ML) Techniques.

1. Introduction

The deliverable D2.2 describes the work of task 2.5 and provides information about a plant trial performed to test if a fast slag analysis can be used as an online analysis tool to obtain a new process parameter for the adaption of slag conditioning practices.

The aim of work was the calibration, commissioning and validation of a laser induced plasma spectroscopy device (LIBS) in the spectrometer laboratory (see **Figure 1**). For this purpose, VD slag samples were taken from the steel plant, pressed into tablets, and these are analyzed by means of an X-ray fluorescence spectrometer (XRF) to determine their composition. Some of the samples analyzed in this way were used for the basic calibration of the LIBS (SECOPTA analytics, SlagLIBS). The basic calibration had already been started, so that analyzed samples were at first transferred to Excel and sent to the instrument supplier. Subsequently, the validation took place. For this purpose, samples from the current production were additionally measured on the LIBS using the same procedure. These data were processed, evaluated, and were used in the next step to recalibrate the instrument.

Figure 1: LIBS device in the laboratory (left) and measuring room with cover (laser protection glass) and controls (right)

2. Preparation and commissioning

Before commissioning the SlagLIBS system, a compressed air connection was established in the laboratory. The Ethernet access was released by GMH-Systems, and the device transported to the incoming goods inspection. After the device had been set up, Secopta carried out a Site Acceptance Test on two days of commissioning, including functional tests, setting up the software communication and subsequent briefing of the SWG staff.

An overview of the control panel on the instrument and the output of the analysis in the 2D program can be found in Annex Figure A 1. The 3D program offers a variety of settings (see Annex Figure A 2). Typically, the selection is limited to the area to be analysed (selected by touchscreen or keyboard), to the scan mode (e.g. "Line" or "Point by Point") and the measuring point density ("Increments"). The output offers a variety of analysis options. In addition to the actual analysis spectra are also displayed. Via a 2D false colour image the distribution over the measuring area can be viewed and analyses of individual measuring points can be selected.

The 2D program is characterized by a rapid analysis of the slag powder by means of a sample holder and disposable tray (see **Figure 2**). The measuring field, the measuring height and the measuring method are already defined in this program. Since the height scan is not carried out, the surface of the powder must be smooth and finish with the upper edge of the disposable tray (see Annex Figure A 3).

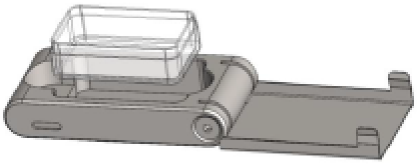


Figure 2: Sample holder and disposable tray for the 2D program [1].

In order to prevent carryover of sample material after each 2D measurement, the disposable tray is cleaned with 2-propanol and the holder with the machine bed is vacuumed out. The compressed air at the measuring head is also checked after the instrument is switched on. An approx. two-week check for contamination and, if necessary, replacement is scheduled for the protective glass in the measuring head.
An exhaust system has not been installed, but this could help to keep the instrument and the sensor clean during regular use and thus also save time for the operator (especially in the 2D program). The question remains open as to a positive influence of the exhaust system on the analysis values.

During the commissioning there were software problems of the device, which were solved in contact with Secopta by means of remote access. For example, the height scan could abort prematurely in the 3D program. The height scan may also be aborted if the measurement area in the 3D program is larger than approx. 100mm-100mm. Furthermore, during repeated measurement of a specimen the height scan must be performed again. Otherwise, the analysis terminates without results.
Thus, until the successful integration of the instrument into the running production the support with RDP access is very helpful.

3. Evaluation of the slags

After calibration and commissioning, 45 VD slags and two reference samples were measured for validation. The analyses of the composition were compared with the XRF measured values or the certificates of the reference slags. The evaluated measured values can be found in Annex Figure A 4 to Figure A 6. Only elements/compounds were presented for which a counter comparison was desired and for which a comparison was possible due to the base calibration. From the calculated relative deviations, in following chapters 3.1 and 3.2 boxplots were created.

A planned 2D-EAF program could not be implemented, because no XRF analyses of EAF slags were available. The production of the tablets is laborious due to the high Fe content. Until now, the tablets often broke during pressing. During the practical course, a routine was found, and six tablets were produced as examples. An implementation of an EAF program is possible in the future, albeit with increased effort. EAF process optimization via the slag would then also be conceivable.

The evaluated validation samples were then included in the recalibration of the 2D programs. Annex Figure A 7 shows the linear model fit of the base calibration is shown as an example for SiO_2 with an R^2 = 0, 856. Opposite to this Annex Figure A 8 shows the model with an R^2 = 0.911 after the recalibration. The coefficient of determination as a measure of the quality of the linear fit indicates an improved model. However, it can easily lead to an "overfitting" with the consequence that measured values which are not close enough to the calibrated range are ignored. The diagrams Annex Figure A 9 - Figure A 10 [2] for the recalibration of the 2D-VD program of the 2D-VD program only serve as an overview.

3.1 Certified reference specimens

Two certified standard slags SWG-STD5 and SWG-STD7 were each measured five times at the LIBS. The objective of the series of tests was to quantify possible measurement errors from the XRF, to the calibration of the LIBS. The background is that laboratory instruments were previously calibrated using certified standard samples.

The standard samples were measured in separate disposable trays. The extracted material was then poured into labeled containers and stored in the incoming goods inspection area, including disposable trays. They can thus be used as a standard for regular quantitative "counter measurement".

The certified compositions are compared to the LIBS analyses in Annex Figure A 4 and Figure A 5 contrasted. The mean, median and coefficient of variation were calculated. The relative deviation in percent was formed from the averaged measured values with respect to the certified reference. The lowest relative deviation has SiO_2 (SWG-STD5) with 4,4%. The majority of the relative deviations in the double-digit range. The values marked in red in Annex Figure A 4 and Figure A 5 were not considered due to missing calibration/calculation formula of the LIBS.

The reference material SWG-STD5 shows a coefficient of variation (RSD) between 1,73 (TiO_2) and 27,88 (Al_2O_3), indicating low repeatability. The reference material SWG-STD7 shows a (RSD) between 0,00 (K_2O) to 7,4 (Cr_2O_3), indicating a rather high repeatability. Since the expert opinion of the reference material attests a 95% confidence interval below 0,05% (up to 0.001%), the partly high RSD values cannot be explained by this.

From the relative deviations of all plausible values, scatter and position measures were calculated in **Table 1** and presented as boxplots (**Figure 3**). The relative deviation of the reference material SWG-STD5 is on average 76%, the median is 50%. The maximum deviation of 251% can be calculated on the basis of the Interquartile Range (IQR) >> 1,5 can be excluded as an extreme outlier. The relative deviation of the reference material SWG-STD7 is on average 48% and the median is 35%.

