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High repetition rate laser-induced breakdown spectroscopy using acousto-optically gated detection

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This contribution introduces a new type of setup for fast sample analysis using laser-induced breakdown spectroscopy (LIBS). The novel design combines a high repetition rate laser (up to 50 kHz) as excitation source and an acousto-optical modulator (AOM) as a fast switch for temporally gating the detection of the emitted light. The plasma radiation is led through the active medium of the AOM where it is diffracted on the transient ultrasonic Bragg grid. The diffracted radiation is detected by a compact Czerny-Turner spectrometer equipped with a CCD line detector. Utilizing the new combination of high repetition rate lasers and AOM gated detection, rapid measurements with total integration times of only 10 ms resulted in a limit of detection (LOD) of 0.13 wt.% for magnesium in aluminum alloys. This short integration time corresponds to 100 analyses/s. Temporal gating of LIP radiation results in improved LODs and consecutively higher sensitivity of the LIBS setups. Therefore, an AOM could be beneficially utilized to temporally detect plasmas induced by high repetition rate lasers. The AOM in combination with miniaturized Czerny-Turner spectrometers equipped with CCD line detectors and small footprint diode pumped solid state lasers results in temporarily gateable compact LIBS setups. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4890337]

I. INTRODUCTION

In recent years laser-induced breakdown spectroscopy (LIBS) has become an increasingly popular analytical method. Its major advantages are its multi-element capacity, experimental simplicity, and the lack of sample preparation.1–4 Briefly, a strong non-resonant laser pulse is used to ablate, atomize, excite, and ionize a small amount of the sample, thus forming transient microplasmas. While relaxing, the matter inside the formed plasma plume emits light. In the first few hundred nanoseconds the plasma is typically very hot; its radiation mainly stems from electron-ion recombination and bremsstrahlung. The radiation is spectrally broad and contains no information on the elemental composition of the plasma. After this period, atoms and ions of the analyte undergo relaxation between well-defined energy states and emit light with characteristic wavelengths. These optical emission spectra are often very dense, since they contain spectrochemical information from all elements present in the ablated matter. To obtain maximum information, the emitted light should, therefore, be (a) temporally gated to discriminate against the early broadband emission and (b) detected with a sufficiently high spectral resolution to resolve contributions from all individual species involved.

LIBS has been successfully applied for quantitative analysis of trace elements in solids,5,6 liquids,7–9 and gases;10,11 Numerical experimental setups have been introduced with different laser sources and spectrometer types.12 Because no sample preparation is needed, LIBS is perfectly suited for sorting and mapping applications.13 Since the recorded plasmas have lifetimes of only several μs, subsequent spectra can be recorded within a short time interval; this makes LIBS also a perfect candidate for mapping 2D surfaces. Typical plasma lifetimes are ~10 μs so the duty cycle loosely dictates a ~100 kHz upper limit for the repetition rate of subsequent measurements. When a purged sample chamber is used, this upper limit is in the order of the minimal required interval for a gas exchange in the plasma region.

The most commonly used excitation sources in LIBS are Nd:YAG lasers operating at different harmonics. Both combine high pulse energies with repetition rates of typically around 10 Hz. These lasers, however, have extremely low duty cycles, of the order of 10−7 taking into account their short pulse durations of ~10 ns. To increase the duty cycle and, correspondingly, the probing efficiency per given time, low power/high repetition rate lasers can alternatively be used. Several such systems have recently been introduced, e.g., diode pumped Nd:YVO4 microchip lasers and fiber lasers. These lasers counterbalance the significantly lower pulse energies by their higher repetition rates of typically several (up to hundreds) kHz. At comparable temporal pulse widths this corresponds to duty cycles of 10−5 to 10−3, i.e., ~2–4 orders of magnitude higher than that of the conventional lasers. Depending on the chosen detector, the increase in observable number of plasmas per unit time can result in better counting statistics or shorter duration of individual experiments.

