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Interlaboratory Comparison for Quantitative Chlorine Analysis in Cement Pastes with Laser Induced Breakdown Spectroscopy

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Abstract

Concrete structures experience severe damage during service, for example due to pitting corrosion of rebars caused by the ingress of chlorine (Cl) into the porous concrete structure. The ingress can be monitored using laser-induced breakdown spectroscopy (LIBS), a recently introduced civil engineering technique used to detect Cl in concrete structures in addition to conventional wet chemistry methods. The key advantages of LIBS are high spatial resolution, which is important when analyzing heterogeneous concrete samples, as well as the almost complete absence of sample preparation. To assess LIBS as a reliable analytical method, its accuracy and robustness must be carefully tested. This paper presents the results of an interlaboratory comparison on the analysis of Cl in cement paste samples conducted by 12 laboratories in 10 countries. Two sets of samples were prepared with Cl content ranging from 0.06-1.95 wt.% in the training set and 0.23-1.51 wt.% in the test set, with additional variations in the type of cement and Cl source (salt type). The overall result shows that LIBS is suitable for the quantification of the studied samples: the average relative error was generally below 15 %. The results demonstrate the true status quo of the LIBS method for this type of analysis, given that the laboratories were not instructed on how to perform the analysis or how to process the data.

Keywords: LIBS interlaboratory comparison round robin test cement chlorine

1. Introduction

One of the most common reasons for the deterioration of reinforced concrete structures is the pitting corrosion of reinforcing steel bars, which can be initiated by the ingress of chlorides. Therefore, structures and buildings at risk are regularly inspected to assess the ingress depth of chlorides and evaluate the service life. Typical infrastructure exposed to chlorides are bridges, garages, highways, and offshore structures. In Germany, the maximum permissible content of chlorides in relation to the mass of cement for reinforced concrete is limited to 0.4 wt.% for new structures [1, 2] and 0.5 wt.% for existing structures [3].

The most common methods for determining the concentration of chlorides in concrete are potentiometric titration, direct potentiometry or photometry as described in DIN EN 14629 and brochure 401 DAfStb [4, 5]. The validity of these methods has been demonstrated through interlaboratory comparisons (ILC) [6–12]. However, the common disadvantages of these methods are their complexity and duration, as well as the impossibility of assessing the surface and volume distribution of chlorides in heterogeneous concrete samples, since the concrete is crushed and homogenized before analysis.

A recently introduced method for determining the content of chlorine (Cl) in concrete is laser-induced breakdown spectroscopy (LIBS). The advantages of LIBS over standard methods are its multi-element capability, high measurement throughout and high spatial resolution, as well as minimal sample preparation. Measurements with spatial resolution using LIBS make it possible to take into account the heterogeneity of concrete by separately measuring the chemical composition of aggregates and binder matrix [13, 14]. Limitations of the method include lack of sensitivity for some elements, low reproducibility due to small ablation mass, and the need to calibrate using standards that match the matrix. In addition, there are no established protocols for conducting LIBS analysis. A review on the determination of Cl in cement materials using LIBS can be found in Ref. [15].

This study presents the results of an interlaboratory comparison (ILC) conducted in 2021 by 12 laboratories in 10 countries to quantify Cl in hardened homogenized cement paste using LIBS. The main goal was to determine the trueness and repeatability of the method when no protocol or standardized methodology was provided to the participating laboratories. Each laboratory was free to choose its own experimental setup and data analysis procedure. This made it possible to evaluate the differences between laboratories and to identify important factors affecting the accuracy of the analysis. The results of this test can serve as a useful guide for the analysis of Cl in cement paste and concrete using LIBS.

2. Materials and Methods

2.1. Sample preparation

For the ILC, a training set of 12 samples (K01-12) and a test set of 8 samples (T01-08) with known Cl content, types of cement, and salts were made. To obtain various types of cement, ordinary Portland cement, limestone and blast-furnace slag were mixed in the ratios prescribed by DIN EN 197-1 [16]. The Cl content was adjusted for each sample by dissolving a certain amount of salt in deionized water. Cement and water were mixed with a water/cement ratio of 0.5 and homogenized in a mortar mixer to obtain cement paste prisms with dimensions of 40 mm × 40 mm × 160 mm. After an initial hydration process that lasted 24 hours, the formwork was removed, and the prisms were stored in a climate chamber at 23 °C and 60 % relative humidity for 27 days. During the curing process, the prisms were packed in plastic bags to minimize water loss. The prisms were then dried at 105 °C to constant weight, crushed and ground to a maximum particle size of about 90 µm. To exclude the influence of different sample handling and preparation by the participants, the samples were sent in the form of compacts by pouring the powder into small aluminum cups and pressing into compacts at a pressure of 100 N/mm^2 for two minutes. The composition of both sets of samples is shown in Table 1. The Cl content in sample K01 (without salt addition) is due to the natural Cl content of the cement used for its production. This value was determined on the material of sample K01 by potentiometric titration. The Cl values of the other samples are calculated from the base content (sample K01) and the amount of salt added during sample preparation.