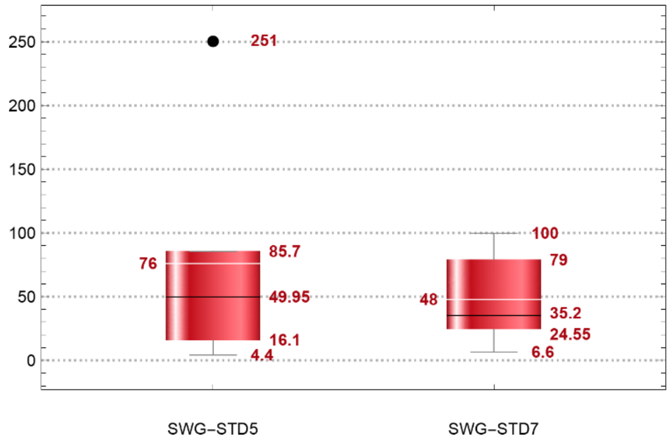


Figure 3: Boxplots of the reference samples

Table 1: Statistical evaluation of the reference samples (in %)

	SWG-STD5	SWG-STD7
Maximum	251,00	100,00
75%-Quantil	85,70	79,00
Median	49,95	35,20
25%-Quantil	16,10	24,55
Minimum	4,40	6,60

Since the powder structure of the reference material is comparable to that of the steel plant specimens, matrix effects cannot explain these large deviations. Also, the powder was mixed after each measurement at the LIBS to ensure representative and homogeneous samples. Part of the deviations could be explained by the small measurement series of five samples. Likewise, with regard to the composition, the material is comparable, but not identical. Also missing elements/compounds in the calibration can lead to errors in the LIBS analysis, since some of the compounds are calculated stoichiometrically.

The trial is informative because it shows the limited applicability of LIBS with changing process parameters. It shows that a universal analysis (on the RFA as an "Omnian" program) is not technologically possible without prior basic calibration.

3.2 LF/VD samples

To validate the 2D-VD slag program, 45 LF/VD slag samples were measured. Statistically evaluated were Al_2O_3, SiO_2, CaF_2, CaO, Ca, MgO, which are compared with the relative deviations in Annex Figure A 6.
Due to a missing calculation formula in the base calibration, CaF_2 was calculated stoichiometrically via fluorine (see formulas (1) – (3)).

$$CaO + F = CaF_2 + CaO_{ber.} \quad (1)$$

$$CaO_{ber.} = CaO - F * 1{,}4758 \quad (2)$$

$$CaF_2 = F * 2{,}0549 \quad (3)$$

For fluorine there were very large deviations, since the LIBS mostly did not recognize the low fluorine contents. In Annex Figure A 6, the negative XRF values for fluorine are marked in red. Since there were also problems with the fluorine measurements at the XRF due to negative values, the statistical evaluation was omitted for CaF_2. The reason for this cannot be conclusively answered. It is striking that the contents are very low. One assumption is that these are measurement errors due to the very reactive element. It will have to be observed whether the results change after the next calibration of the XRF.

CaO was also calculated stoichiometrically via Ca. The high relative deviations of CaO can be traced back to a missing/incorrect calculation formula within the LIBS software. Since the values are consistent in themselves and thus can be assumed to be a systemic error, the CaO values were included in the evaluation (see **Figure 4**). The calculation formula of $CaO_{ber.}$ and CaF_2 was discussed with Secopta and should be considered in the recalibration.

For creating **Table 2**, three measured values of Al_2O_3, Ca and two measured values of Ca with values above 80% rel. deviation were identified as extreme outliers. These are marked in blue in Annex Figure A 6 and are not included in the evaluation.

From the relative deviations of all plausible values in Table 2 scatter and position measures were calculated from the relative deviations of all plausible values in Table 2 and presented as boxplots in Figure 4.

On average, MgO has the smallest relative deviation with 7%. Also, the median of MgO is also the smallest with 6,06%. If CaO is left out of the equation, Al_2O_3 has the largest median with 8,17% and the largest mean value of 11%. The smallest relative deviation has a SiO_2 measurement with a value of 0,09%, followed by Ca with 0,17% and MgO with 0,35%.

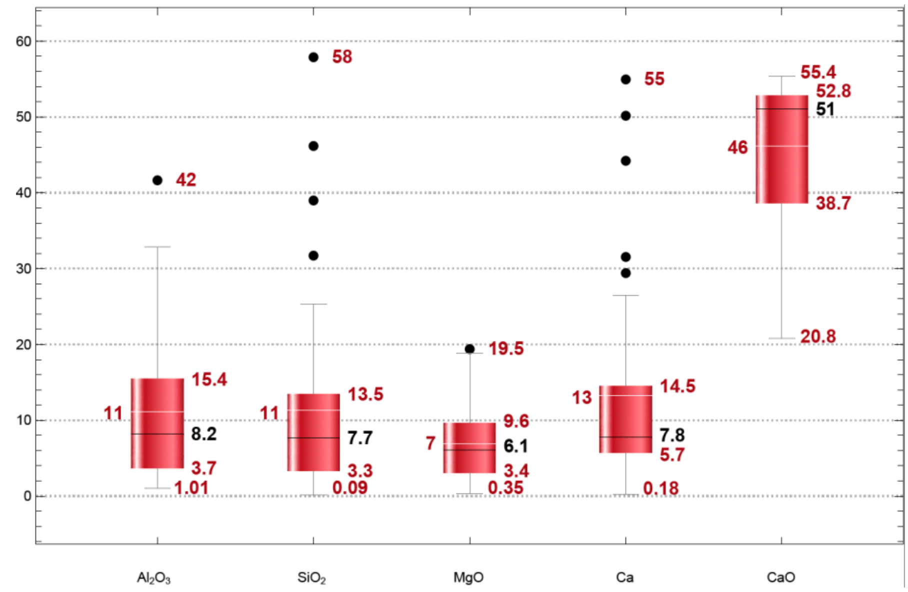


Figure 4: Boxplots of the LF/VD samples

Table 2: Statistical evaluation of the LF/VD samples (in %)

	Al_2O_3	SiO_2	MgO	Ca	CaO
Maximum	41,76	57,96	19,50	55,07	55,37
75%-Quantil	15,43	13,46	9,60	14,50	52,83
Median	8,17	7,65	6,06	7,78	51,00
25%-Quantil	3,67	3,34	3,05	5,715	38,66
Minimum	1,01	0,09	0,35	0,18	20,79

Thus, only the 25% quantiles of Al_2O_3, SiO_2 and MgO are in the range of the target corridor of 2-3%. The median of all elements/compounds is a factor of 2 to 3 above the target corridor.

Since the base calibration is very small with 26 samples, it should be checked in a next step, whether the target corridor can be achieved for all compounds by recalibration.

