



Quantification of chloride in concrete samples using LA-ICP-MS



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ABSTRACT

Inspection of the chloride content in concrete samples is an important factor for determination and planning of maintenance measures. The standard method given by European legislative for chloride determination is the titrimetric Volhard method. However, it requires significant experimental effort, and knowledge about the cement content in the concrete is required. In this work, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is proposed as an alternative method to the commonly used wet-chemical approach. LA-ICP-MS allows analysis of drilled core concrete samples with increased depth resolution, minimal workload for sample preparation, and fast analysis time. Furthermore, exploiting the multi-elemental capabilities of ICP-MS, an in-depth analysis of the sample composition, allowing a differentiation between cement phase and aggregates is feasible. Using this information, selective determination of chloride in the cement phase becomes possible, which helps to increase the reliability of the determined chloride concentrations.

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1. Introduction

Free chloride can locally weaken the passivation layer of the reinforcing steel [1], and the induced corrosion of the steel can severely affect structural stability. The chloride content near the reinforcement is therefore an essential parameter to determine and plan maintenance measures for concrete structures [2].

Concrete consists of multiple main components: aggregates (stones, rocks, or sand, in variable mixtures), water, admixtures, and cement as a binding agent. Even though the use of chloride containing aggregates is permitted by European standards (EN 12620:2013), completely chloride-free environments are not economically realizable. Additionally, external sources of chloride, such as de-icing salts, play a considerable role for chloride intake into the concrete structure.

The standard method for chloride determination specified by the European standard EN 14629:2007 [3] is the titrimetric Volhard method, which exploits precipitation of solubilized chloride with silver nitrate. Concrete samples are collected by drilling holes into the structures, and collecting either complete cores, or borehole dust. Cores are typically cut into slices of 10–20 mm thickness, and ground for further analysis. Borehole dust can be used directly without homogenization. The powdered samples are solubilized using nitric acid, and the chloride concentration in the solution is determined by titration. The cement content (the chloride concentration is referenced to the amount of cement in the concrete) is either known from the concrete production, or estimated by conservative rules dictated by the standards [3]. Using both methods for concrete sampling, depth profiles at depth resolutions

of around 10–20 mm can be collected. Higher depth resolutions can be obtained by specialized techniques (e.g., by grinding of slices). However, as the chloride content is determined as a chloride concentration in the cement fraction, in such cases the inhomogeneity of the aggregates has to be taken into account. The determination thereof will become less accurate with smaller sampling volumes (i.e., higher depth resolution). Alternative methods for chloride determination in concrete samples are other titrimetric methods, such as potentiometric titration, or the use of ion selective electrodes. Also, more advanced instrumental analytical methods, such as X-ray fluorescence (XRF) [4], laser induced breakdown spectroscopy (LIBS) [5–8], or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [9] have already been used for the determination of chloride in concrete. Those methods allow some improvements in depth resolution compared to titrimetric approaches. In addition to improving the limits of detection and the specificity of the analysis, the workload for such analyses could be reduced.

LA-ICP-MS is a method with a broad application range in the environmental and geological sciences [10]. Allowing for direct solid sample analysis, excellent detection limits for most elements, and a wide linear range, this method is very powerful for elemental analysis. In this work, the analysis of concrete core samples using LA-ICP-MS is presented. The objective of the presented work is to provide a more sensitive and more accurate determination of the chloride content in concrete compared to the standard method. In a novel approach, selective quantification of chloride in the cement phase is performed. As only the chloride content in the cement phase is determined, the total chloride content can be correlated with the free chloride content, which is responsible for rebar corrosion. In preliminary experiments, in-house prepared concrete samples with different types of aggregates

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and known chloride and aggregate contents were analyzed. Chloride containing aggregates are excluded from data evaluation and thus, a very reliable determination of the chloride content in the cement phase combined with high depth resolution can be obtained. The developed method was applied to drilled core samples from a retaining wall beside a city highway obtained from different sampling positions; the obtained depth profiles and the chloride quantification were compared with results from conventional titration.

2. Material and methods

2.1. Sample preparation and collection of drilled core samples

In order to produce concrete samples with known aggregate content and chloride concentration, some specimens were prepared in-house. Commercially available cement powder (baumit, Austria) was mixed in a ratio of 7:2 (v/v) with NaCl-containing water (conc. 3.79 g L⁻¹), yielding a total chloride content of 0.5 m% in the cement mixture. Preliminary titrations showed that the used cement does not have a considerable chloride content (i.e., not quantifiable by titration). Approx. 60.0 m% aggregates were added to each concrete mixture, the exact aggregate content was determined by weighing. The used aggregates originated from different areas in Austria, resembling varying compositions: River gravel, limestone, and granite had a grain size distribution between 1.0 and 16 mm. Aggregates and cement were thoroughly mixed and molded into cylindrically shaped PE molds with an inner diameter of 50 mm. The concrete was allowed to harden for 3 days at room temperature and 40% relative humidity until further processing.