The dispersive systems used in LIBS are usually monochromators or spectrometers; the latter are preferred because of their multielemental capability. Typically three
complementary types of spectrometers are used: (a) Paschen-
Runge spectrometers with individual photomultiplier tubes
for each detected spectral line, (b) small portable Czerny-
Turner spectrometers with linear charged coupled device
(CCD) detectors, and (c) high resolution echelle spectrom-
eters with 2D CCD or intensified CCD, i.e., ICCD detec-
tors. Among these types, Paschen-Runge spectrometers have
some intrinsic benefits.\textsuperscript{1} They can be built very robust with
very broad spectral range. The use of individual detectors
per line of interest allows for an adjustment of the sensitiv-
ity of individual photomultiplier tubes (PMTs) depending on
the spectral lines, with the possibility to use the cathodes with
optimized sensitivity in the UV and near-infrared (NIR) re-
regions. Different delay and integration times can be adjusted
for individual PMTs which brings a vast variability into the
spectroscopic measurement. Typically, Paschen-Runge spec-
trometers cover a wide spectral range, however, only a set of
selected wavelengths can be detected if PMTs are used. An-
other disadvantage that Paschen-Runge and echelle spectrom-
eters have in common is a lower light transmittance compared to
a Czerny-Turner setup.

Recently, Gravel et al.\textsuperscript{14} directly compared an echelle
spectrometer and a Czerny-Turner spectrometer, with respect to
the limits of detection (LODs) for trace elements in alu-
minum and copper alloys. They found that compact spectrom-
eters are especially favorable in combination with high repe-
tition rate lasers. The Czerny-Turner spectrometers are more
compact and affordable; they usually have a fiber-coupled
input slit and a CCD line detector that only needs several
milliseconds for readout. Their spectral resolution is rela-
tively low (typically about 5000) but suffices for most LIBS
applications.\textsuperscript{15,16} However, the detector cannot be temporally
gated to circumvent accumulation of the white light from
early stages of the plasma evolution.

Operation of echelle spectrometers with two-dimensional
ICCDs or CCDs on the other hand is relatively slow (the read-
out takes a fraction of a second) but have spectral resolu-
tions of up to 100 000. Using a CCD with a mechanical chap-
per or gated ICCD allows for temporal discrimination of the
plasma radiation. In ICCDs the gating is realized by applying
a rectangular high voltage (HV) pulse to the intensifying mi-
rochannel plate (MCP). Apart from the high cost and large
size of these systems, the repetitive gating is usually limited to
a few kHz. This is due to the inertia of HV switches whose
speed is limited by high capacitance of the MCP. Another
drawback of pixel-structured detectors is their susceptibility
to blurring the detected images by intensity spilling between
neighboring pixels.\textsuperscript{17} The accompanying loss in spectral res-
olution is in strong contrast to the original resolution of the
systems.

Apart of the better duty cycle, the high repetition LIBS
technique benefits from good spatial profiles of microchip
lasers as well as from their very low pulse-to-pulse fluctu-
tations in terms of laser power. The lower pulse en-
ergy of the microchip lasers has to be well focused to
reach the breakdown threshold of sampled materials and
produce radiant micro-plasmas. Due to the lower pulse
energy microchip laser-induced plasmas have shorter life
times and significantly lower background compared to laser-
induced plasmas produced by commonly used high-energy
lasers.\textsuperscript{18}

Freedman et al.\textsuperscript{19} highlighted the benefits of the use of a
microchip laser and a non-gated, CCD array detector in LIBS
measurements of aluminum alloys. Nonetheless, the obtained
limits of detection (LOD) are roughly two orders of magni-
tude higher compared to temporally gated detection. Cristo-
foretti et al.\textsuperscript{20} measured aluminum alloy standards with vari-
ous trace elements employing a high repetition rate microchip
laser and two detection systems: an Echelle spectrometer cou-
pled to an ICCD and a Czerny-Turner spectrometer coupled
to a CCD. Both systems yielded LODs in the ppm range with
slightly better LODs for the Czerny-Turner-CCD sys-
tem. Lopez-Moreno et al.\textsuperscript{15} used microchip LIBS for analysis
of low-alloy steel standards and detected various trace ele-
ments in the ppm level. Hoehse et al.\textsuperscript{21} directly compared
the analytical performance of a low repetition rate but high energy
Nd:YAG and a high repetition rate but low energy microchip
lasers using an Echelle-CCD detection. With both systems
comparsable LODs at the low ppm level could be achieved for
Cu, Cr, and Ni in iron samples with a slightly better perfor-
mance of the microchip laser spectrometer.