4. Summary and conclusion

The LIBS determines total contents of each element and not elemental compounds. Thus, for example, the CaF_2 content is determined based on the measured Fluor-content by means of a constant calculation formula, and this Ca content is subtracted from the CaO content. Since the calculation formulas of CaO and CaF2 in the base calibration were not complete, large relative deviations occurred.

To obtain meaningful values, the XRF analysis must be significantly above the target analysis of the LIBS. Using CaF_2 as an example, it was shown that the fluorine-accuracy of the XRF measurement should be checked/improved (cf. chapter 3.2).

A basic calibration of the EAF program can be carried out with the experience gained. Based on this, it can be investigated whether an online optimisation of the process via slagging of alloying elements is possible.

For the following calibrations, care must be taken to ensure a robust data set with the greatest possible scatter of the contents. For this purpose, the analyses of the certified reference samples can be included in the calibration.

For automated evaluation during ongoing production operation, it is necessary to set up an interface between the analysis results and the SAP/ERP system.

The 3D program is time-consuming, depending on the choice of the measuring surface, the scan mode and the distances of the measuring increments, but it is suitable e.g. to analyze alloy elements within the incoming goods inspection. In a next step, it can be investigated which ratio of time and accuracy is optimal for integration into the running production process.

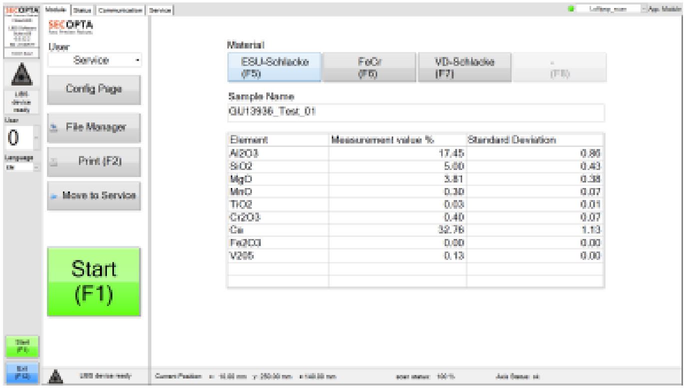
To finally conclude, within the trials it was found that the LIBS measurements were promising, but calibration is challenging and at the moment not precisely enough for mutli-component slag systems (the number of samples was not large enough for the wide-ranging spectrum of SWG slags). Hence no stable in-process measurement of the slags is possible. However, the analysis system was purchased by SWG and is in standard usage for chemical analysis of ferroalloys for secondary metallurgy, which shows very promising results.

References

[1] SECOPTA ANALYTICS. SlagLIBS: Technical specifications. Handbook. 2021.

[2] SECOPTA ANALYTICS. Update VD-Calibration. Powerpoint-slides from internal meeting. 2021.

Annex



Material

ESU-Schlacke (F5) | FeCr (F6) | VD-Schlacke (F7) | - (F8)

Sample Name

GU13936_Test_01

Element	Measurement value %	Standard Deviation
Al2O3	17.45	0.86
SiO2	5.00	0.43
MgO	3.81	0.38
MnO	0.30	0.07
TiO2	0.03	0.01
Cr2O3	0.40	0.07
Ca	32.76	1.13
Fe2O3	0.00	0.00
V2O5	0.13	0.00

Figure A 1: Output screen 2D programme (Screenshot)

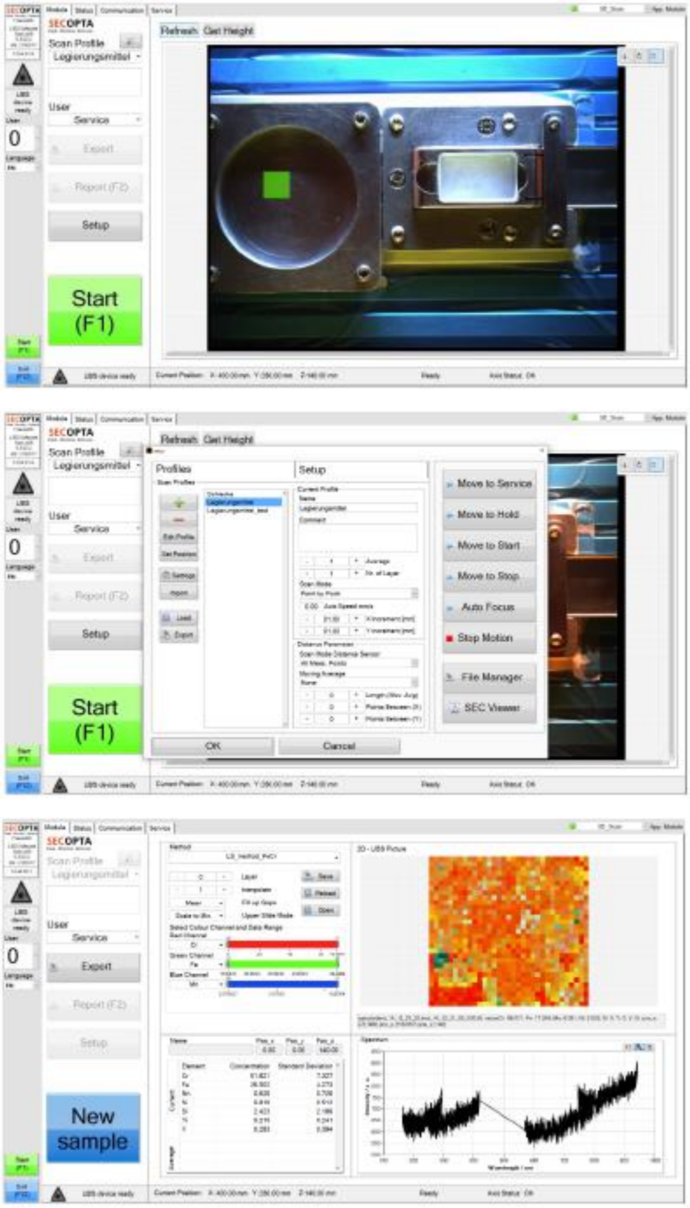


Figure A 2: Testing in the 3D programme (Screenshots)