Drilled core samples were taken from a retaining wall beside a city highway in Vienna (Austria). Sampling from the concrete structure was performed at four different heights (0.8, 1.8, 2.6, and 4.6 m above street level), facing the roadway; six core samples were taken at each height with a horizontal distance of 1.5 m between the sampling spots. All cores had a diameter of 45 mm, with a length of approximately 100 mm.

All cylinders, molded concrete samples as well as drilled core samples were cut along the length of the sample into two semicircular halves by dry cutting, in order not to mobilize chloride. Until further processing, the samples were stored at 25 °C and a relative humidity of 40% separately in plastic bags. Storage time was never longer than two weeks. The flat side of one half-cylinder was used for LA-ICP-MS analysis. Parts of the other half of the molded concrete samples were ground using a tungsten carbide mortar to a maximum particle size below 1 mm for subsequent titrimetric analysis.

2.2. Instrumentation

All measurements were performed using a quadrupole ICP-MS device (iCAP Q, ThermoFisher Scientific, Bremen, Germany) coupled to an NWR213 laser ablation unit (ESI, Fremont, CA). The connection between the instruments was established using PTFE tubing. The sample material was ablated under a constant stream of helium,

which was mixed with argon as make-up gas before introduction into the ICP-MS. Tuning of the instrumental performance was performed daily using a glass standard (NIST612, trace elements in glass, National Institute of Standards and Technology, Gaithersburg, MD) for highest intensity of the ¹¹⁵In signal. Additionally, the oxide ratio was monitored by the ¹⁴⁰Ce¹⁶O/¹⁴⁰Ce ratio, which was below 1.9% for all experiments. Laser parameters and gas flows were optimized in preliminary experiments to yield the best achievable signal stability as well as signal intensity for the sample measurements. To prevent detector saturation, less abundant isotopes were chosen for the bulk elements expected in the concrete samples. Polyatomic interferences were not expected, as only major sample constituents were analyzed. Typical instrumental parameters used for the experiments are listed in Table 1.

2.3. Chloride determination using titration

Chloride determination using the Volhard method was performed according to the European norm EN 14629:2007 [3]. 50 mL high purity water dispensed from a Barnstead EASYPURE II water system (ThermoFisher Scientific, Marietta, OH) were added to 1–3 g of the ground sample material, which was deposited into PTFE beakers and weighed exactly. After addition of 10 mL conc. nitric acid (p.a., Merck, Darmstadt, Germany), another 50 mL of water were added. The mixture was heated until boiling and kept boiling for at least 3 min. After complete cooling to room temperature, 5 mL silver nitrate solution (0.05 mol L⁻¹, p.a., Merck, Darmstadt, Germany) was added. The reaction mixture was stirred to ensure quantitative precipitation of the formed silver-chloride. Subsequently, freshly prepared ammonium iron-(III)-sulfate solution was added and the excess of silver ions was titrated using ammonium thiocyanate solution (0.05 mol L⁻¹, Merck, Darmstadt, Germany) until color change from white to a brownish-red color. A blank sample was treated in the same way, but without addition of ground concrete.

2.4. Preparation of cement standards for LA-ICP-MS analysis

Pressed pellets from cement mixed with powdered sodium chloride were manufactured to be used as standards. Milling of sodium chloride and homogenization of standard materials was performed using an ultrasonic mill (MM 400, RETSCH, Haan, Germany). Titrimetric chloride analysis was performed to determine the chloride concentration of the cement. 3.0 g cement powder was treated in the same way as the concrete samples described above. Color change of the mixture appeared after addition of the same titrant volume as for the blank sample, indicating that the used cement has a chloride concentration of below 0.01 mg g⁻¹. Additionally, a blank pressing was prepared to investigate the cement powder by LA-ICP-MS. The ³⁵Cl signal was not different from the gas blank, i.e., also by LA-ICP-MS, chloride was not detectable in the blank cement.

For preparation of the standards, 2.0 g cement powder was mixed with various amounts of previously milled sodium chloride (p.a., Merck, Darmstadt, Germany). After homogenization, 300 mg of the mixture were pressed using a pneumatic press at 10 bar for 30 s,

Table 1
Typical instrumental parameters used for sample measurement.

Laser ablation		ICP-MS	
Wavelength	213 nm	Plasma power	1550 W
Pulse duration	4 ns	Cool gas flow	14.0 L min ⁻¹
Laser repetition rate	10 Hz	Auxiliary flow	0.8 L min ⁻¹
Laser beam diameter	250 μm	Cones	Ni
Laser energy	1.38 mJ	Scanning mode	Peak hopping
Laser scan speed	40 μm s ⁻¹	Dwell time per isotope	10 ms
Laser beam geometry	Circular	Monitored isotopes	¹³ C, ²⁵ Mg, ²⁷ Al, ²⁹ Si, ³⁵ Cl, ⁴² Ca, ⁴⁹ Ti, ⁵⁷ Fe
He gas flow	0.4 L min ⁻¹	Mass resolution	300 m/Δm
Ar make-up flow	0.8 L min ⁻¹		

yielding round cement pellets with a diameter of 12 mm. This procedure yielded standard pellets containing 0.077, 0.23, 0.49, and 1.01 m% chloride and a blank pellet. The concentrations were chosen to be in the expected concentration range of the concrete samples.