For field applications where LIBS systems with a min-
imal footprint are desired, a particularly beneficial combina-
tion consists of a small diode pumped solid state (DPSS) laser
operating at a high repetition rate and a portable spectrometer
with a non-intensified CCD detector. Previously, such setups
have been utilized by several groups\textsuperscript{18–20} to quantify trace ele-
ments in aluminum and steel alloys with promising detection
limits of hundreds of ppm. In these works, a direct compari-
son of non-intensified CCD spectrometers with high resolu-
tion ICCD spectrometers showed that the additional dark cur-
rent noise from the microchannel plates in the ICCDs led to
an increase (i.e., worsening) of the LODs. However, in the ex-
periments with non-intensified CCD detectors no means were
employed to block the initial plasma continuum. Such detec-
tors would obviously perform even better if the continuum
would be temporally eliminated by an inexpensive, portable,
and robust gating device.

A desirable improvement of the above mentioned setups
would, thus, be the introduction of an optical switch in front
of the spectrometer to mask the undesired emission during
or directly after the plasma formation. There are several de-
mands to the switching device other than its size, cost, and
robustness. A typical delay time between the laser pulse and
the ideal detection window is several hundreds of nanosec-
onds; hence the switch needs fast opening time of \(t_0 \sim 100\) ns.
Furthermore, a typical plasma lifetime is between 5 \(\mu s\) and
20 \(\mu s\) resulting in a maximal optical shutter frequency \(f_{\text{shutter}} \sim 200\) kHz.

Sakka et al.\textsuperscript{22} described a new LIBS detection scheme in
which the first order diffraction of an acousto-optical modu-
lator (AOM) was used to temporally control the displacement
of the beforehand collimated plasma light. The light diffracted
into the first order was guided into the spectrometer at a pre-
scribed delay time with respect to the laser pulse. In that way
the AOM acted as an optical switch fulfilling the requirements
listed above. For the “conventional” 10 Hz LIBS experiment,
the authors demonstrated a dramatic improvement in quality

of the obtained spectra using the AOM as compared to the non-gated detection. Yet, until now the main advantage of this new approach, namely, its compatibility with high repetition rate experiments, remained unexplored.

The present contribution fills this gap. It introduces a LIBS setup which includes a high repetition rate DPSS laser and a miniature Czerny-Turner spectrometer with a fast linear CCD detector gated by an AOM. Because of the overall lower emission of DPSS laser-induced plasmas and additional light losses in the AOM based gating process, the Czerny-Turner setup with its high light transmission appears as ideal candidates for this approach. The original advantages of the small and robust high speed instrument are now complemented by the temporal gating of the detected signal.

II. EXPERIMENTAL

A schematic view of the experimental setup is depicted in Fig. 1(a). A passively Q-switched Nd:YVO₄ DPSS laser (Blade IR25, Compact Laser Solutions GmbH, DE) operates at its fundamental wavelength of $\lambda = 1064$ nm at discrete repetition rates of 1, 2, 5, 10, 20, and 50 kHz. The pulse energies and widths of the individual laser pulses are 1.44, 1.44, 1.26, 0.96, 0.58, and 0.35 mJ/pulse and 18, 18, 18, 24, 36, and 70 ns full width at half maximum (FWHM), respectively. The laser beam is focused onto the sample from above by an off-axis parabolic mirror (102 mm focal length, 38 mm in diameter) to create the repetition rate-dependent irradiances of 710, 710, 620, 350, 140, and 45 MW cm⁻² and ignite transient plasmas. The emitted light is collimated with the same parabolic mirror and then focused with another off-axis parabolic mirror into an aperture of an optical fiber (600 $\mu$m). The light is displaced by diffraction, electric transducer in the modulator, a Bragg grating is induced in the AOM crystal; the light is displaced by diffraction, and spectrally dispersed.