The training samples were used by laboratories to develop appropriate quantification models. The Cl concentration in all test samples was within the range of the training samples. Test samples T01-04 were used to evaluate whether the LIBS laboratory systems used were sensitive enough to reliably detect Cl at various concentrations. Samples T05-07 were used to check whether problems in quantification with different LIBS instruments or in data analysis were caused by differences in cement type or Cl source (salt type). Systematic studies on the influence of the sample matrix have been performed in the past on samples of this type [15], so that a direct comparison with the ILC results was possible. Sample T08 was prepared from the same powder as sample T02 to ensure that each laboratory correctly determined the same concentration in two identical samples.

Table 1: Composition of the training (first segment) and test samples (second segment).

sample	cement type	salt type	Cl in wt.%
K01	CEM I	-	0.06
K02	CEM I	NaCl	0.19
K03	CEM I	NaCl	0.32
K04	CEM I	NaCl	0.46
K05	CEM I	NaCl	0.59
K06	CEM I	NaCl	0.72
K07	CEM I	NaCl	0.85
K08	CEM I	NaCl	0.98
K09	CEM I	NaCl	1.15
K010	CEM I	NaCl	1.43
K011	CEM I	NaCl	1.71

K012	CEM I	NaCl	1.95
T01	CEM I	NaCl	1.51
T02	CEM I	NaCl	0.50
T03	CEM I	NaCl	1.02
T04	CEM I	NaCl	0.23
T05	CEM II/B-LL	NaCl	0.41
T06	CEM III/A	NaCl	0.87
T07	CEM I	KCl	0.59
T08a	CEM I	NaCl	0.50

[a] Samples made of same powder as T02

2.2. Participating laboratories and report

A total of 31 laboratories were invited to the ILC. 14 laboratories from 10 countries accepted the invitation and 12 laboratories submitted results. These laboratories are listed in Table 2, except for one laboratory that wished to remain anonymous. Note that the various laboratories are listed in alphabetical order and do not follow the order of the custom lab code used in the following sections.

The pressed samples were packaged in resealable zipper bags to minimize possible environmental impact during transport and laboratory storage. Samples were mailed to all participating laboratories, including a form to request basic information about the experimental setup, measurement procedure, and results obtained (see Section 3.1). Only the concentration of Cl in the training samples was provided to the participants and the sample preparation process was briefly explained. The participants were not informed about the different cement types or salts used. Furthermore, no suggestions regarding an experimental setup or a procedure for data analysis have been made.

Table 2: List of participants in the interlaboratory comparison.

participating laboratories	country
- Central European Institute of Technology, Brno University of Technology	Czech Republic
- Grid Innovation Research Laboratory, Central Research Institute of Electric Power Industry	Japan
- HafenCity Universität Hamburg	Germany
- Institute of Applied Construction Research Weimar	Germany
- Isotopic and Elemental Nuclear Analytical Development Laboratory, French Alternative Energies and Atomic Energy Commission	France
- Laser and Plasma Spectroscopy Group, University Oviedo	Spain
- National Research Council of Canada, Energy Mining and Environment	Canada
- Physics department, Ariel University	Israel
- Secopta analytics GmbH	Germany
- University of Szeged	Hungary
- Valtest AG	Switzerland

2.3. Performance metric

For the evaluation of ILC, the trueness and precision performance (within and between labs) is determined according to relevant standards [17–19] and calculated from the following equations for each sample k

$$\delta_k = \sqrt{\frac{1}{L}\sum_{l=1}^{L}(x_{lk} - x_{ref,k})^2} \tag{1}$$

$$\sigma_{v,k} = \sqrt{\frac{1}{L-1}\sum_{l=1}^{L}(x_{lk} - \overline{x}_{lk})^2} \tag{2}$$

$$\sigma_{r,k} = \sqrt{\frac{1}{L}\sum_{l=1}^{L}{s_{lk}}^2} \tag{3}$$

$$\sigma_{R,k} = \sqrt{{\sigma_{v,k}}^2 + \frac{n-1}{n}{\sigma_{r,k}}^2} \tag{4}$$

where δ_k, σ_v, σ_r and σ_R are the standard deviations of bias, variability, repeatability and reproducibility. The quantities n, s, x, x_{ref} and L are the numbers of replicate measurements, relative standard deviation of replicate measurements, test result, reference value and number of participating laboratories, respectively.

3. Results and discussion

3.1. Experimental setups and data evaluation methods

The LIBS setups and experimental conditions in participating laboratories varied greatly, including different lasers and types of spectrometers, the atmosphere in which LIBS was performed, sampling and data collection methods. These parameters are summarized in Table 3-4.

Most laboratories used single-pulse excitation. Two laboratories chose double-pulse LIBS and one LIBS-LIF configuration. The laser irradiance varied from 4 - 130 GW/cm^2, and the spot diameter in the focal plane varied from 60 - 750 µm. Plasma emission was recorded using both compact spectrometers and high-resolution echelle spectrometers, so that the resolution ranged from 2800 - 18600. Both elemental and molecular emissions were used to quantify Cl in concrete.

Elemental emission was collected with no or little delay (< 2 µs), while molecular emission was usually detected with a longer delay. To improve signal quality and compensate for sample inhomogeneity, various data acquisition strategies have been used, such as accumulation and/or averaging using software and hardware, as well as obtaining multiple spectra from different locations on the sample surface. Various atmospheres were also used, since gases such as helium or argon can have a significant effect on the emission of atoms and molecules, as is known from the literature [20– 22].