2.5. LA-ICP-MS measurement of standards and samples

Before analysis, loose dust was removed from the sample surface using clean and dry pressurized air. After placing samples and standards in the ablation chamber, it was purged for 20 min with helium before starting the analysis. Time resolved intensity data for the selected isotopes were collected using Qtegra software, provided by the manufacturer of the ICP-MS instrument. For analysis of standards, straight lines 5.0 mm in length were ablated; analysis of the samples was performed by ablating lines 37.0 mm in length. On each core sample, 24 lines with a distance of 3.3 mm between lines were measured; the scan direction was perpendicular to the drilling axis for drilled core samples. After every two samples, one standard was measured, to control possible instrumental drifts. Analysis time for each core sample was approx. 20 min.

For signal evaluation, the transient signal intensity profiles obtained from linescans of the standards were divided into 18 segments with equal length. Data points in each segment were averaged and a blank value for the signal obtained without material ablation was subtracted. This procedure was found necessary to determine representative depth profiles, as chloride concentrations showed to vary significantly on discrete sampling positions in the real samples.

As the ablation behavior between concrete samples and pressed cement standards might differ significantly, an internal standard was employed. This internal standard can compensate changes in material ablation due to variations in laser focus resulting from a rough surface of the concrete samples. Since calcium is a major constituent of cement with rather constant concentrations in different cement types (around 55–65 m% CaO), this element was considered being a suitable internal standard. Minor variations in the Ca-concentration of different concrete types were neglected due to the overall positive effect of the internal standardization on signal stability. Thus, the measured chloride intensities (^{35}Cl) were normalized to the corresponding calcium signal (^{42}Ca) as an internal standard. Subsequently, the values for the 18 segments were averaged to obtain representative mean values for each investigated line.

2.6. Imaging experiments

Investigation of elemental distributions was performed using consecutive linescans over the sample surface. A laser beam diameter of 100 μm at 10 Hz repetition rate with 300 $\mu\text{m s}^{-1}$ scan speed was used. Image construction from the acquired time resolved intensity profiles and further processing of the obtained elemental distribution images was accomplished using ImageLab [11] (v.1.02, Epina GmbH, Pressbaum, Austria). Detailed information about image acquisition and construction can be found elsewhere [12]. Corresponding light microscopic images were obtained using a Leica DM2500M microscope (Leica Microsystems, Wetzlar, Germany) in reflective-light mode.

3. Results

3.1. Sample analysis using titration

3.1.1. Analysis of cement-sodium chloride mixtures used as standards for LA-ICP-MS analysis

For verification of the chloride concentrations in the standards, all cement-sodium chloride mixtures were analyzed using titration. Approximately 500 mg of each standard were exactly weighed and used for the analysis. The chloride determination was performed in four replicates for all standards. Between 5.0 and 20 mL of ammonium

thiocyanate solution were required until the endpoint of the titration was reached. The analysis yielded chloride contents with relative standard deviations of below 5%. Considering a single standard deviation, none of the actual results differed from the desired concentrations.

3.1.2. Chloride content in the in-house prepared concrete samples

In contrast to the standards (pure cement), cured concrete samples do not only consist of cement, but also of aggregates. In case of the in-house prepared concrete samples, the chloride content, as well as the amount of aggregates in the concrete was exactly known. The used cement did not contain detectable amounts of chloride. Thus, the chloride content in the resulting cement could be adjusted by a given NaCl concentration in the water used for preparation of the concrete. Based on this knowledge, a wet-chemical analysis of these samples was performed and the results were compared with the actual values. Yielded chloride concentrations were 0.49 ± 0.03 m% (granite as aggregate), 0.737 ± 0.02 m% (limestone as aggregate), and 1.03 ± 0.03 m% (river gravel as aggregate). Except from the granite sample, the chloride contents differed significantly from the value of 0.50 m% chloride in the cement fraction of the prepared concretes. To explain these deviations, all aggregate types were analyzed for their chloride content using titration. For granite, no significant acid-soluble chloride content ($<0.01 \text{ mg g}^{-1}$) could be found. Chloride concentrations for limestone were 0.867 ± 0.08 m% and for river gravel 1.37 ± 0.05 m%. When considering the known aggregate amount of 60%, chloride contents in the cement phase of 0.542 ± 0.05 m% (limestone) and 0.521 ± 0.03 m% (river gravel) can be calculated. Taking slight changes in aggregate-cement ratio into consideration, these values correspond well with the nominal chloride concentration of 0.50 m%.