A razor blade was carefully positioned in front of the second focusing lens to block the zero-order light from entering the collection optics. The first order spectrally diffracted light was re-collimated (to minimize the spectral dispersion by the AOM and use it merely as an optical switch) by a 75 mm planoconvex lens and refocused by a 50 mm planoconvex lens into a second fiber that was connected to the spectrometer (USB 4000, Ocean Optics, USA). This miniaturized spectrometer is in the asymmetrical crossed Czerny-Turner configuration with f/4 and 1800 grooves/mm grating, set to a spectral range of 200–430 nm, with the spectral resolution $\Delta \lambda = 0.4$ nm at 315 nm. A pulse generator (DG535, Stanford Research Systems, USA) was used for synchronization of the individual events. This spectrometer is provided with a linear CCD-array detector (with 3648 pixels of $8 \times 20 \mu$m dimension). The data readout and processing was done with a standard computer. The diffraction efficiency of the AOM was determined experimentally as the ratio of spectrally integrated intensity diffracted into the first order and that of the non-diffracted light. This value was 20%. This efficiency is not as high as could be desired, however, LIBS is not a low-light application. A desirable increase in detected light can be readily obtained by integrating the collected plasma emission over a larger solid angle or/and larger number of laser pulses. The rise time of the AOM, i.e., the time needed to build up the transient grating in the active medium, was experimentally determined to $t_r = 70$ ns.

The time sequence of the individual events is depicted in Fig. 1(b). At a prescribed time after the laser pulse, a 24 V boxcar pulse with 10 $\mu$s width (Gw) (plus twice the empirically determined rise time $t_{r,v}$) was sent to the AOM. After the time $t_{r,v}$, the AOM had established a stable grating and diffracted a constant fraction of the plasma light towards the detector.

The delay time (Gd) was experimentally determined in order to take into account the rise time of the AOM as well as the internal delay between the Q-switch pulse and the actual firing of the laser. This cycle of the plasma ignition and
gated detection was then repeated at different repetition rates and different delays of the detection window \( G_w \). For a direct comparison of experiments with different repetition rates, the light was accumulated using a constant exposure time of the CCD-chip. To demonstrate the capability of the setup for fast spectrochemical analysis, the integration time was set to a short value of 10 ns that corresponds to 100 readouts per second and 100 laser pulses per readout (for 10 kHz repetition rate experiments). This setting allows for fast detection of elemental composition (100 Hz) while in each individual analysis the signal-to-noise statistics benefit from 100 individual consecutive plasma events. For LIBS measurements without temporal gating, the plasma radiation was collected with the same collection optics and introduced into the working area of the AOM. For detection of ungated signal, however, the Bragg grid was constantly present inside the AOM so the entire plasma light including the continuous radiation and bremsstrahlung was diffracted with no temporal gating. Only radiation dispersed into the 1st order of diffraction was accumulated on the CCD line detector. This setting was used to obtain non-gated spectra for later comparison with gated spectra. It is worth mentioning that the AOM only deflected \( \sim 20\% \) of the incident beam. Thus, \( \sim 80\% \) of the signal detected in the ungated experiments was merely lost in the Bragg grating diffraction and never reached the detector. Signal statistic dictates that this inefficiency leads to a decrease in signal to noise of factor \( \sqrt{0.2} = 2.24 \). Even though the factor 5 in light collection efficiency can readily be compensated in most setups by using more efficient collection optics, this signal loss is an intrinsic drawback of the proposed gating. The described effect can, however, be minimized by the use of more efficient AOM materials.

At each operational mode, three individual spectra were recorded and mean values of line intensities were used to optimize the setup. The spectral range of the spectrometer exceeds the transmittance range of the AOM crystal material. Therefore, beyond the overlapping region, the recorded data contained only dark current and stray light but no plasma emission. The aluminum standard 309 with low Mg content was used as a blank sample; a linear fit to the baseline of this sample spectrum in the region of 380–385 nm served for the background correction of plasma spectra. For data analysis, standard software was employed. Every spectrum was smoothed with a 3 point Savitzky-Golay algorithm and all peaks were fitted with a Gaussian profile. The authors are aware of the Voigt beam profile of the spectral lines. However, as a good approximation Gaussian beam profiles were used throughout. As a further simplification, the heights of the peaks were taken as line intensities, neglecting changes in the peak widths.

### III. RESULTS AND DISCUSSION

The feasibility study of the proposed approach started with optimization of the temporal and spatial parameters of the conducted experiment. In a subsequent study to estimate the analytical applicability, the LOD for Mg in Al alloy standard reference materials (SRM) (BAM, Germany) was obtained.