Table 4 lists the data processing strategies used by the laboratories. The first three columns show basic spectrum pre-processing such as outlier detection, smoothing, and baseline correction. In addition, internal standardization of spectra was carried out in some laboratories either using CaO molecular band radiation or using continuous background radiation. Ten of twelve laboratories opted for a univariate approach. In most cases, the Cl atomic emission line at 837.6 nm was used. Due to the limited spectral range of the spectrometer, the insufficient intensity of the Cl spectral lines and/or the ability to measure only in air, several laboratories have decided to measure Cl indirectly using the CaCl molecular band. The analytical signal used in laboratories is either the integral or peak line intensity. The calibration plot was built using either linear or quadratic regression. Two laboratories used a multivariate approach in which either the entire spectrum or a selected spectral window was used for data processing. In all cases, LOD and LOQ were calculated using an univariate approach.

Table 3: Selected characteristics of the experimental setups used by participating laboratories.

lab	typea	irradianceb	λ_{Laser}	spot Ø	$\lambda / \Delta\lambda$	delay t	intg. t	no. spectra	ATM
-	-	GW/cm^2	nm	µm	-	µs	µs	-	-

A	SP	42.4	266	60	6600	1.0	1000	200	Ar
B	SP	11.3	1064	160	2800	-	2000	6084	He
C	DP	11.9	532 (532)	200	4200	0.5	5	30000	Air
D	SP	129.4	1064	60	4000	10.0	100	1000	Air
E	LIBS-LIF	4.4	1064 (377.5)	500	7700	20.0	0.03	900	Air
F	SP	3.8	1064	750	18600	2.0	3.5	400	He
G	DP	50.9	532 (1064)	100	6000	0.5	50	500	He
H	SP	15.9	1064	400	3700	50.0	15	200	Air
I	SP	6.4	1064	100	2800	-	2000	57600	He
J	SP	11.3	1064	150	2800	-	2000	2205	He
K	SP	25.5	1064	100	2800	-	2000	59049	He
L	SP	3.7	1064	400	6400	0.5	9.5	1000	Ar

[a] SP - single Pulse, DP - Double Pulse

[b] for DP LIBS and LIBS-LIF only the irradiance for the ablation laser is given

Table 4: Summary of data evaluation procedures performed by participating laboratories.

lab	OD	SM	BC	IS[b]	line/band[b]	signal eval.	calibration	LOD / LOQ[a]
A	×	×	✓	×	CaCl 593.5	integral intensity	OLS-regression, 2nd ord. Polynom	0.08 / 0.27
B	✓	×	×	be	Cl 837.6	peak intensity	OLS-regression, linear	0.03 / 0.12
C	×	×	✓	×	Cl 837.6	integral intensity	OLS-regression, linear	0.08 / 0.27
D	✓	×	×	CaO	CaCl 593.5	integral	OLS-regression, 2nd ord.	0.07 /

				615		intensity	Polynom	0.20
E	×	✓	✓	CaO 387.6	CaCl 382.8, 382.9	integral intensity	OLS-regression, linear	0.02 / 0.07
F	×	×	✓	×	Cl 837.6	peak intensity	OLS-regression, 2nd ord. Polynom	0.01 / 0.03
G	×	×	×	×	250 - 900	-	SPLS-R	0.48 / 1.60
H	✓	×	✓	be	CaCl 593.5	integral intensity	OLS-regression, linear	0.04 / 0.13
I	×	×	×	be	Cl 837.6	peak intensity	OLS-regression, linear	0.02 / 0.05
J	×	×	×	be	835-839		PLS-R	0.05 / 0.09
K	×	×		be	Cl 837.6	peak intensity	OLS-regression, linear	0.10 / 0.33
L	×	×		×	Cl 837.6	peak intensity	OLS-regression, linear	- / -

lab - laboratory code, OD - outlier detection, SM - smoothing, BC - baseline correction, IS - internal standard, signal eval. - signal evaluation, OLS - ordinary least squares, be - background emission

[a] in units of wt.%. Underlining indicates the calculation of LOD and LOQ according to the calibration line method, otherwise according to the blank value method (DIN 32645 [23])

[b] in units of nm

3.2. Laboratories excluded from ILC

With a small number of participating laboratories, individual laboratories whose results differ significantly from the results of others have a significant impact on the assessment of the validity of the method. Therefore, such laboratories should be identified and excluded from further evaluation. The Cl concentrations determined in the test samples are given in 5. Comparing the reference Cl concentrations in the test samples with the data provided by the participants, the results of laboratory L differ significantly from the results of other laboratories. Application of the generalized Student's test of extreme deviations (ESD) [24] confirms that this laboratory is an exception.

Also, many of the results from Laboratories A, E, and G are identified as outliers; however, only laboratory L results unreasonably exceed the reference concentration range and are therefore excluded from further data evaluation (5 out of 7 sample results had a relative error greater than 100 %).