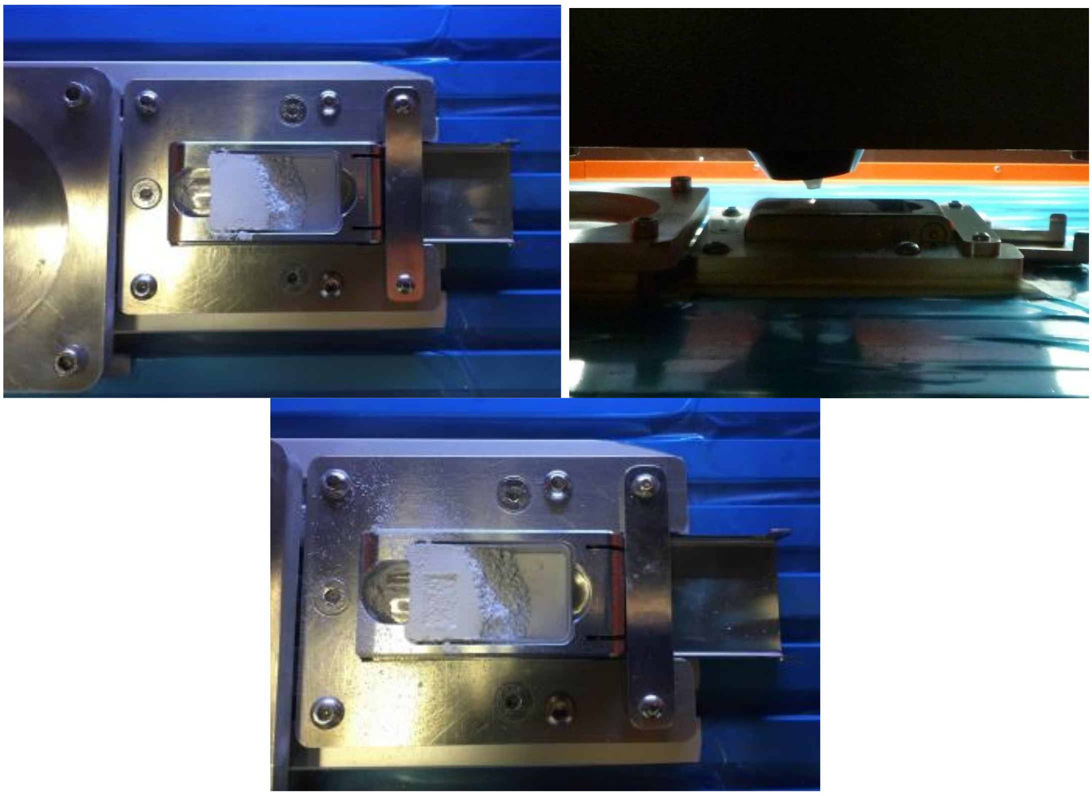
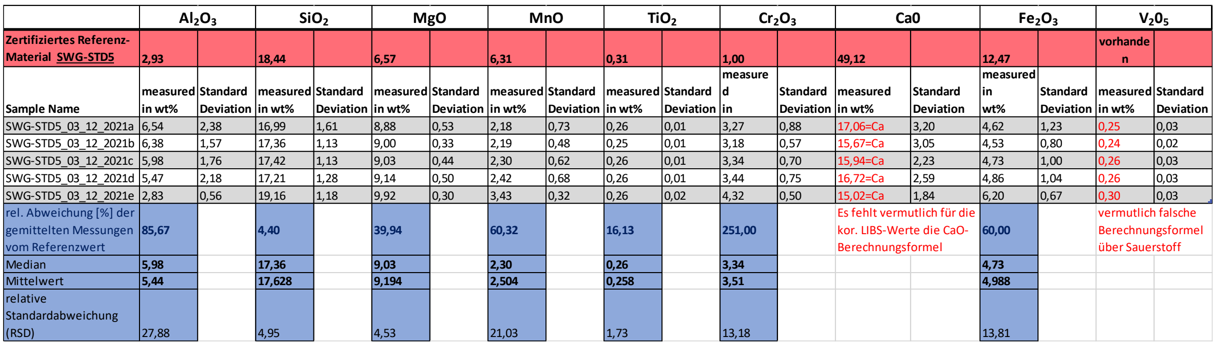
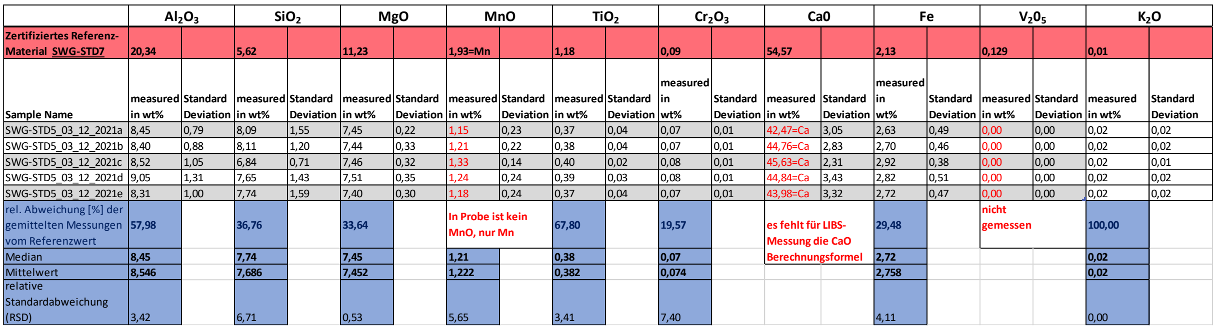


Figure A 3: Testing in the 2D programme: Sample with plain measuring area before measurement (top left), during measurement laser scans surface line by line (top right), and sample after measurement (bottom)