### A. Optimization of experimental parameters

To provide the correct timing for experiments with different repetition rates, the internal delay between the trigger of the Q-switch and the actual emission of the laser pulse was determined for each repetition rate individually using a fast photodiode (DET10A, Thorlabs). For the repetition rates between 1 kHz and 50 kHz, the delays varied between 450 ns and 730 ns.

Consecutively, the rise time \( t_{rt} \) of the Bragg grid inside the AOM was experimentally determined by probing the diffracted part of a continuous light source by the photodiode. The acoustic wave is created on one side of the AOM and is propagated to the working area within a finite time interval. This causes the delay in establishing the stable grating inside the AOM and determines the rise time during which the fraction of the diffracted light increases. The internal delays of both devices, DPSS laser and AOM, were taken into account in all subsequent measurements.

The geometrical design of the setup, i.e., the mutual arrangement of optical elements, was optimized by maximizing the intensity of the Al (I) line at \( \lambda = 396.1 \) nm in the aluminum alloy 312 (see Table I). Even though this line could be self-absorbed, a maximum signal on the detector still corresponded to the most efficient collection and coupling of the emitted light. Temporal optimization of AOM gating was conducted at a fixed repetition rate of the DPSS laser (10 kHz) while the detection window at a fixed width of 10 μs was altered by shifting the AOM gating pulse with respect to the laser pulse from \(-400 \) ns to 600 ns.

The results are depicted in Fig. 2(a) and several interesting features can be identified from these spectra. From 100 ns on, the overall intensity of the Al (I) doublet at \( \lambda = 394.4 \) and 396.1 nm decreases with further increase of the gate delay (Gd). This decrease can be explained by detection of less plasma continuum and by gradual plasma cooling. There is another broad spectral feature around 358–359 nm that appears only in the early plasma and completely vanishes by 300 ns after the formation of the plume. This feature is attributed to a strong Al (II) triplet at 358.6 nm, 358.7 nm, and 358.7 nm; the upper state of this triplet at 15.3 eV can only be significantly populated in early and hot plasmas.

Even though the overall intensity of the Al (I) doublet decreases

### TABLE I. Elemental composition of aluminum standards from Federal Institute for Materials Research and Testing (BAM, Germany).

<table>
<thead>
<tr>
<th>Al alloy</th>
<th>The amount of the element (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no.</td>
<td>Al</td>
</tr>
<tr>
<td>---------</td>
<td>----</td>
</tr>
<tr>
<td>307</td>
<td>93.72</td>
</tr>
<tr>
<td>308</td>
<td>90.21</td>
</tr>
<tr>
<td>309</td>
<td>88.02</td>
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<td>310</td>
<td>98.81</td>
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<td>91.86</td>
</tr>
<tr>
<td>312</td>
<td>98.79</td>
</tr>
<tr>
<td>313</td>
<td>94.73</td>
</tr>
<tr>
<td>314</td>
<td>82.98</td>
</tr>
</tbody>
</table>
towards later detection window, an increase in the slope of the profiles, i.e., a better contrast, can be observed.

One sees from Fig. 2(a) that spectral background between the spectral bands decreases as well with increasing the delay time. The signal-to-background ratio (SBR) for the Al (I) line at 396.1 nm is plotted in Fig. 2(b) as a function of the delay time. A 7-fold increase in SBR due to the temporal gating can be observed starting from 200 ns. The SBR starts rising at around $G_d = 100$ ns, then reaches the maximum at 300 ns and saturates. Therefore, all subsequent measurements were conducted with the AOM delay time fixed at $G_d = 300$ ns.

Subsequently, the effect of the laser repetition rate on the absolute intensity of detected emission signal was tested. Fig. 3 shows the Al alloy spectra recorded at a fixed gate delay of $G_d = 300$ ns for different repetition rates ranging from 1 kHz to 50 kHz. For the rates between 1 and 10 kHz an almost linear increase in line intensities can be observed, while at the rates higher than 20 kHz the emission signal significantly drops. This is because the DPSS laser has an almost constant pulse power only at rates below 5 kHz. At higher repetition rates the power of the pumping diodes does not suffice to maintain a constant population inversion within the lasing media; this results in the decrease of output pulse energy, and, hence, of irradiance on the sample surface. Another reason for the decrease in irradiance is the longer pulse durations at higher repetition rates. Even though the gate width of
$G_w = 10 \mu s$ would allow for repetition rates of up to 100 kHz, all subsequent measurements were conducted at 10 kHz.

