



# Sulfur determination in concrete samples using laser-induced breakdown spectroscopy and limestone standards

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## ABSTRACT

A LIBS equipment operating at 532 nm was optimized and used for sulfur determination in concrete samples. The influence of He atmosphere in a gas-tight chamber (1000–200 mbar) on S I 921.29 nm line sensitivity, signal-to-background and signal-to-noise ratio was studied at gate delays 100–2000 ns. Wide range of gate delays from 500 to about 1000 ns and pressures from several hundreds of mbar to the atmospheric pressure can be used for the desired detection of sulfur. The LIBS quantification was done using a simple calibration method. A synthetic limestone enriched by defined amounts of sodium sulfate was newly employed for direct quantification of S in concrete. This powder material was pressed into pellets and ablated with the LIBS system. The average content of sulfur as SO<sub>3</sub> in the samples was 0.41–0.70 wt% by LIBS and 0.43–0.61 wt% by a reference standard procedure employing gravimetry and Inductively Coupled Plasma Triple Quad Mass Spectrometry (ICP-QQMS). The uncertainty of the yielded LIBS results covers also the dispersion of the points in the calibration line and ranges from 16 to 28% at the probability level of 95%. The uncertainty of the ICP-QQMS results was almost 10%. No correction on different signal response on the limestone and on the concrete was necessary.

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## 1. Introduction

Concrete is a widely used composite building material. Basically it is a mixture of cement as an adhesive powder component and stone aggregates as a filling component with water. Analysis of concrete and other building materials is an extremely important issue. One of the important analytes is sulfur. Sulfur compounds form a natural component in building materials such as gypsum or concrete panels. However, the ingress of sulfates or sulfuric acid constitutes a major risk of chemical aggression for concrete. There is a need for a fast method, which can be used on-site and is able to investigate a wide range of different measuring points, so that damages can be characterized on a large scale [1]. A suitable method for sulfur determination in solids is Laser-Induced

Breakdown Spectroscopy (LIBS) [1,2]. In the last two decades LIBS has been established as a common technique used for determination of non-metal compounds in concrete. Main advantage of this technique is direct determination of elements (including non-metals) from solid sample. Relatively high limits of detection (LOD) of non-metals makes this method restrictive for many samples. However, sulfur and chlorine [3–6] in concrete can be successfully determined with LIBS. Distribution of chlorine in concrete cores and an overall spatially resolved analysis is also feasible using LIBS [7–9]. The structure of the concrete must be taken into account because the sulfur natural content is close to zero in aggregates (such as mainly SiO<sub>2</sub> [1]) while in the cement mortar it is typically about 10<sup>-1</sup> wt% [8]. More specifically, chlorine LOD 1500 mg kg<sup>-1</sup> [7] can be improved using a double pulse LIBS system [3,4] with LOD down to 50 mg kg<sup>-1</sup>. With a double pulse LIBS, even the use of the weak S II 545.38 nm line was reported by Gondal et al. [6] and the LOD was 38 mg kg<sup>-1</sup>. Unfortunately this line was not visible in other studies on sulfur determination in concrete [3]. For both sulfur

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and chlorine on near IR lines Labutin et al. [3] reported LOD about  $10^3 \text{ mg kg}^{-1}$  for a mobile LIBS system. Thus chlorine local corrosion can be efficiently monitored using a LIBS system.

The choice of available lines for these non-metals is quite limited because strong lines fall into the VUV range [10] and their radiation is strongly absorbed by the ambient air and optical components. The relatively less intensive spectral lines present in the NIR range are often out of the sensitivity range of used detectors [11]. If the LIBS system is not able to directly detect a sulfur line advanced chemometric tools as Partial Least Squares regression can be helpful. The multivariate data analysis algorithms reveal latent variables (dependence of detected spectra on the content of S). In turn, those algorithms can provide quantitative analysis, in this case, of building materials without direct detection of any sulfur line [12].