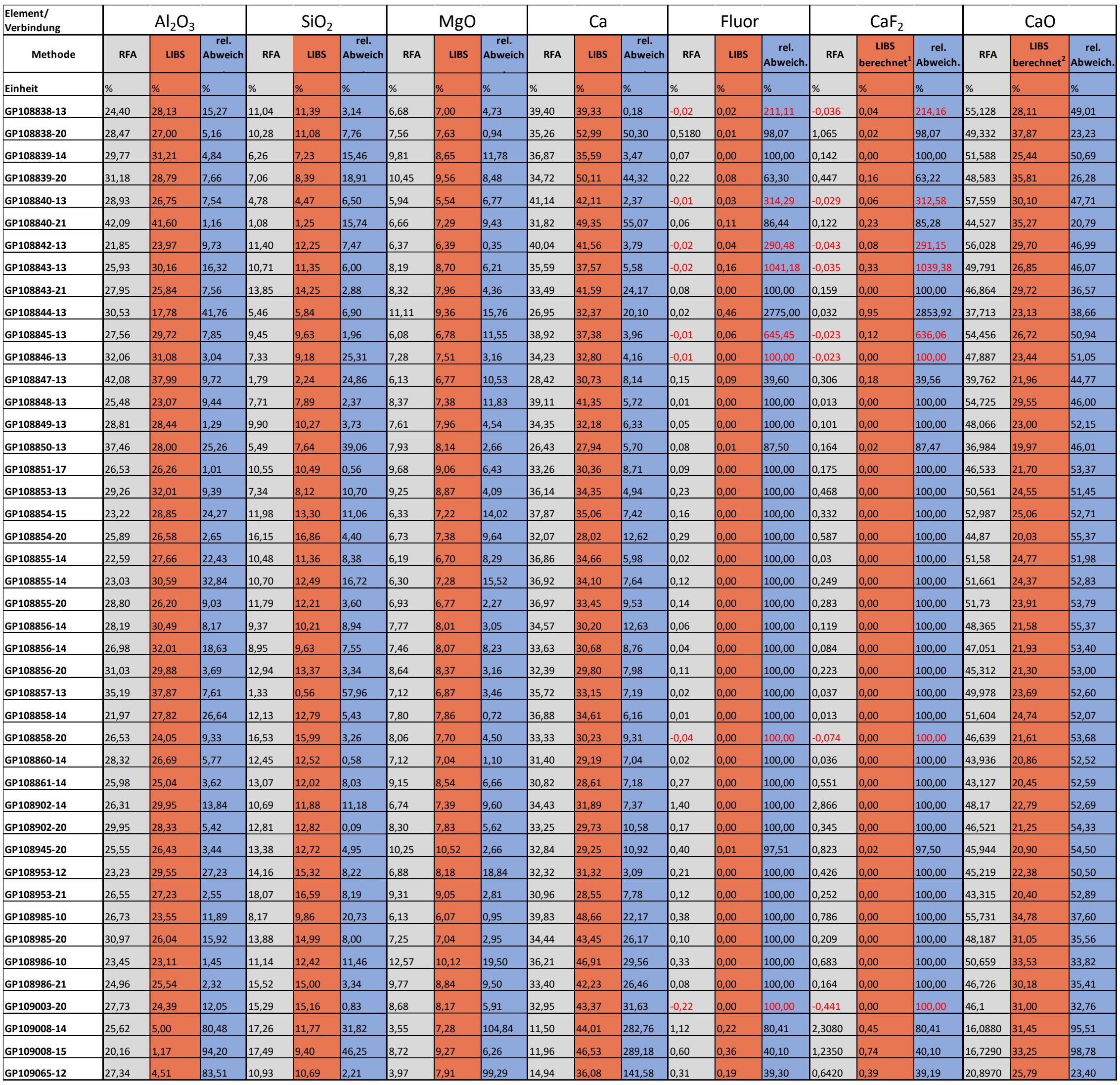
	Al_2O_3		SiO_2		MgO		MnO		TiO_2		Cr_2O_3		Ca0		Fe_2O_3		V_20_5	
Zertifiziertes Referenz-Material <u>SWG-STD5</u>	**2,93**		**18,44**		**6,57**		**6,31**		**0,31**		**1,00**		**49,12**		**12,47**		**vorhanden**	
Sample Name	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**
SWG-STD5_03_12_2021a	6,54	2,38	16,99	1,61	8,88	0,53	2,18	0,73	0,26	0,01	3,27	0,88	17,06=Ca	3,20	4,62	1,23	0,25	0,03
SWG-STD5_03_12_2021b	6,38	1,57	17,36	1,13	9,00	0,33	2,19	0,48	0,25	0,01	3,18	0,57	15,67=Ca	3,05	4,53	0,80	0,24	0,02
SWG-STD5_03_12_2021c	5,98	1,76	17,42	1,13	9,03	0,44	2,30	0,62	0,26	0,01	3,34	0,70	15,94=Ca	2,23	4,73	1,00	0,26	0,03
SWG-STD5_03_12_2021d	5,47	2,18	17,21	1,28	9,14	0,50	2,42	0,68	0,26	0,01	3,44	0,75	16,72=Ca	2,59	4,86	1,04	0,26	0,03
SWG-STD5_03_12_2021e	2,83	0,56	19,16	1,18	9,92	0,30	3,43	0,32	0,26	0,02	4,32	0,50	15,02=Ca	1,84	6,20	0,67	0,30	0,03
rel. Abweichung [%] der gemittelten Messungen vom Referenzwert	**85,67**		**4,40**		**39,94**		**60,32**		**16,13**		**251,00**		Es fehlt vermutlich für die kor. LIBS-Werte die CaO-Berechnungsformel		**60,00**		vermutlich falsche Berechnungsformel über Sauerstoff	
Median	**5,98**		**17,36**		**9,03**		**2,30**		**0,26**		**3,34**				**4,73**			
Mittelwert	**5,44**		**17,628**		**9,194**		**2,504**		**0,258**		**3,51**				**4,988**			
relative Standardabweichung (RSD)	27,88		4,95		4,53		21,03		1,73		13,18				13,81			

Figure A 4: Evaluated measured values of the standard sample SWG-STD5



	Al_2O_3		SiO_2		MgO		MnO		TiO_2		Cr_2O_3		Ca0		Fe		V_20_5		K_2O	
Zertifiziertes Referenz-Material <u>SWG-STD7</u>	**20,34**		**5,62**		**11,23**		**1,93=Mn**		**1,18**		**0,09**		**54,57**		**2,13**		**0,129**		**0,01**	
Sample Name	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**	**measured in wt%**	**Standard Deviation**
SWG-STD5_03_12_2021a	8,45	0,79	8,09	1,55	7,45	0,22	1,15	0,23	0,37	0,04	0,07	0,01	42,47=Ca	3,05	2,63	0,49	0,00	0,00	0,02	0,02
SWG-STD5_03_12_2021b	8,40	0,88	8,11	1,20	7,44	0,33	1,21	0,22	0,38	0,04	0,07	0,01	44,76=Ca	2,83	2,70	0,46	0,00	0,00	0,02	0,02
SWG-STD5_03_12_2021c	8,52	1,05	6,84	0,71	7,46	0,32	1,33	0,14	0,40	0,02	0,08	0,01	45,63=Ca	2,31	2,92	0,38	0,00	0,00	0,02	0,01
SWG-STD5_03_12_2021d	9,05	1,31	7,65	1,43	7,51	0,35	1,24	0,24	0,39	0,03	0,08	0,01	44,84=Ca	3,43	2,82	0,51	0,00	0,00	0,02	0,02
SWG-STD5_03_12_2021e	8,31	1,00	7,74	1,59	7,40	0,30	1,18	0,24	0,37	0,04	0,07	0,01	43,98=Ca	3,32	2,72	0,47	0,00	0,00	0,02	0,02
rel. Abweichung [%] der gemittelten Messungen vom Referenzwert	**57,98**		**36,76**		**33,64**		**In Probe ist kein MnO, nur Mn**		**67,80**		**19,57**		**es fehlt für LIBS-Messung die CaO Berechnungsformel**		**29,48**		**nicht gemessen**		**100,00**	
Median	**8,45**		**7,74**		**7,45**		**1,21**		**0,38**		**0,07**				**2,72**				**0,02**	
Mittelwert	**8,546**		**7,686**		**7,452**		**1,222**		**0,382**		**0,074**				**2,758**				**0,02**	
relative Standardabweichung (RSD)	3,42		6,71		0,53		5,65		3,41		7,40				4,11				0,00	