3.2. LA-ICP-MS measurements

3.2.1. Calibrations for signal quantification

For calibration of the signal intensities, pressed pellets from the cement-sodium chloride mixtures were used. The standards containing 0.077 m% chloride were not used for the calibration but considered as a sample for validation of the calibration function. Thus, the cement pellets containing 0.23, 0.49, and 1.01 m% chloride, as well as a blank sample were used to determine a calibration function for the LA-ICP-MS procedure. Intensity values for ^{35}Cl between 3500 cps (blank) and 180,000 cps (highest standard) were obtained. After signal normalization using ^{42}Ca as an internal standard, a linear regression model was calculated from the known chloride concentrations in the pressed pellets. The calibration yielded a correlation coefficient of 0.997. The limit of detection (LOD) and limit of quantification (LOQ) were determined by adding three times (LOD) and nine times (LOQ) the standard deviation of the blank to the signal of the blank. An LOD of 0.008 m% and an LOQ of 0.021 m% chloride were obtained.

The standard with 0.077% Cl was considered as a sample with unknown chloride content for validation of the calibration function. Quantification resulted in a chloride content of 0.072 ± 0.006 m% ($\alpha = 0.95$, $n = 4$). The found chloride content does not differ significantly from the actual concentration; thus, the validity of the quantification procedure was demonstrated.

3.2.2. Elemental distribution in the concrete samples

For differentiation between aggregates and cement phase by elemental patterns, the samples needed to be investigated in closer detail. Especially differences between the compositions of the aggregates were a point of interest. Criteria for the differentiation between aggregates and cement phase were defined for automated distinction of cement and aggregates using the time-resolved ICP-MS data. To enable reliable conclusions, elemental imaging of multiple sample areas on all three in-house prepared concrete types was performed. Investigation of the elemental distributions on the concrete surface revealed deeper information about the components of the concrete, especially the

composition of the aggregates. All of the five shown elements could be detected in every part of the three samples. However, their intensities varied significantly based on the composition of the sample area of interest.

For granite (Fig. 1), silicon and aluminum can be identified as major components of the aggregates. This fact correlates well with the chemical composition of granite. Carbon and calcium are only detected at background level on areas with aggregates. The chloride signal in the cement phase is around 40,000 cps (approx. 0.5 m% Cl) and the distribution is very homogeneous. In contrast, in the aggregate phase only chloride signals around 10,000 cps can be detected, indicating the presence of chloride in a lower concentration in this aggregate type.

When limestone is used as aggregate (Fig. 2), calcium and carbon are the main elements detected in the aggregate phase. Calcium can also be detected in cement, however with significantly lower intensities (approx. three times lower) than in the aggregates. Silicon and aluminum are solely detected in the cement phase, indicating the absence of siliceous aggregates. The chloride distribution in the cement phase is very homogeneous, with average signals of 40,000 cps (approx. 0.5 m% Cl). However, chloride can also be detected in the aggregates with intensities up to 40,000 cps (approx. 0.9 m% Cl according to the determination by titration). Discrepancies in concentration and signal intensity comparing cement phase and aggregates can be explained by varying ablation behavior, material transport, and analyte ionization. This phenomenon is commonly referred to as matrix effect, leading to the fact that cement powder used for chloride quantification in the cement phase is not a suitable calibration standard for chloride in the aggregates.

In the case of river gravel being used as aggregate (Fig. 3), two types of aggregates can be found: On the one hand carbonates with high signals of carbon and calcium, and on the other hand siliceous minerals

with high silicon and aluminum signals. Carbon and calcium cannot be detected in the siliceous aggregates. Chloride is distributed evenly in the cement phase with average signals of around 40,000 cps (approx. 0.5 m% Cl). However, as in the case of limestone, it can also be detected above background level in most aggregates. Signal intensities for ^{35}Cl up to 50,000 cps have been found, indicating high abundance of chloride in those aggregates. As for the limestone aggregate type, also in the case of river gravel, the absolute signal intensities depend on the ablated matrix material. Therefore, chloride concentrations found in the aggregates by titration do not correlate with the detected signal intensities when compared to the calibration function using cement powder.

Notable concentrations of chloride were found in all aggregate types. Thus, the results from the elemental distribution analysis underline the need for a selective quantification method of chloride in the cement phase.