Another method for determination of both metals and some non-metals is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). There are, however, some limitations like influence of spectral interferences caused by polyatomic species and non-spectral interferences [13–15]. For example phosphorus and sulfur are difficult elements to determine at low levels by quadrupole based ICP-MS due to their high ionization potentials and intense polyatomic interferences:  $^{31}\text{P}^+$ ,  $^{32}\text{S}^+$  and  $^{34}\text{S}^+$  suffer spectral overlaps from  $^{15}\text{N}^{16}\text{O}^+$ ,  $^{14}\text{N}^{17}\text{O}^+$ ,  $^{14}\text{N}^{16}\text{O}^{1}\text{H}^+$ ,  $^{12}\text{C}^{18}\text{O}^{1}\text{H}^+$ ,  $^{13}\text{C}^{16}\text{O}^+$ ,  $^{14}\text{N}^{18}\text{O}^+$ ,  $^{16}\text{O}_2^+$ ,  $^{15}\text{N}^{16}\text{O}^{1}\text{H}^+$ ,  $^{14}\text{N}^{16}\text{O}^{1}\text{H}_2^+$ ,  $^{33}\text{S}^{1}\text{H}^+$ ,  $^{32}\text{S}^{1}\text{H}_2^+$ ,  $^{16}\text{O}^{18}\text{O}^+$ ,  $^{16}\text{O}^{17}\text{O}^{1}\text{H}^+$ ,  $^{16}\text{O}^{16}\text{O}^{1}\text{H}_2^+$ ,  $^{15}\text{N}^{18}\text{O}^{1}\text{H}^+$  and  $^{16}\text{O}^{18}\text{O}^+$ , respectively [16,17]. Polyatomic interferences limiting the detection power of ICP-MS for these elements can be effectively removed with a type of instrument based on the concept of tandem mass spectrometry. Therefore, a triple quadrupole (QQQ) ICP-MS has been used for the effective reduction of the most interferences. For the first time Fernandez et al. used QQQMS (with oxygen as reaction gas) for the determination of sulfur and phosphorus present in the proteins as a new concept of polyatomic interference removal in ICP-MS [17]. The method is typically used in molecular MS but with a new focus: the reaction cell is not employed to breakdown organic molecules but to form new molecules by ion–molecule reaction. This system offers consistent reaction conditions in the collision/reaction cell, even with changing sample composition. In reaction mode oxygen can react with the analyte ion or the on-mass interfering ion to eliminate or avoid the respective interference. The second quadrupole can be tuned independently of the first one. The mass of the product ions generated by the reaction with the cell gas or the mass of analyte ions without interferences is detected [14]. This method provides achievement of the low detection limits in the  $\text{ng l}^{-1}$  range limited by blanks, and the removal of all possible spectral interferences.

Sulfur and phosphorus are contained both in the environment and in biological materials and, therefore, the determination of sulfur and phosphorus is needed in many fields such as peptide/protein analysis, pharmaceutical research, industrial analysis and environment analysis. Commonly used instrumentation for the determination based on ICP-MS resolving spectral interferences include except classical quadrupole ICP-MS instruments with reaction cells [18] also high resolution ICP-MS instruments, sector field instruments [19,20], triple quadrupole ICP-MS, hyphenated techniques [21–23], [10,11] and laser ablation (LA)-ICP-MS [24]. Using such systems, absolute detection limits achieved are in the low pmol and medium-high fmol range [16]. ICP-QQQMS method seems to be good choice with a big potential of applications with good limits of detection. Thanks to good interference removing the method is suitable for determination of sulfur and chlorine in a wide variety of samples including concrete.