Figure A 5: Evaluated measured values of the standard sample SWG-STD7



Element/ Verbindung	Al_2O_3			SiO_2			MgO			Ca			Fluor			CaF_2			CaO		
Methode	RFA	LIBS	rel. Abweich	RFA	LIBS	rel. Abweich	RFA	LIBS	rel. Abweich	RFA	LIBS	rel. Abweich	RFA	LIBS	rel. Abweich.	RFA	LIBS berechnet[1]	rel. Abweich.	RFA	LIBS berechnet[2]	rel. Abweich.
Einheit	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
GP108838-13	24,40	28,13	15,27	11,04	11,39	3,14	6,68	7,00	4,73	39,40	39,33	0,18	-0,02	0,02	211,11	-0,036	0,04	214,16	55,128	28,11	49,01
GP108838-20	28,47	27,00	5,16	10,28	11,08	7,76	7,56	7,63	0,94	35,26	52,99	50,30	0,5180	0,01	98,07	1,065	0,02	98,07	49,332	37,87	23,23
GP108839-14	29,77	31,21	4,84	6,26	7,23	15,46	9,81	8,65	11,78	36,87	35,59	3,47	0,07	0,00	100,00	0,142	0,00	100,00	51,588	25,44	50,69
GP108839-20	31,18	28,79	7,66	7,06	8,39	18,91	10,45	9,56	8,48	34,72	50,11	44,32	0,22	0,08	63,30	0,447	0,16	63,22	48,583	35,81	26,28
GP108840-13	28,93	26,75	7,54	4,78	4,47	6,50	5,94	5,54	6,77	41,14	42,11	2,37	-0,01	0,03	314,29	-0,029	0,06	312,58	57,559	30,10	47,71
GP108840-21	42,09	41,60	1,16	1,08	1,25	15,74	6,66	7,29	9,43	31,82	49,35	55,07	0,06	0,11	86,44	0,122	0,23	85,28	44,527	35,27	20,79
GP108842-13	21,85	23,97	9,73	11,40	12,25	7,47	6,37	6,39	0,35	40,04	41,56	3,79	-0,02	0,04	290,48	-0,043	0,08	291,15	56,028	29,70	46,99
GP108843-13	25,93	30,16	16,32	10,71	11,35	6,00	8,19	8,70	6,21	35,59	37,57	5,58	-0,02	0,16	1041,18	-0,035	0,33	1039,38	49,791	26,85	46,07
GP108843-21	27,95	25,84	7,56	13,85	14,25	2,88	8,32	7,96	4,36	33,49	41,59	24,17	0,08	0,00	100,00	0,159	0,00	100,00	46,864	29,72	36,57
GP108844-13	30,53	17,78	41,76	5,46	5,84	6,90	11,11	9,36	15,76	26,95	32,37	20,10	0,02	0,46	2775,00	0,032	0,95	2853,92	37,713	23,13	38,66
GP108845-13	27,56	29,72	7,85	9,45	9,63	1,96	6,08	6,78	11,55	38,92	37,38	3,96	-0,01	0,06	645,45	-0,023	0,12	636,06	54,456	26,72	50,94
GP108846-13	32,06	31,08	3,04	7,33	9,18	25,31	7,28	7,51	3,16	34,23	32,80	4,16	-0,01	0,00	100,00	-0,023	0,00	100,00	47,887	23,44	51,05
GP108847-13	42,08	37,99	9,72	1,79	2,24	24,86	6,13	6,77	10,53	28,42	30,73	8,14	0,15	0,09	39,60	0,306	0,18	39,56	39,762	21,96	44,77
GP108848-13	25,48	23,07	9,44	7,71	7,89	2,37	8,37	7,38	11,83	39,11	41,35	5,72	0,01	0,00	100,00	0,013	0,00	100,00	54,725	29,55	46,00
GP108849-13	28,81	28,44	1,29	9,90	10,27	3,73	7,61	7,96	4,54	34,35	32,18	6,33	0,05	0,00	100,00	0,101	0,00	100,00	48,066	23,00	52,15
GP108850-13	37,46	28,00	25,26	5,49	7,64	39,06	7,93	8,14	2,66	26,43	27,94	5,70	0,08	0,01	87,50	0,164	0,02	87,47	36,984	19,97	46,01
GP108851-17	26,53	26,26	1,01	10,55	10,49	0,56	9,68	9,06	6,43	33,26	30,36	8,71	0,09	0,00	100,00	0,175	0,00	100,00	46,533	21,70	53,37
GP108853-13	29,26	32,01	9,39	7,34	8,12	10,70	9,25	8,87	4,09	36,14	34,35	4,94	0,23	0,00	100,00	0,468	0,00	100,00	50,561	24,55	51,45
GP108854-15	23,22	28,85	24,27	11,98	13,30	11,06	6,33	7,22	14,02	37,87	35,06	7,42	0,16	0,00	100,00	0,332	0,00	100,00	52,987	25,06	52,71
GP108854-20	25,89	26,58	2,65	16,15	16,86	4,40	6,73	7,38	9,64	32,07	28,02	12,62	0,29	0,00	100,00	0,587	0,00	100,00	44,87	20,03	55,37
GP108855-14	22,59	27,66	22,43	10,48	11,36	8,38	6,19	6,70	8,29	36,86	34,66	5,98	0,02	0,00	100,00	0,03	0,00	100,00	51,58	24,77	51,98