3.2.3. Selective quantification of chloride in the cement phase

Based on the findings from the elemental distribution analysis, it is possible to use LA-ICP-MS for the differentiation between cement and aggregates. For the three investigated concrete/aggregate types, a distinction criterion using the signal intensities of aluminum and calcium was found suitable. However, for other aggregate types it might be necessary to adjust the criterion accordingly. Areas with either low aluminum or calcium signal (or both) would be denoted as aggregates. The complete range of data points acquired during 1 day of analysis was taken into consideration for definition of the criterion. The median value of all data points acquired for ^{27}Al and ^{42}Ca was calculated. These values were multiplied by empirically selected factors to define the threshold intensities. Factors of 0.5 (^{27}Al) and 0.3 (^{42}Ca) were found to be suitable. For selective quantification of chloride in the cement phase, every data point was checked for their ^{27}Al and ^{42}Ca intensity. If either of the

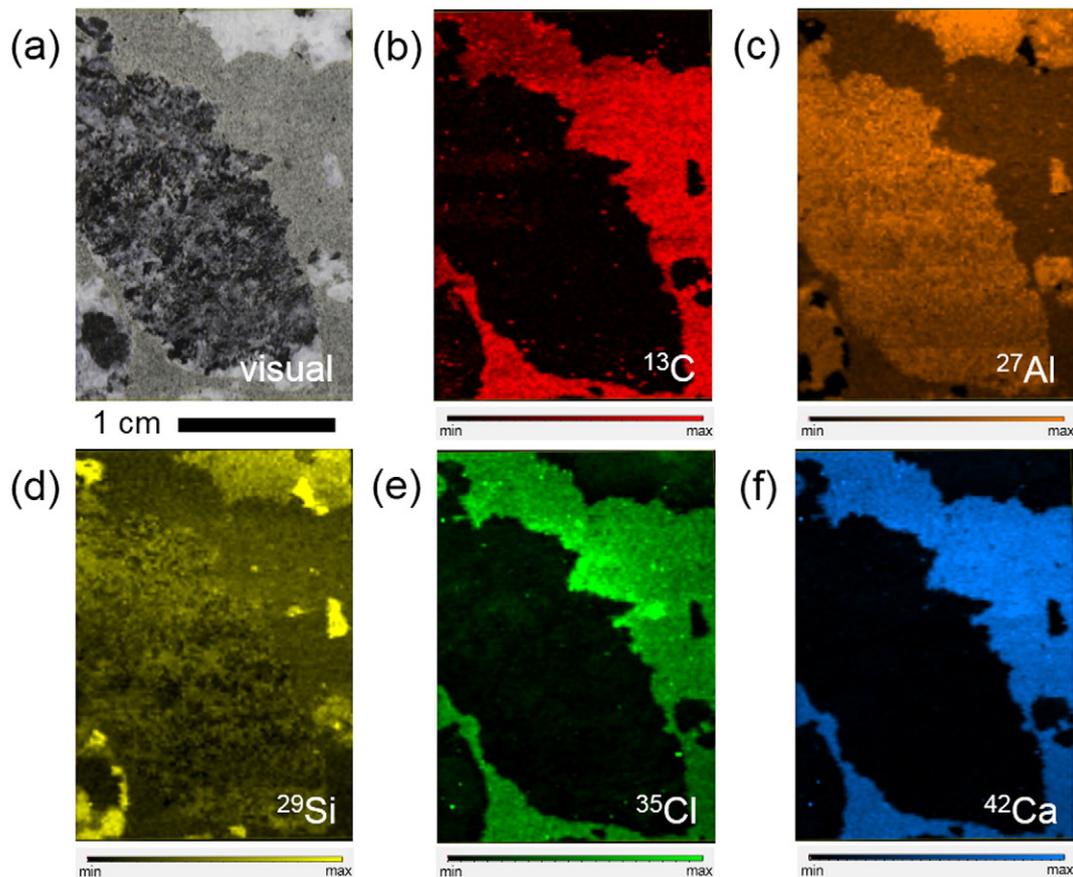


Fig. 1. Elemental distributions on an in-house prepared concrete sample using granite as aggregates measured using LA-ICP-MS, visual image (a), as well as the elemental distributions of ^{13}C (b), ^{27}Al (c), ^{29}Si (d), ^{35}Cl (e), and ^{42}Ca (f).