An ICP-QQQMS instrumentation was used for comparative analysis of several concrete samples. These concrete samples were subjected to LIBS determination of sulfur. In contrast to the previous LIBS studies dealing with the concrete standards here we demonstrate a simplified method of bulk (a couple of square cm) sulfur determination in concrete samples using synthetic limestone with defined additions of sodium sulfate as a calibration standard. This is a substantial simplification

against the aforementioned quantitative studies of concrete composition with LIBS using laboratory-made concrete containing defined additions of elements of interest.

## 2. Experimental part

### 2.1. LIBS instrumentation

The measurements were performed using the LIBS Sci-Trace instrument (AtomTrace, Czech Republic). The sample was placed in the LIBS Interaction Chamber (AtomTrace, Czech Republic) where the 3-axis motorized stage enables the sample manipulation with sub- $2 \mu\text{m}$  lateral resolution. Laser pulse created using CFR 400 laser (532 nm, 10 ns pulse duration, 7 mm beam diameter; Quantel, France) was guided into the Interaction Chamber by the series of dielectric laser line mirrors (dielectric; ThorLabs, USA) and focused on the sample by a doublet lens (focal length 30 mm). The position of the focusing optics was moved by motorized translation in respect to sample surface. This enabled changes in laser spot diameter. LIP radiation was collected by the refractive collimator built by a combination of UVFS and  $\text{CaF}_2$  lenses (focal length 44.5 mm) and transmitted to the echelle spectrometer EMU-65 (Catalina Scientific, USA) via optical cable (400  $\mu\text{m}$  core diameter; ThorLabs, USA). Dispersed radiation was captured by the EMCCD camera Falcon Blue (Raptor Photonics, Ireland). The gate delay was controlled using a pulse generator AC-DDG4 (AtomTrace, Czech Republic) and custom developed control electronics (AtomTrace, Czech Republic).

#### 2.1.1. LIBS experimental conditions for the samples and calibration

Intensities of the Si 921.28 nm line were used, helium atmosphere in the chamber at 600 mbar, laser pulse energy 100 mJ, 5 pulses per spot, accumulation of 20 spectra, 5 values of intensity (each value from accumulation of 20 spectra) for each calibration point and each sample were used, crater diameters on pellets were about 0.23 mm.

#### 2.1.2. Concrete samples and pelletized standards preparation for LIBS measurement

Concrete samples were building material and were drilled cores (cylinders) 10 cm in diameter and about 30 cm length. All the concrete samples were cut with a diamond saw to obtain blocks of about  $5 \times 4 \times 2 \text{ cm}$ . These blocks from the appr. middle of the drilled core were taken for LIBS analysis. No more sample treatment (as surface polishing) was applied. Synthetic limestone powder (NCS DC 73344, China) enriched by defined amounts of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  was pressed to 12 mm pellets (17 MPa, 90 s, press: Mobiko, Hranice, CZ). This formed 4-points calibration set. Samples with calibration pellets were fixed onto the table in the interaction chamber.

### 2.2. ICP-QQQMS instrumentation

The measurements were performed using the inductively coupled plasma triple quadrupole mass spectrometer (Agilent 8800; Agilent USA) with two quadrupoles Q1, Q2, and an octopole reaction cell (ORC) working in the mass shift mode. First quadrupole transmits the analyte  $m/z$  with all interferences at the same  $m/z$ . The reaction gas (oxygen) collides with the analyte ions and the interfering ions. The second quadrupole transmits only the  $m/z$  of the new created molecular ion of the analyte and the reaction gas, here  $^{32}\text{S}^{16}\text{O}^+$ .

#### 2.2.1. Settings of the used ICP-QQQMS

The forwarded RF power was 1550 W, carrier gas flow rate  $1.07 \text{ l min}^{-1}$ , integration time per isotope was 0.1 s and cell gas (oxygen) flow rate  $0.177 \text{ l min}^{-1}$ .

#### 2.2.2. Samples preparation for gravimetric and ICP-QQQMS measurement

The whole individual cylindrical concrete sample (except a couple of cut pieces used for LIBS – described above) was crushed by crusher and

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