GP108855-14	23,03	30,59	32,84	10,70	12,49	16,72	6,30	7,28	15,52	36,92	34,10	7,64	0,12	0,00	100,00	0,249	0,00	100,00	51,661	24,37	52,83
GP108855-20	28,80	26,20	9,03	11,79	12,21	3,60	6,93	6,77	2,27	36,97	33,45	9,53	0,14	0,00	100,00	0,283	0,00	100,00	51,73	23,91	53,79
GP108856-14	28,19	30,49	8,17	9,37	10,21	8,94	7,77	8,01	3,05	34,57	30,20	12,63	0,06	0,00	100,00	0,119	0,00	100,00	48,365	21,58	55,37
GP108856-14	26,98	32,01	18,63	8,95	9,63	7,55	7,46	8,07	8,23	33,63	30,68	8,76	0,04	0,00	100,00	0,084	0,00	100,00	47,051	21,93	53,40
GP108856-20	31,03	29,88	3,69	12,94	13,37	3,34	8,64	8,37	3,16	32,39	29,80	7,98	0,11	0,00	100,00	0,223	0,00	100,00	45,312	21,30	53,00
GP108857-13	35,19	37,87	7,61	1,33	0,56	57,96	7,12	6,87	3,46	35,72	33,15	7,19	0,02	0,00	100,00	0,037	0,00	100,00	49,978	23,69	52,60
GP108858-14	21,97	27,82	26,64	12,13	12,79	5,43	7,80	7,86	0,72	36,88	34,61	6,16	0,01	0,00	100,00	0,013	0,00	100,00	51,604	24,74	52,07
GP108858-20	26,53	24,05	9,33	16,53	15,99	3,26	8,06	7,70	4,50	33,33	30,23	9,31	-0,04	0,00	100,00	-0,074	0,00	100,00	46,639	21,61	53,68
GP108860-14	28,32	26,69	5,77	12,45	12,52	0,58	7,12	7,04	1,10	31,40	29,19	7,04	0,02	0,00	100,00	0,036	0,00	100,00	43,936	20,86	52,52
GP108861-14	25,98	25,04	3,62	13,07	12,02	8,03	9,15	8,54	6,66	30,82	28,61	7,18	0,27	0,00	100,00	0,551	0,00	100,00	43,127	20,45	52,59
GP108902-14	26,31	29,95	13,84	10,69	11,88	11,18	6,74	7,39	9,60	34,43	31,89	7,37	1,40	0,00	100,00	2,866	0,00	100,00	48,17	22,79	52,69
GP108902-20	29,95	28,33	5,42	12,81	12,82	0,09	8,30	7,83	5,62	33,25	29,73	10,58	0,17	0,00	100,00	0,345	0,00	100,00	46,521	21,25	54,33
GP108945-20	25,55	26,43	3,44	13,38	12,72	4,95	10,25	10,52	2,66	32,84	29,25	10,92	0,40	0,01	97,51	0,823	0,02	97,50	45,944	20,90	54,50
GP108953-12	23,23	29,55	27,23	14,16	15,32	8,22	6,88	8,18	18,84	32,32	31,32	3,09	0,21	0,00	100,00	0,426	0,00	100,00	45,219	22,38	50,50
GP108953-21	26,55	27,23	2,55	18,07	16,59	8,19	9,31	9,05	2,81	30,96	28,55	7,78	0,12	0,00	100,00	0,252	0,00	100,00	43,315	20,40	52,89
GP108985-10	26,73	23,55	11,89	8,17	9,86	20,73	6,13	6,07	0,95	39,83	48,66	22,17	0,38	0,00	100,00	0,786	0,00	100,00	55,731	34,78	37,60
GP108985-20	30,97	26,04	15,92	13,88	14,99	8,00	7,25	7,04	2,95	34,44	43,45	26,17	0,10	0,00	100,00	0,209	0,00	100,00	48,187	31,05	35,56
GP108986-10	23,45	23,11	1,45	11,14	12,42	11,46	12,57	10,12	19,50	36,21	46,91	29,56	0,33	0,00	100,00	0,683	0,00	100,00	50,659	33,53	33,82
GP108986-21	24,96	25,54	2,32	15,52	15,00	3,34	9,77	8,84	9,50	33,40	42,23	26,46	0,08	0,00	100,00	0,164	0,00	100,00	46,726	30,18	35,41
GP109003-20	27,73	24,39	12,05	15,29	15,16	0,83	8,68	8,17	5,91	32,95	43,37	31,63	-0,22	0,00	100,00	-0,441	0,00	100,00	46,1	31,00	32,76
GP109008-14	25,62	5,00	80,48	17,26	11,77	31,82	3,55	7,28	104,84	11,50	44,01	282,76	1,12	0,22	80,41	2,3080	0,45	80,41	16,0880	31,45	95,51
GP109008-15	20,16	1,17	94,20	17,49	9,40	46,25	8,72	9,27	6,26	11,96	46,53	289,18	0,60	0,36	40,10	1,2350	0,74	40,10	16,7290	33,25	98,78
GP109065-12	27,34	4,51	83,51	10,93	10,69	2,21	3,97	7,91	99,29	14,94	36,08	141,58	0,31	0,19	39,30	0,6420	0,39	39,19	20,8970	25,79	23,40