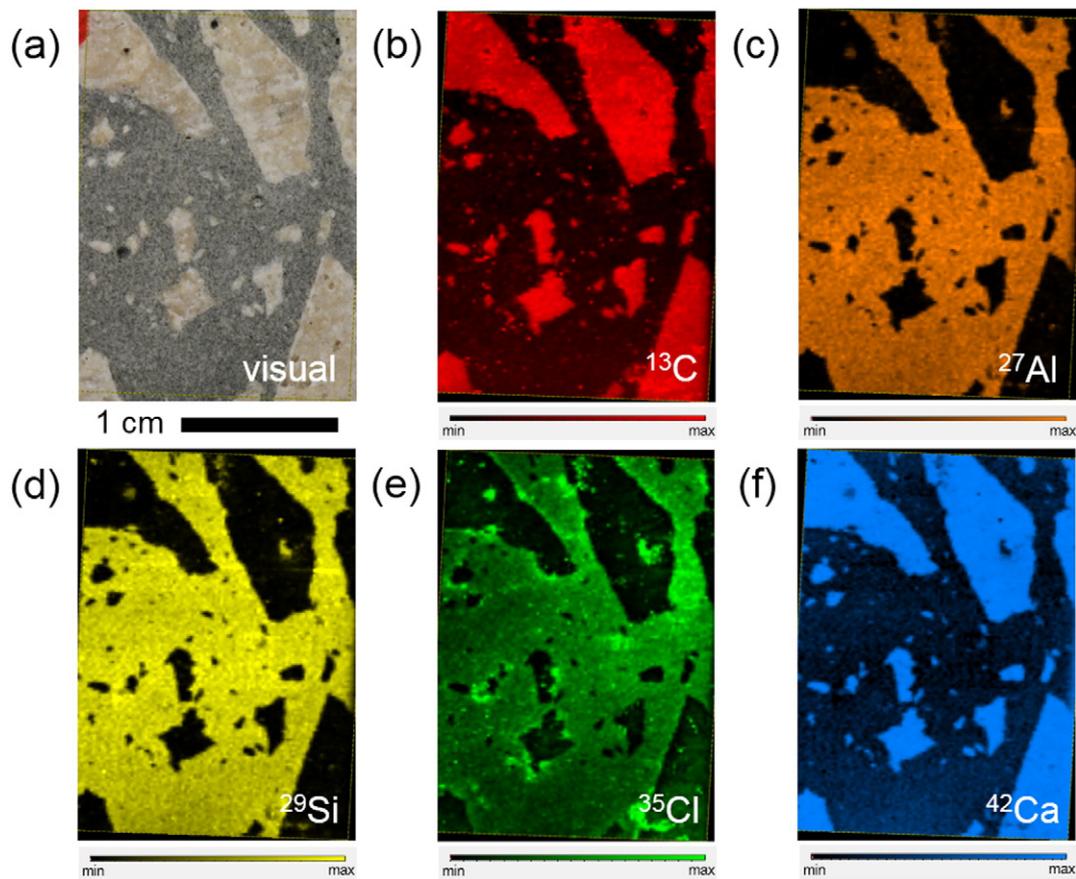


Fig. 2. Elemental distributions on an in-house prepared concrete sample using limestone as aggregates measured using LA-ICP-MS, visual image (a), as well as the elemental distributions of ^{13}C (b), ^{27}Al (c), ^{29}Si (d), ^{35}Cl (e), and ^{42}Ca (f).

intensities was below the threshold, this data point would not be taken into consideration for the chloride quantification. In Fig. 4, an elemental distribution image of the river gravel sample after application of the threshold is shown. Compared with the visual image, a good distinction between aggregates (and pores) and the cement phase is provided.

For analysis of the in-house prepared concrete, 10 parallel lines with a distance of 5 mm were measured. An average was calculated, as chloride was expected to be homogeneous in those samples. ^{35}Cl signals were between 40,000 and 50,000 cps for all samples, resulting in chloride concentrations of around 0.5 m% in the cement phase. Those values are in good agreement with the expected chloride concentrations in the concretes. For the drilled core samples, depth profiles with 3.3 mm depth resolution were obtained, resulting in 24 data points per drilled core sample. ^{35}Cl signal intensities ranged between 4000 cps and 300,000 cps. Chloride concentrations between 2.0 and 0.03 m% were calculated.

4. Discussion

4.1. Comparison of the results from titration and LA-ICP-MS measurement

Titrimetric analysis yielded varying results for three concrete types despite the fact that the same cement with a chloride content of 0.5 m% was used for all mixtures. As indicated by the elemental mapping experiments, some aggregates contain considerable amounts of chloride. Based on the results, the titration does not seem feasible for the exact determination of chloride in the cement phase. The found carbonate minerals will readily dissolve during acidic treatment of the sample as a sample preparation step for the titrimetric chloride determination. As shown in the elemental images, most of the carbonate aggregates also exhibit chloride signal significantly higher than the

background signal. These findings underline the weakness of the titrimetric analysis: Aggregates may be soluble under acidic conditions, and they may also contain significant amounts of chloride, thus, contributing to the determined chloride concentration in the cement. Additionally, the determination of the aggregate content in unknown concrete mixtures may be problematic and wrong estimations might provoke further errors.

However, the influence of acid-soluble aggregates on the determined chloride content strongly depends on the analyzed concrete type: While LA-ICP-MS analysis and titration yielded consistent results in the case of granite (acid insoluble) as aggregate material, the values differed significantly for the aggregate type river gravel and limestone. A comparison of the determined chloride concentrations is given in Fig. 5. As expected, LA-ICP-MS analysis of all three cement types yielded consistent results of around 0.5 m% chloride in the cement phase (for all concretes the same cement was used), the results of the Volhard titration method varied significantly from each other.

The results of the two analysis methods only match for the granite sample. As indicated by the elemental mapping experiment, this aggregate type does not contain acid-soluble constituents. The aggregates form a solid residue in the mixture and are not dissolved by the nitric acid used during sample pretreatment for titration. Thus, only the total chloride content in the cement phase is determined. As a comparison, the other two aggregate types contain acid-soluble minerals (e.g., limestone), which itself contain chloride. Thus, the effective chloride content determined by the Volhard titration overestimates the chloride content in the cement. LA-ICP-MS measurement deliver correct results as the above described distinction criterion can be used to selectively quantify chloride in the cement phase. This will lead to correct results, disregarding the chloride concentration in the aggregates and if they are acid-soluble or not.