3.3. *Trueness and precision*

Comparison of reference values with determined Cl concentrations in all samples by all laboratories is shown in Figure 1. For most laboratories and most samples, the found concentrations of Cl are scattered around the reference values with a deviation of ± 0.1 wt.%. On closer inspection, these laboratories show systematically high or low concentrations, indicating some procedural errors in the analysis. On average, the overall relative error is about 16 %, and for individual samples the error reaches 125 %.

The normality of the distribution of the data was checked and the corresponding statistical parameters are shown in Table 5. The median and means show a significant deviation for some samples, and the p-values for skewness, kurtosis and the Shapiro-Wilk test also indicate a deviation from the normal distribution, as expected. These deviations occur mainly at the edges of distributions due to multiple outliers from multiple laboratories. For reasons of generality and because of the small number of laboratories involved, these outliers are not discarded.

Figure 2(a) shows the results of analysis based on the Youden plot [25]. It is assumed that well-functioning laboratories not only provide reproducible results for the same sample, but also recognize identical samples (T02 and T08). When comparing the position of the ideal point (0.5 wt.%, 0.5 wt.%) with the median in Figure 2(a), a slight shift of around 0.02 wt.% is visible. However, the fact that the results of most laboratories lie on the bisector ensures high intralaboratory reproducibility. From Figure 2(a) is also seen that the significant outliers are Laboratories A, E and G, which have already been identified as such in section 3.2. In general, they are characterized by low reproducibility and high bias. It should be noted that lab G was aware of this problem based on internal review and poor LOD and LOQ but was unable to improve their results.

To better understand the relationship between intra-laboratory trueness and precision, Figure 2(b) compares the bias of the reference value from the estimated concentrations (averaged over all samples) with the measurement repeatability of the duplicate sample (T02/T08). Measurement repeatability is determined by the relative standard deviation (coefficient of variation). For all but two laboratories, the relative bias was less than 15 % and reached ～45 % for laboratories E and G. For all but three laboratories, measurement repeatability was less than 5 %; laboratory A showed poor measurement repeatability of ～25 %. In general, laboratories that showed a large margin of error also reported poor repeatability.

Figure 1: Results of analysis of Cl content for all samples by all laboratories.

Table 5: Key statistics for the distribution mean, including mean, median, standard deviation (SD), absolute median deviation (MAD), and p-values for skewness, kurtosis, and Shapiro-Wilk test for normality, rounded to two decimal places.

	sample							
	T01	T02	T03	T04	T05	T06	T07	T08
mean	1.37	0.51	0.97	0.25	0.44	0.99	0.52	0.5
median	1.48	0.53	1.01	0.25	0.43	0.88	0.53	0.53
SD	0.21	0.09	0.09	0.08	0.19	0.19	0.09	0.11
MAD	0.06	0.03	0.02	0.02	0.03	0.06	0.06	0.02
skewness	0.03	0.00	0.02	0.13	0.15	0.01	0.95	0.00
kurtosis	0.29	0.01	0.34	0.06	0.02	0.02	0.65	0.00
shapiro	0.01	0.00	0.00	0.10	0.02	0.00	0.80	0.00

Figure 2: (a) Youden-Plot for duplicate sample T02/T08. True value, median, 45° fiducial line, and 95 % coverage circle are marked. (b) Mean relative laboratory error versus measurement repeatability.

3.4. Performance of LIBS analysis

The performance values given by equations 1-4 are calculated and presented in Table 6. The arithmetic mean of the concentrations determined by all laboratories was taken as a consensus value. Repeatability and reproducibility could only be determined for the duplicate samples (T02, T08), as no further repeat measurements on individual samples were requested by the participants.

As can be seen from Table 6, the reference and consensus values are generally in good agreement, with the relative error for most samples being less than 10 %. The standard deviations of the bias and variability, averaged over all samples, are 0.16 wt.% and 0.15 wt.%, while the standard deviations of repeatability and reproducibility, averaged only over duplicate samples T02 and T08, are 0.09 wt.% and 0.12 wt.%, respectively.

Metrics are recalculated after excluding data from underperforming laboratories A, E, and G; the results are shown in Table 7. Performance improves as the relative error between reference and determined values is less than 10 % for all samples except T04. In addition, the standard deviations of bias, variability, repeatability and reproducibility are significantly lower.

In addition to high precision and trueness, it is important that LIBS demonstrates high detection sensitivity for practical use. Based on the limit values given in the introduction for the maximum allowable Cl content in reinforced concrete, the LIBS system must reliably determine a Cl concentration of at least 0.2 wt.%. This value was obtained assuming a water-cement ratio of 0.5. Based on the limit-of-quantification (LOQ) values shown in Table 4, Laboratories A, C, G, and K do not meet this requirement. This is consistent with the low confidence in the T04 Cl concentrations determined by these laboratories compared to other laboratories. However, lab E shows the largest discrepancy for sample T04, although it shows a low LOQ of 0.07 wt%. It should be noted that the consensus value for all laboratories differs from the reference value in the T04 sample by only 0.02 wt.% (~10 % rel. error).