Figure A 6: Evaluated measured values of the LF/VD samples

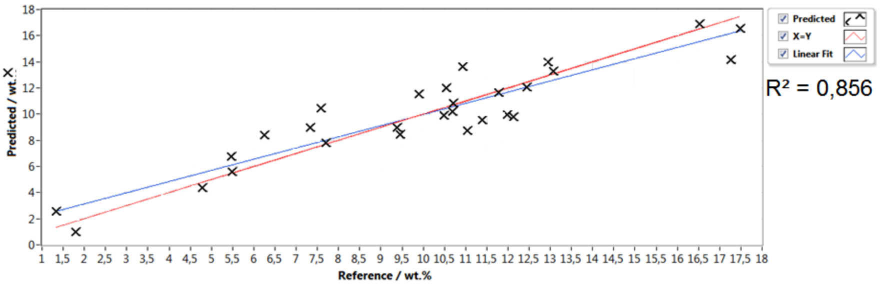


Figure A 7: Basic calibration using the example of SiO_2

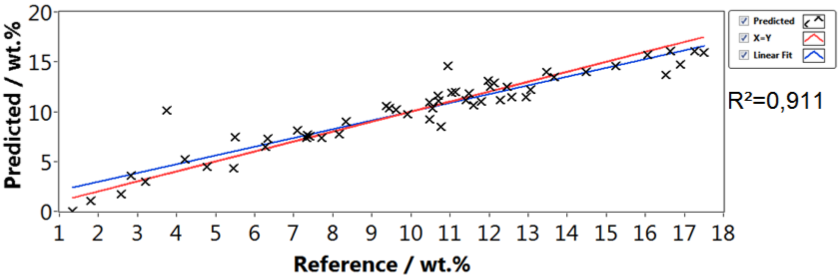


Figure A 8: Recalibration using the example of SiO_2

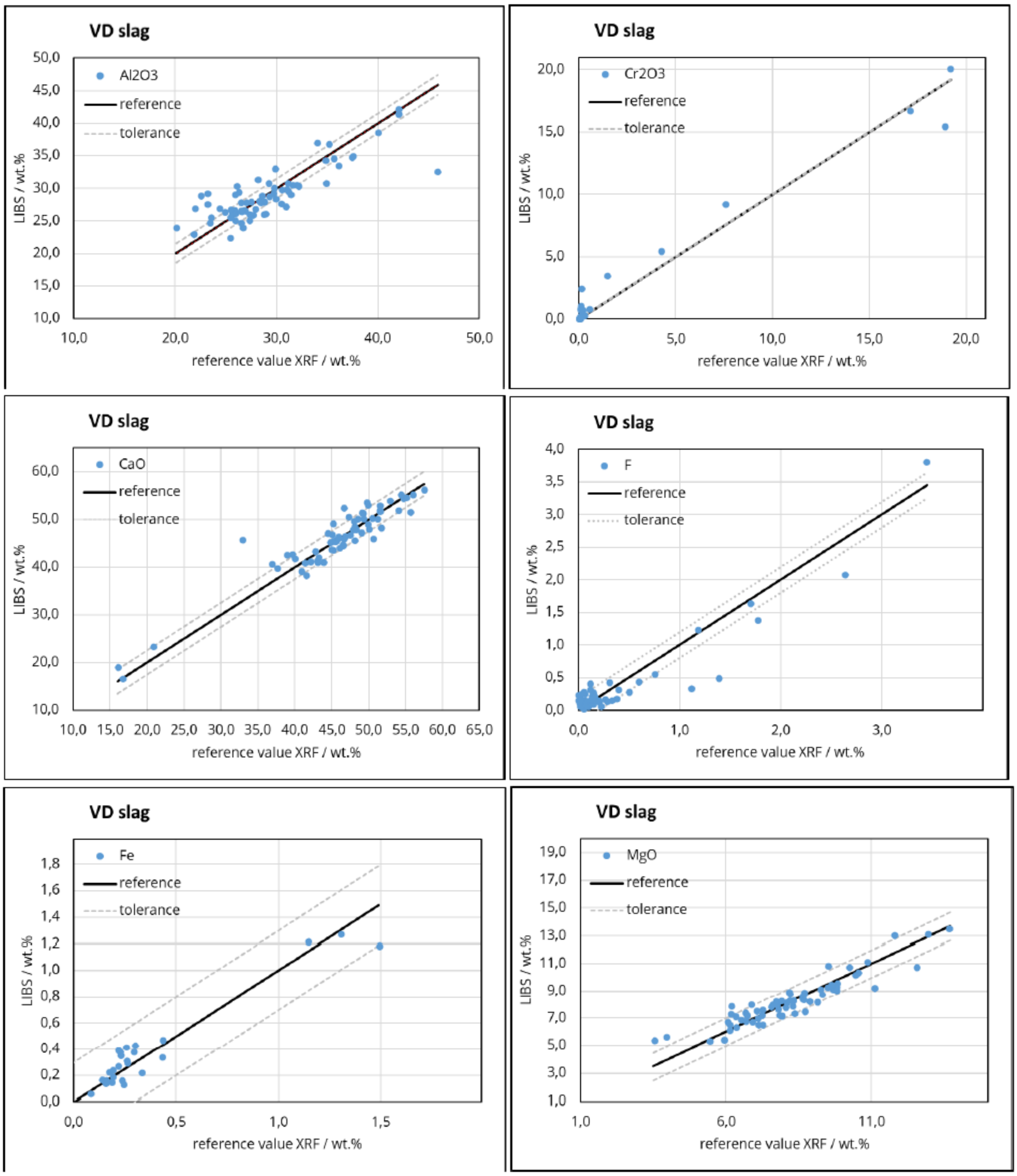


Figure A 9: Recalibration of the VD programme Part 1 [2]

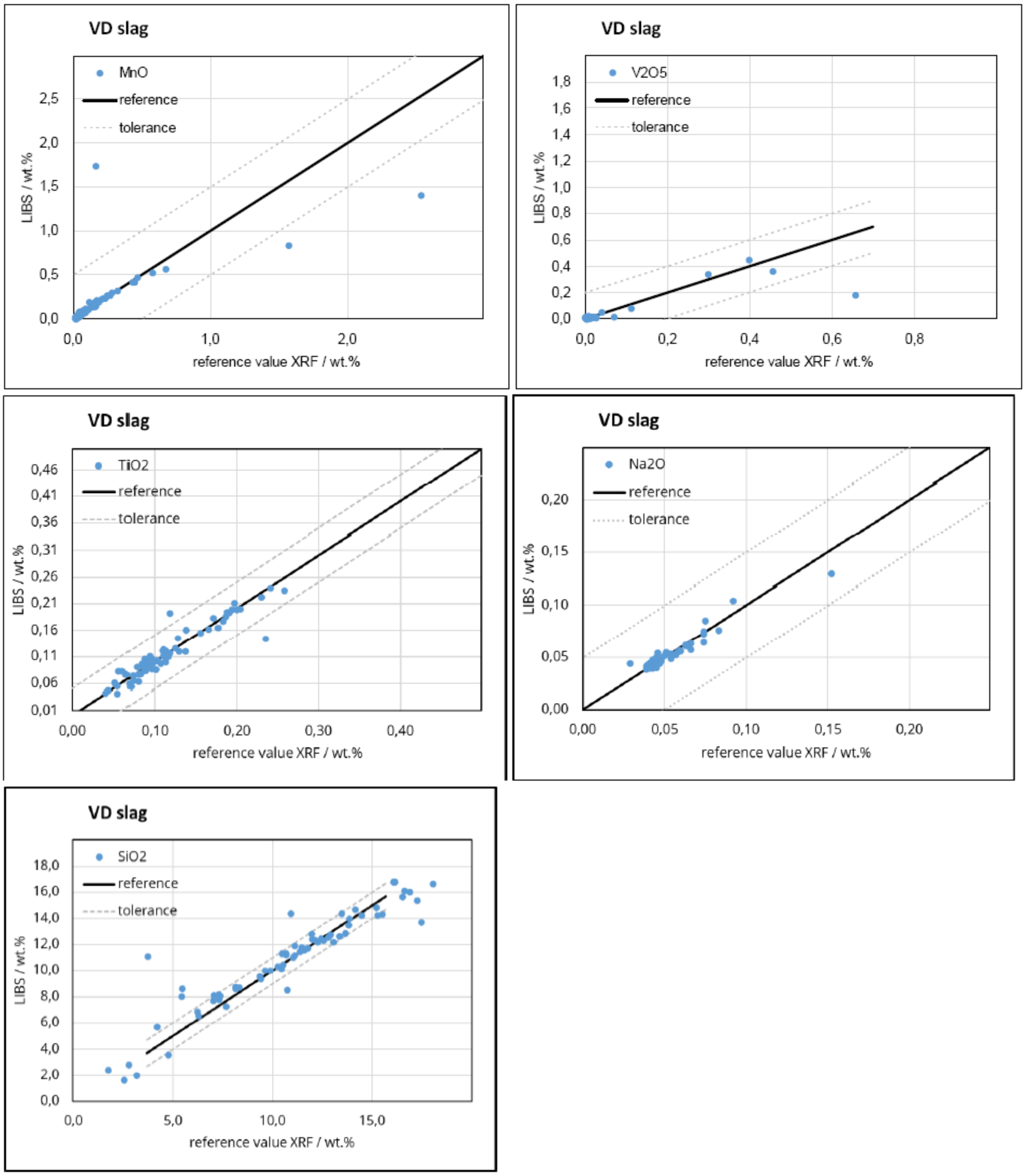


Figure A 10: Recalibration of the VD programme Part 2 [2]