As discussed in the LIBS literature, multiple laser pulses impinging on the same sample spot affect the signal intensity. A positive effect is the so-called laser cleaning where subsequent laser pulses ablate a fresh surface after a corrosion layer has been removed. However, after a certain number of laser pulses, the laser drills a hole through the surface and light from later pulses is trapped inside the crater or blocked by the crater’s rim. In the case of the angular or side-view observation geometries this light does not reach the detector. The effect is more pronounced at larger numbers of laser pulses and higher fluencies. In experiments with high repetition rate lasers, the laser hits the target repeatedly within a short time interval (100 $\mu s$ at 10 kHz). After the impact of each laser pulse on a metal target the interaction spot partially melts and a LIP is produced. At repetition rates of above 1 kHz it is reasonable to expect that the melted phase does not re-solidify prior to the subsequent laser pulse and thus hampers the plasma formation since a melted metallic phase exhibits a higher optical breakdown threshold compared to their solid counterparts.\(^{15,18}\) The higher the repetition rate, the less time the melt phase has to cool down and solidify. The heat conduction within the sample is not able to transport a sufficient amount of the absorbed energy for solidification of the interaction region. The same effect could be observed in an earlier study using the same laser system at comparable repetition rates.\(^{21}\) Gornushkin et al.\(^{15}\) recommended to move the target during the analysis to avoid the occurrence of a melt phase, which does not have time to solidify, in the interaction region. This phenomenon was observed when two consequent laser pulses were delivered with the delay $\sim 0.2$ ms, corresponding to 5 kHz laser repetition rate.

As mentioned earlier, in typical LIBS experiments either a low number of high power laser pulses at repetition rates of several Hz or a vast number of low power laser pulses at rates of several kHz are applied to collect an analytical signal. In the present experiment the untypical sequence of only 100 quickly succeeding laser pulses with low fluence was used. For this experiment, the influence of the sample movement on the analytical signal was tested. For this, the signal obtained from a constantly moving sample (achieved by mounting the sample onto the chuck of a handheld drill operated at a rotational speed of 33 000 rounds/min) was directly compared to the signal recorded with simple manual movement of a handheld sample. A thorough comparison, however, showed only negligible differences in the spectral intensities. Hence, for the relatively small number of 100 subsequent laser pulses, manual movement of the samples was applied throughout.

### B. Al samples

To emphasize the benefits arising from the temporal gating with the AOM, Fig. 4 comparatively shows the two spectra recorded with (bold) and without gating. For easier visual comparison, the spectra were normalized to the highest intensity of the aluminum line at 396.1 nm. Apart from the significantly increased SBR, two other features become visible from Fig. 4. The reduced background appears only in the region of transparency of the AOM medium, from 340 to 420 nm. The spectra show a strongly broadened Al (II) triplet at 358.6–358.7 nm. The reduction of the ionic line intensity is evident for the measurement utilizing AOM temporal gating set at 300 ns. This effect agrees with our previous observation that the contribution of ionic lines is mostly important at early stages (\(< 300 \text{ ns}\)) of the plasma evolution.

To estimate the analytical applicability of the suggested approach, aluminum alloy standard reference materials (BAM, Germany) whose elemental composition is listed in Table I, were measured. Special emphasis was put onto the observation of trace elements, especially magnesium, see Fig. 5(a). The two magnesium lines, Mg (I) 383.2 nm and Mg (I) 383.8 nm, strongly overlap due to the low spectral resolution of the Czerny-Turner spectrometer. The amount of Mg in the sample 309 is lower than LODs in proposed system. In Fig. 5(a) the sample 309 is depicted however no Mg peaks can be observed.

The calibration curves for magnesium in aluminum alloys obtained with and without the AOM temporal gating are shown in Fig. 5(b). The analytical signal was corrected by the background intensity employing a blank sample measurement (aluminum standard no. 309 containing merely $6.8 \times 10^{-5}$ wt.% of magnesium was considered as the blank sample). In the complete analysis the height of the Mg I peak at 383.8 nm served as the analytical signal. The LODs were computed employing the $3\sigma$-IUPAC criterion.\(^{23,24}\) Accordingly, the LODs were computed by the equation $LOD = \frac{3\sigma}{s}$, where $\sigma$ is the standard deviation of the background at the wavelength in a blank sample and $s$ is the slope of the calibration curve, respectively. For this quantification analysis the raw data served as input, no further normalization or internal standardization was used throughout.