Table 6: Calculated performance characteristics based on results from all laboratories.

	sample								μ
	T01	T02	T03	T04	T05	T06	T07	T08	
reference value in wt.%	1.51	0.50	1.02	0.23	0.41	0.87	0.59	0.50	-
consensus value in wt.%	1.37	0.51	0.97	0.25	0.44	0.99	0.52	0.49	-
rel. error in %	9.33	1.27	4.72	9.49	8.43	13.38	12.63	1.09	-

bias δ in wt.%	0.26	0.09	0.10	0.08	0.19	0.22	0.11	0.11	0.16
variability σ_v in wt.%	0.23	0.10	0.09	0.09	0.20	0.20	0.09	0.12	0.15
repeatability σ_r in wt.%	-	0.09	-	-	-	-	-	-	-
reproducibility σ_R in wt.%	-	0.12	-	-	-	-	-	-	-

Table 7: Calculated performance characteristics based on results from well-performing laboratories.

	sample								μ
	T01	T02	T03	T04	T05	T06	T07	T08	
reference value in wt.%	1.51	0.50	1.02	0.23	0.41	0.87	0.59	0.50	-
consensus value in wt.%	1.48	0.52	1.01	0.26	0.43	0.94	0.55	0.52	-
rel. error in %	2.32	3.00	1.23	14.6	5.79	8.33	7.20	3.75	-
bias δ in wt.%	0.09	0.03	0.03	0.05	0.07	0.13	0.09	0.03	0.07
variability σ_v in wt.%	0.09	0.03	0.03	0.04	0.07	0.11	0.08	0.03	0.07
repeatability σ_r in wt.%	-	0.02	-	-	-	-	-	-	-
reproducibility σ_R in wt.%	-	0.03	-	-	-	-	-	-	-

3.5. Factors affecting performance

It is instructive to see how laboratory performance depends on the type of experimental setup, calibration method, and sample matrix.

For the repeatability and trueness of LIBS analysis, the relationship between the size of the laser spot and the grain diameter is usually of great importance [26, 27]. The larger the laser spot, the more grains are involved in the measurement, and thus the material appears to be more uniform. To reduce the effect of sample grain size on a single measurement, a large spot diameter can be selected or a large number of acquired spectra can be set to statistically compensate for inhomogeneity.

It is also advantageous to work with high irradiance to remove more material. Comparing laboratories with each other (Figure 3) shows that laboratories with low irradiance and small spot diameters, as a rule, recorded more spectra (Laboratory I, K). In contrast, laboratories with large spot diameters (Laboratory E, F, H) or high irradiance (Laboratory A, D, G) tended to record fewer spectra. However, this observation cannot be generalized because Laboratories B, C, and J chose intermediate settings. With regard to the optimal spot diameter, the number of spectra recorded or the irradiance, no clear conclusion can be drawn from the present results on the best parameters, since all settings provide both high and low repeatability and accuracy.

In terms of spectral resolution, high resolution spectrometers are more favorable for LIBS experiments because they reduce spectral interference. However, high resolution is not required for the current analysis because for this samples Cl 837.6 nm is a separate emission line. For the CaCl molecular band, high resolution is also not important, since the bands are wide (provided that they are also completely or partially free from spectral interference).

High repeatability and accuracy can be achieved with both high and low resolution spectrometers (see Figure 3). However, it was observed that higher resolution spectrometers performed time-resolved measurements to improve the signal-to-noise ratio, while lower resolution spectrometers performed time-integrated measurements because they were typically equipped with non-gating detectors (see Table 3).

Concerning the choice between Cl emission line or CaCl molecular band, it can be observed that laboratories that used the CaCl molecular band showed on average lower trueness and repeatability compared to laboratories that used the Cl emission line (e.g. lab A, D, E, H vs. B, C, F, I, J, K). However, this statement cannot be generalized, because if laboratories A and E (designated as outliers) are excluded from the comparison, the remaining laboratories show comparable results and thus using the Cl emission line or the CaCl molecular band gives comparable results for the samples studied.

It should be noted that the laboratories that used single-pulse setups also used the Cl emission line for analysis and worked in an atmosphere of an inert gas He or Ar. In contrast, laboratories with double-pulse setups and laboratories that used indirect Cl quantification via CaCl emission detection operated in air (except Laboratory A). This choice is consistent with previous Cl detection studies [22, 21, 28, 29] and justifies the decisions made by individual laboratories (see section 3.1).

Both univariate and multivariate calibrations were used for quantification, and only two of the twelve laboratories (laboratories G and J) chose multivariate calibration. Laboratory J used a narrow spectral range of 835-839 nm for the multivariate calibration, which contained only one Cl line, so little or no difference is expected between the univariate and multivariate calibration results. Lab G performed poorly compared to other labs. Due to the limited number of examples, no clear conclusion can be drawn about the effect of the calibration method.

Regarding the effect of the Cl source (salt type), KCl-doped sample T07, compared to T02 and T08 (NaCl) with similar Cl concentrations, similar deviations were found for all laboratories (Table 6). This is consistent with the results of previous studies [15]. Interestingly, when only good performing laboratories are considered, an improvement in trueness is observed for samples T02 and T08 (NaCl), but not for sample T07 (KCl).

When examining the effect of cement type, namely samples T05 (CEM II/BLL) and T06 (CEM III/A) compared to T02 and T03 (both CEM I) with the same Cl concentrations, an increased deviation was found in all laboratories (Tables 6,7). At least for the T05 sample, this was also found in a previous study [15]. As a possible cause, the authors suggest that limestone does not participate or only slightly participates in the process of hydration and phase formation in cement, and thus a possible matrix effect may be the result.