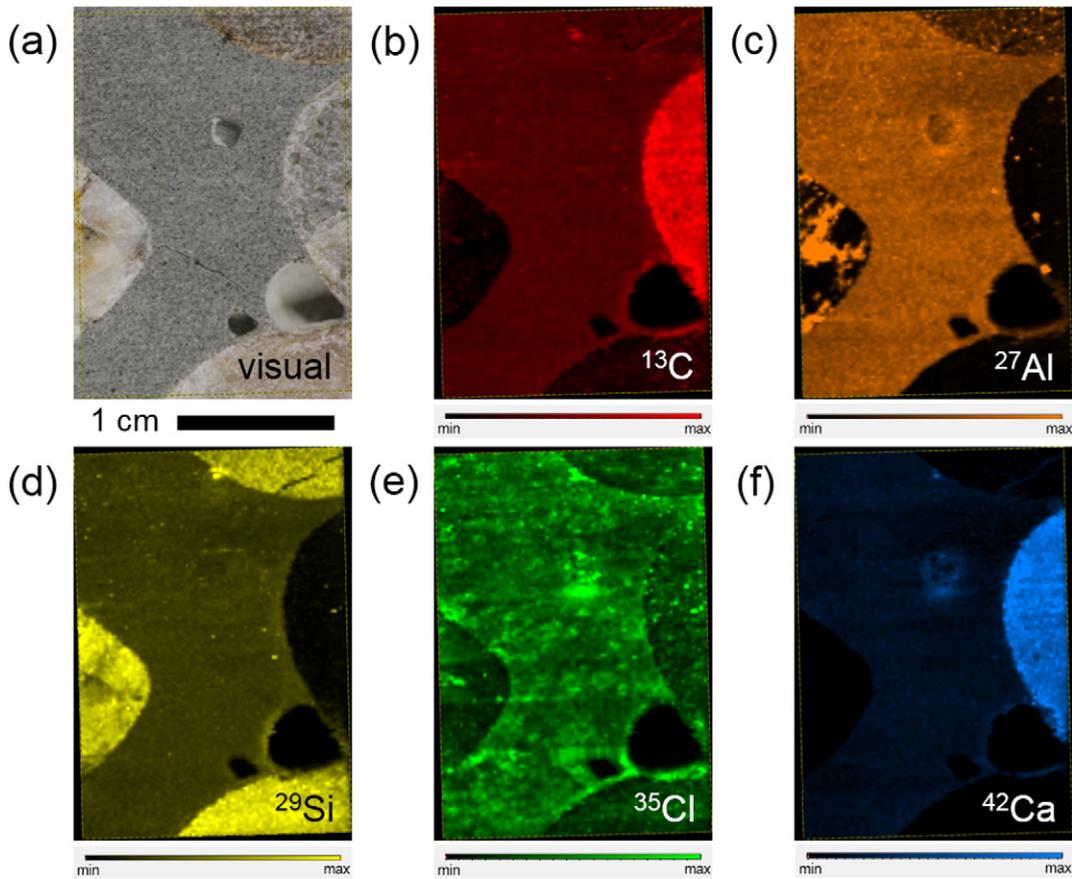


Fig. 3. Elemental distributions on an in-house prepared concrete sample using river gravel as aggregates measured using LA-ICP-MS, visual image (a), as well as the elemental distributions of ^{13}C (b), ^{27}Al (c), ^{29}Si (d), ^{35}Cl (e), and ^{42}Ca (f).

4.2. Comparison of Cl diffusion profiles

Within this study depth profiles were measured from samples collected at different heights. Averages from six samples taken at the same height above the roadway were calculated; one data point was acquired every 3.3 mm. The profiles for all four sample heights are presented in Fig. 6.

The overall maximum chloride concentration is 1.11 ± 0.07 m%, for the samples taken 0.8 m above the roadway. Generally, the maximum chloride concentrations decrease with increasing height of sampling.

The maxima of the chloride depth profiles for every height consistently occur at a depth of 15–20 mm, not in the outermost region of the drilled core sample. Significant differences between heights can be observed, considering the standard deviation of six replicate sample measurements.