The improvement of the LODs due to the use of the AOM is already obvious from Fig. 4. The lowest detectable concentration of Mg was 0.13 wt.% obtained with the setup with the DPSS laser and AOM and with accumulation of 300 laser pulses per sample. The LOD of 0.625 wt.% for the LIBS setup with AOM.
without the AOM gating are significantly higher than that in
the case of the gated detection. Even though the gating mecha-
nism sacrifices roughly 80% of the emitted light before it
reaches the detector, the observed fivefold improvement in
LODs outweighs the improvement that can be estimated from
collecting the entire light entering the AOM (factor 2.24, see
above). Future improvements can be expected from AOMs
built from different active media with a more efficient diffrac-
tion. This result strengthens the importance of temporal gating
of laser-induced plasma emission and usability of the AOM
for this application. Compared to results from the literature,20
the obtained LODs employing the AOM-gated setup appear
to be large. However, the previous experiments were not aiming
towards fast detection and a vast portion of the improve-
ment in LODs are likely to stem from the significantly lower
amount of accumulations employing the AOM-gated setup (100)
compared to the number of accumulations used in Ref.
20 (160 000). Furthermore, in Ref. 1 (p. 451) a limit of de-
tection is reported for the same Mg (I) line (383.8 nm) in Al
matrix of 0.057%. Those LODs were achieved with so-called
FML system (Flexible Measuring System based on LIBS)
with a sequence of 100 laser pulses. The FML system consists
of compact Nd:YAG laser with pulse energy of 50 mJ and a
Paschen-Runge spectrometer equipped with three CCDs cov-
ering the spectral range from 278 to 560 nm.

Though the results presented here seem to be unsatisfac-
tory compared to the references, the aim of our investiga-
tion was a mere proof of principle. The lower detection limits in
Ref. 1 most likely result from the higher irradiance of individ-
ual laser pulses and the better spectral resolving power of the
used spectrometer. In future experiments the obtained LODs
can be improved using AOMs with better throughputs, bring-
ing more efficient light transmittance.

In summary, an AOM can be used for temporal gating of
light emitted from transient laser-induced plasmas. In LIBS
applications, this gating can be used to significantly decrease
the limits of detection. Since AOMs are small and robust
components with low power consumption and no mecha-
nical parts, they seem ideal for the future development of com-
pact high-rate LIBS devices. On the other hand, AOMs limit
the wavelength range and as well the intensity of transmitted
plasma radiation. Optical system for collecting the plasma ra-
diation is of high importance. AOMs essentially decrease the
intensity of temporally gated radiation, which is diffracted on
Bragg grid within the active medium of AOM. Therefore, the
choice of AOMs has to be adapted to the case of the study.

IV. CONCLUSIONS

The use of acousto-optical modulators as fast optical
shutters allows convenient time gating in LIBS experiments
with high repetition rate lasers. Due to the low price, small
size, and the possibility of fiber coupling of these optical shut-
ters to spectrometers, almost any experimental setup can be
easily equipped with an AOM gating unit. The small and com-
 pact LIBS setup with the AOM temporal gating was success-
fully utilized for the detection of traces of Mg in aluminum al-
loy standard reference materials. Moreover, improved signal-
to-background ratio (SBR) for the lines of Mn, Si, and Cr in
the analyzed aluminum alloys was observed, not shown in the
article. The achieved LODs for Mg employing AOM-gated
setup were ~0.13 wt.%. These results show improvement in
comparison with non-gated detection (0.625 wt.%). The rela-
tively poor LODs in general result from the short integration
time of the individual experiments in combination with the
high-rate laser source when a temporal detection cannot be
provided utilizing conventional ICCDs. Additionally, none of
the state of the art normalization procedures to the intensity
of a matrix elemental line has been applied. However, even at
an integration time of only 10 ms, the described experimental
LIBS setup could satisfy the needs of semi-quantitative spec-
trochemical analysis of up to 100 spots/s. Additionally, the
absence of any moving parts makes the AOM-shutter an ideal
gating device in harsh environments.

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