Figure 3: Comparison of normalized characteristic features of the experimental setup among laboratories, as well as comparison of the associated performance parameters.

4. Conclusion

This study presents the results of the first international interlaboratory comparison (ILC) for the determination of Cl in cement paste samples by the LIBS method. The samples consisted of homogenized pressed cement paste powders. 12 training samples covered the range 0.06-1.95 wt.% and 8 test ("unknown") samples the range 0.2-1.5 wt.%. Several types of cement and salts were used during the sample preparation stage.

Only one of the 12 laboratories reported overestimated data. The remaining 11 laboratories showed a high repeatability of about 0.09 wt.% and an average bias of about 0.16 wt.%. Quality indicators improved when only 8 well-performing laboratories out of 11 were considered for evaluation. In this case, a repeatability of about 0.02 wt.% and an average bias of about 0.07 wt.% were achieved. Laboratories that performed relatively poorly also showed poor measurement repeatability. Neither the cement type studied nor the Cl source (salt type) had a clear effect on performance.

Given the wide variety of experimental setups, measurement protocols, and data analysis methods, the ILC results can be considered satisfactory: the average relative error was generally below 15 %. Overall, the results demonstrate the true status quo of the LIBS method for this type of analysis, given that no instructions were provided to the laboratories on how to perform the analysis or process the data. They were also not informed about the different sample matrices (types of cement and salt) and concentration ranges; only experience in LIBS analysis was required to participate in this test. Laboratories that specialize in Cl analysis or have a standardized workflow are likely to give better results.

No clear recommendations can be made from this ILC as to the best instrumental conditions for Cl analysis with LIBS, since satisfactory results have been obtained using different lasers and spectrometers, and different ambient gases. As a rule, single-pulse setups are preferred over double-pulse setups or other plasma reheat setups.

The signal was evaluated both from the emission line of the Cl atom and from the molecular band of CaCl, and comparable results were obtained for the studied samples. Detection of the Cl atomic emission line required the use of an inert gas atmosphere such as Ar or He in all laboratories, unless an additional plasma reheating method such as double pulse was used. Both univariate and multivariate methods were used for quantification. As only 2 out of 12 laboratories used the multivariate method, recommendations on the quantitation method cannot be given due to the small number of examples.

To further evaluate the suitability of LIBS for applications in civil engineering, further investigations on influences from the sample matrix (e.g. cement type and admixtures) are necessary to cover the possible variability in practice. Also, the heterogeneity of concrete was not considered in this ILC, which is why a subsequent ILC on concrete samples is planned.

Author Contributions

Tobias Völker: Conceptualization, Formal analysis, Writing - Original Draft, Writing - Review & Editing. **Gerd Wilsch**: Conceptualization, Writing - Review & Editing, Resources, Supervision.

Igor B. Gornushkin: Writing - Review & Editing. **Lucie Kratochvilová**: Investigation, Writing - Review & Editing. **Pavel Pořzka**: Investigation, Writing - Review & Editing. **Jozef Kaiser**: Investigation, Writing - Review & Editing. **Steven Millar**: Conceptualization, Resources, Writing - Review & Editing. **Gábor Galbács**: Investigation, Writing - Review & Editing. **Dávid J. Palásti**: Investigation, Writing - Review & Editing. **Patrick M. Janovszky**: Investigation, Writing - Review & Editing. **Shuzo Eto**: Investigation, Writing - Review & Editing. **Christoph Langer**: Investigation, Writing - Review & Editing. **Gesa Kapteina**: Investigation, Writing - Review & Editing. **Marcus Illguth**: Investigation, Writing - Review & Editing. **Jenny Götz**: Investigation, Writing - Review & Editing. **Marina Licht**: Conceptualization, Investigation, Resources, Writing - Review & Editing, Visualization. **Michael Raupach**: Investigation, Resources, Writing - Review & Editing. **Ismail El Hamdaoui**: Investigation, Writing - Review & Editing. **Mohamad Sabsabi**: Investigation, Writing - Review & Editing. **Paul Bouchard**: Investigation, Writing - Review & Editing. **Lev Nagli**: Investigation, Writing - Review & Editing. **Michael Gaft**: Investigation, Writing - Review & Editing. **Yosef Raichlin**: Investigation, Writing - Review & Editing. **Luis Javier Fernández-Menéndez**: Investigation, Writing - Review & Editing. **Cristina Méndez López**: Investigation, Writing - Review & Editing. **Nerea Bordel**: Investigation, Writing - Review & Editing. **Cassian Gottlieb**: Investigation, Writing - Review & Editing. **Christian Bohling**: Investigation, Writing - Review & Editing. **Riccardo Finotello**: Investigation, Writing - Review & Editing. **Daniel L'Hermite**: Investigation, Writing - Review & Editing. **Céline Quéré**: Investigation, Writing - Review & Editing. **Matthias B. Lierenfeld**: Investigation, Writing - Review & Editing. All authors have read and agreed to the published version of the manuscript.

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Appendix A. Submitted Cl concentrations for each test sample of all participants

Table A.8: Determined Cl concentrations and uncertainties of the laboratories, rounded to the second decimal place. For Cl concentrations without uncertainty, no information was provided by the corresponding laboratory.