The influence of de-icing salts used in winter is evident by the very high chloride concentrations found in samples taken at lower heights. Chloride-rich water from the roadway splashes onto the concrete structure and penetrates the material by diffusion. The amount of spray water in contact with the concrete surface is greater at lower

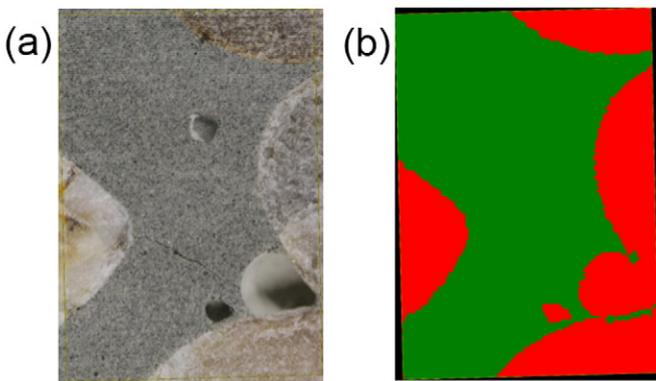


Fig. 4. Application of the distinction criterion between cement phase and aggregates: Concrete with river gravel; microscopic image (a) and distribution image after application of the threshold (b); areas detected as aggregates are marked red, concrete is marked in green.

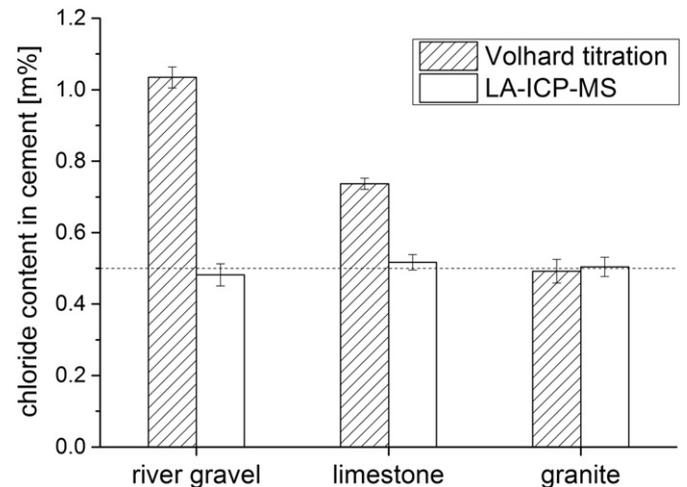


Fig. 5. Comparison between the determination of chloride content by Volhard titration and LA-ICP-MS.

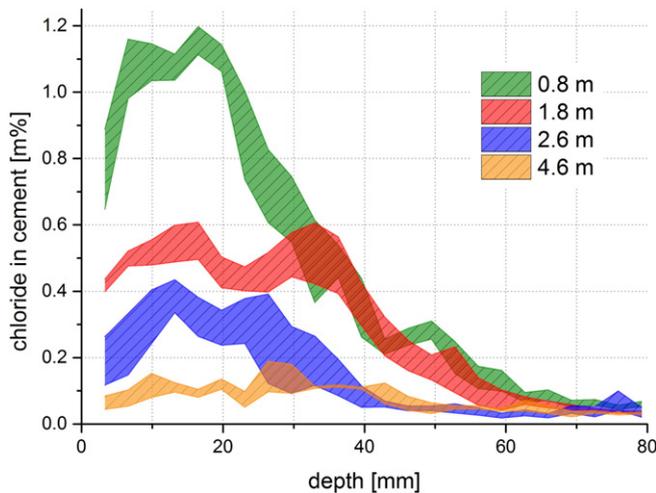


Fig. 6. Depth profiles of drilled core samples taken at four different heights above the roadway (0.8, 1.8, 2.6, and 4.6 m) determined by LA-ICP-MS. The marked areas are displayed with regard to the standard deviation of the average values of six independent samples from the same height.

heights, due to the closer proximity to the roadway, where the chloride-rich water originates from. The samples investigated in this study were removed from the structure in the mid of November 2012. The last freezing day before sampling – and thus, probably the last use of de-icing salts – has been in early March 2012, eight months earlier. It can be speculated that chloride from the outermost layers of the structure has been washed away by rain and splash water from the roadway (with negligible amounts of chloride) during the months where no de-icing salts have been used. This might explain the depth profiles with their maximum chloride content in deeper layers of the material. Consequently, the chloride content (especially in the outer concrete layers) and the found depth profiles might also be dependent on the season and on the amount of de-icing salts used during the last winter periods.

5. Conclusion

In the presented study, a fast and reliable analysis strategy for determination of the chloride content in concrete structures could be developed. It was demonstrated that mineralization and subsequent titration of the concrete samples can lead to systematic errors. The systematic error results from acid-soluble chloride containing aggregates, other deviations may originate from an unknown aggregate content in the samples. While titrimetric analysis yielded inconsistent results for the chloride concentrations of three in-house prepared concrete

samples, LA-ICP-MS analysis resulted in a good match with the expected chloride content.

The proposed LA-ICP-MS approach helps to increase the reliability of the obtained results by selectively addressing three major problems:

- Selective determination of chloride in the cement phase; no wrong results due to dissolving aggregates that contain chloride; no errors due to incorrect determination of the cement-concrete ratio;
- High depth resolution of the chloride profiles that allows an exact assessment at the reinforcement depth and to use data for forecast models;
- The detection of localized maximum chloride concentrations which are inaccessible to the titrimetric method is possible.

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