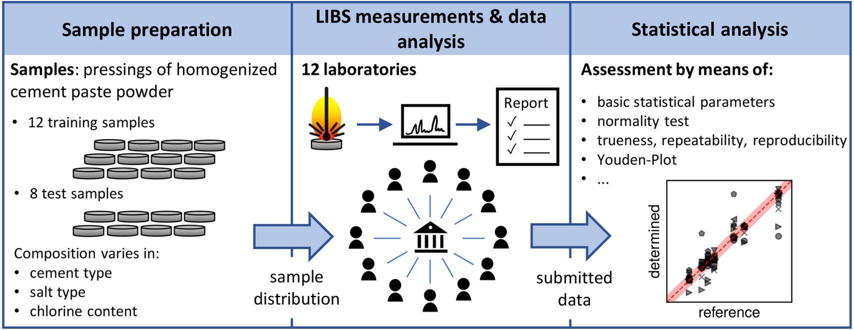
lab code	Cl in wt.%							
	T01	T02	T03	T04	T05	T06	T07	T08
A	0.88 ± 0.13	0.61 ± 0.09	0.81 ± 0.21	0.23 ± 0.05	0.41 ± 0.05	0.82 ± 0.13	0.47 ± 0.05	0.44 ± 0.06
B	1.57	0.53	1.01	0.26	0.50	1.02	0.67	0.54
C	1.48 ± 0.01	0.55 ± 0.02	1.03 ± 0.02	0.31 ± 0.07	0.46 ± 0.03	1.07 ± 0.05	0.55 ± 0.04	0.52 ± 0.04
D	1.51 ± 0.04	0.53 ± 0.03	1.02 ± 0.03	0.24 ± 0.02	0.43 ± 0.03	1.13 ± 0.04	0.60 ± 0.03	0.54 ± 0.04
E	1.02	0.24	0.79	0.05	0.09	0.99	0.40	0.19
F	1.51 ± 0.09	0.49 ± 0.02	1.02 ± 0.02	0.24 ± 0.01	0.45 ± 0.01	0.86 ± 0.05	0.53 ± 0.01	0.49 ± 0.02
G	1.36 ± 0.28	0.60 ± 0.20	1.03 ± 0.21	0.38 ± 0.24	0.92 ± 0.21	1.50 ± 0.38	0.42 ± 0.31	0.66 ± 0.27
H	1.28 ± 0.10	0.46 ± 0.08	0.93 ± 0.07	0.21 ± 0.04	0.28 ± 0.07	0.88 ± 0.06	0.38 ± 0.03	0.46 ± 0.08
I	1.52 ± 0.04	0.51 ± 0.02	1.01 ± 0.05	0.25 ± 0.00	0.43 ± 0.00	0.86 ± 0.01	0.52 ± 0.01	0.53 ± 0.01
J	1.51 ± 0.15	0.50 ± 0.13	1.03 ± 0.13	0.25 ± 0.12	0.42 ± 0.13	0.87 ± 0.15	0.54 ± 0.12	0.52 ± 0.12
K	1.42	0.55	1.01	0.35	0.50	0.85	0.59	0.55
L*	1.29	1.79	0.81	0.55	2.99	14.55	3.84	0.80
reference	1.51	0.50	1.02	0.23	0.41	0.87	0.59	0.50

value								

* outlier, not considered in the analysis

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Sample preparation

Samples: pressings of homogenized cement paste powder

- 12 training samples
- 8 test samples

Composition varies in:

- cement type
- salt type
- chlorine content

sample distribution

LIBS measurements & data analysis

12 laboratories

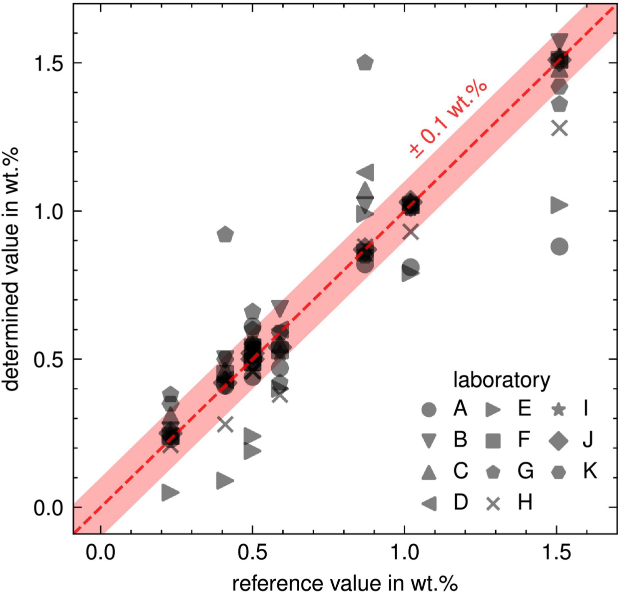
submitted data

Statistical analysis

Assessment by means of:

- basic statistical parameters
- normality test
- trueness, repeatability, reproducibility
- Youden-Plot
- ...

Graphics Abstract



± 0.1 wt.%
1.5
1.0
0.5
0.0
determined value in wt.%
0.0
0.5
1.0
1.5
reference value in wt.%
laboratory
A
B
C
D
E
F
G
H
I
J
K

Figure 1

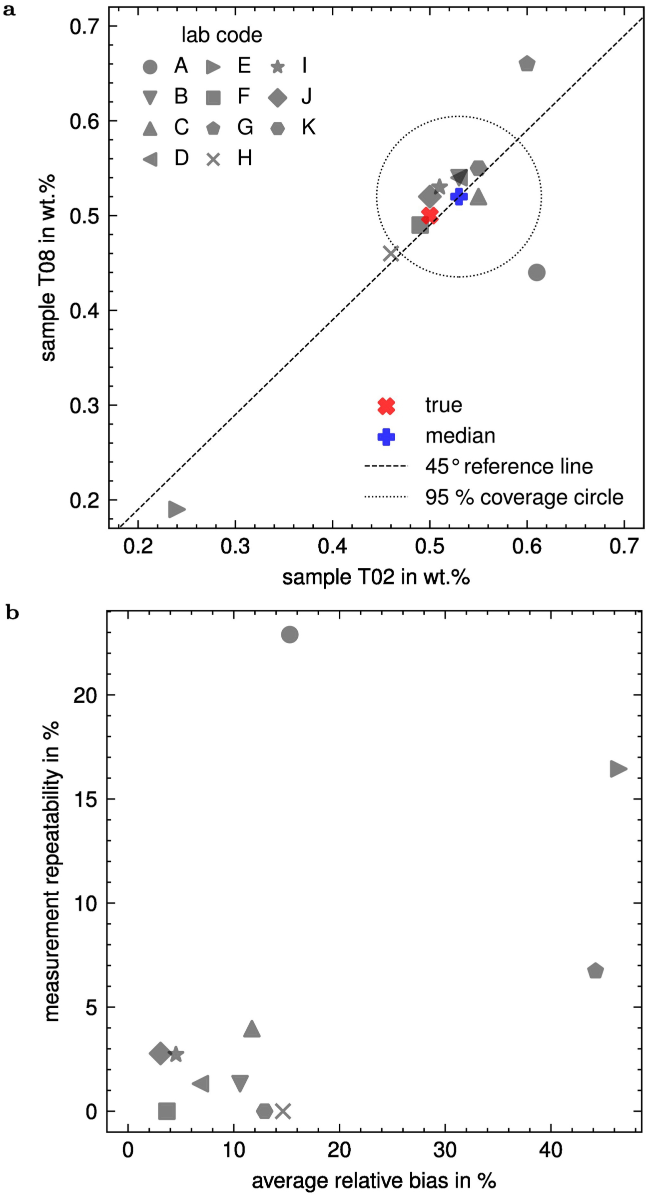
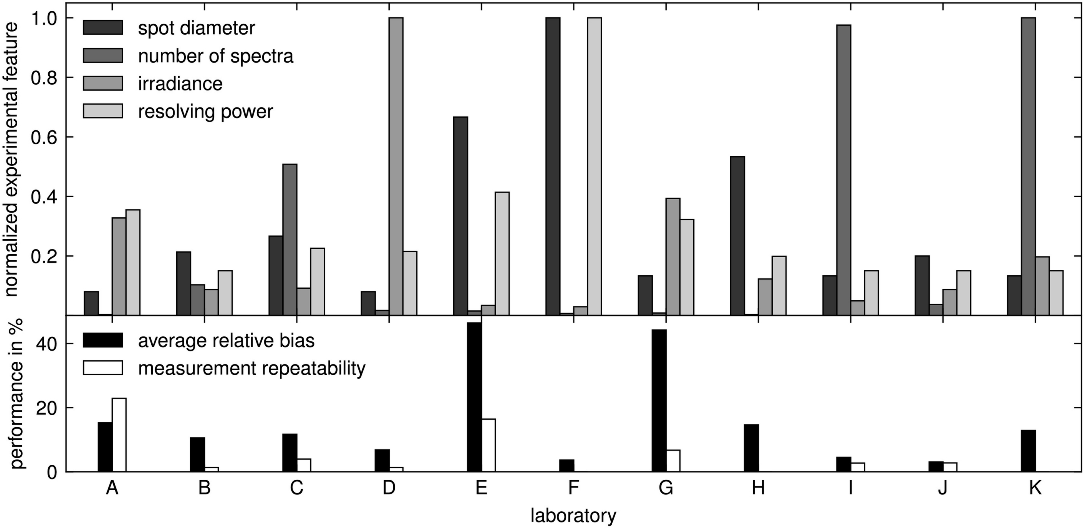

a
lab code
A
B
C
D
E
F
G
H
I
J
K
true
median
45° reference line
95 % coverage circle
0.2
0.3
0.4
0.5
0.6
0.7
sample T08 in wt.%
sample T02 in wt.%
b
0
5
10
15
20
30
40
measurement repeatability in %
average relative bias in %

Figure 2



spot diameter
number of spectra
irradiance
resolving power
normalized experimental feature
1.0
0.8
0.6
0.4
0.2
average relative bias
measurement repeatability
performance in %
40
20
0
A
B
C
D
E
F
G
H
I
J
K
laboratory

Figure 3