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Quantitative analysis of trace elements in technological materials using online-laser ablation of solids in liquids (online-LASIL)

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ABSTRACT

To overcome the challenges of the 21st century, the demand for novel materials which outperforms the limits of previous material classes is high. However, the elemental composition determines crucial material properties from the bulk stoichiometry down to ultra-trace impurities. Therefore, a precise analytical characterization is inevitable to establish a connection between composition and function.

For this purpose, conventional solid sampling techniques could be applied. However, matrix-matched standards are indispensable for quantitative analysis and are often unavailable in the case of technological materials. To overcome this limitation online-Laser Ablation of Solids in Liquids (online-LASIL) has been proposed recently, which combines the advantages of solution-based analysis and solid sampling techniques. However, this technique has only been applied to determine sample stoichiometry.

In this work, major improvements of the online-LASIL approach were reported by the controllable segmentation of the carrier solution, leading to an improved washout behavior of the ablated material, enabling the quantitative investigation at trace levels. The accuracy of this improved measurement setup is validated by the quantitative analysis of trace elements in the standard reference material (SRM) NIST612. To demonstrate the applicability of this method, silicon carbide (SiC), a wide bandgap semiconductor, was analyzed. With the improved online-LASIL method, an Al-doped region, which is only constant for the first 250 nm, was successfully quantified.

1. Introduction

Modern-day challenges like climate change, environmental pollution, and increasing energy consumption have driven the technological progress of the last decade. To achieve the goal of a sustainable future, novel high-performance materials are essential since they enable more efficient and new technologies. However, a precise chemical analysis is indispensable for material design and optimization since crucial material properties are linked to their composition. A conventional approach for this challenge would be converting the sample into a solution and a subsequent liquid measurement with an inductively coupled plasma mass spectrometer (ICP-MS). However, most novel materials, like semiconductors or complex metal oxides, are hard-to-digest materials and therefore require corrosive and harmful chemicals like HF [1] or sample fusion [2], which is very laborious and can lead to inaccurate results during the measurement. Moreover, many scientific questions

revolve around the distribution of trace elements within the sample. Thereby the fusion or digestion of the whole sample wouldn't be helpful since only bulk information is accessible.

Another approach would be solid sampling methods [3] like time of flight secondary ion mass spectrometry (ToF-SIMS), glow discharge mass spectrometry (GD-MS), X-ray photoelectron spectroscopy (XPS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), or laser induced breakdown spectroscopy (LIBS); with all the mentioned methods potential laborious sample digestion can be avoided [4]. In addition, spatially resolved information can be gathered with those techniques, seeming like a perfect fit for the before-mentioned problem. However, considering quantitative analysis, ToF-SIMS, GD-MS, LA-ICP-MS, and LIBS are affected by matrix effects, necessitating the use of matrix-matched standards for accurate measurements [5–7], and the comparatively low sensitivity of XPS [8] wouldn't be suitable for determining trace elements.

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One method that combines the advantages of solid sampling techniques and wet chemical measurements is the laser ablation of solids in liquids (LASIL). This method was initially designed for manufacturing nanoparticles until Muravitskaya et al. [9,10] recognized the analytical value as a solid sampling method. In LASIL the sample is placed in an open pot chamber and covered with liquid. This setup is positioned beneath a LA-system, and the sample is ablated in the presence of a suitable liquid. The nanoparticles generated in this process are suspended in the liquid and can further be analyzed with an ICP-MS [11]. This approach circumvents the laborious sample digestion step required for conventional ICP-MS analysis and enables the use of liquid standards for quantification in contrast to other solid sampling techniques, on condition that elemental ratios are used, or ablation rates are considered. Such standard solutions could be prepared with defined composition (analytes of interest and their concentration levels), thus LASIL offers high flexibility and allows straightforward adjustment to the needs of the research task. The biggest drawback of this method is the separation of the ICP-MS measurement from the preceding ablation step, which requires manual sample manipulation and is, therefore prone to contamination.

Moreover, gathering spatially resolved information is impossible with the previously used LASIL technique. Therefore Bonta et al. [12] developed the online-LASIL approach, where a solid sample is ablated under a continuous stream of a liquid carrier medium, which is then introduced into the plasma of an ICP-MS. This approach minimizes the risk of contamination and enables spatially resolved analysis. In this way, imaging [13] and depth profiling experiments [14] are now possible. However, these measurements are restricted to major components due to limited sensitivity resulting from the strong dilution of the ablated material in the carrier solution. Therefore, previously reported online-LASIL setups only determined sample stoichiometry.

In this work, the online-LASIL setup was further optimized by a controllable segmentation of the carrier solution with gas bubbles that trap the generated nanoparticles in a single liquid segment. In this way, the washout behavior and the transport efficiency of the particles from the online-LASIL cell to the detection system could be improved tremendously, enabling the accurate quantification of trace elements. To validate the implementation of the segmented flow, trace elements of the SRM NIST612 were analyzed quantitatively. The online-LASIL setup with the controlled segmented flow was further used to analyze the semiconductor material SiC. Due to the excellent properties of SiC, more efficient power devices, compared to silicon (Si) based devices, can be realized [15,16]. However, to achieve the desired properties, the dopants' type, concentration, and distribution are crucial to optimize devices [17,18]. Synchronization of the laser pattern with the segmentation of the carrier solution enabled constant ablation conditions, resulting in the correct quantification of the upper 250 nm Al-doped region.

2. Experimental

2.1. Reagents and materials

All solutions were prepared with deionized water (18,2 M Ω cm⁻¹) from a Barnstead EASYPURE II water dispenser (ThermoFisher Scientific, Germany). All used ICP standards had a concentration of 1000 mg/kg and were purchased from Merck (Germany). Concentrated hydrochloric acid and nitric acid were at least of trace element grade and purchased from Merck (Germany). For each measurement dilutions were freshly prepared.

For this work, two different kinds of samples have been used to verify the capability of the improved online-LASIL setup. The first one is the SRM NIST612 trace metals in glass standard (National Institute of Standards and Technologies, USA). The second one is four different Al-implanted SiC, with the following Al concentrations: 3*10²⁰ cm⁻³, 1*10²⁰ cm⁻³, 3*10¹⁹ cm⁻³, 1*10¹⁹ cm⁻³, resulting in Al contents of

4200 μ g/g, 1400 μ g/g, 420 μ g/g and 140 μ g/g.

2.2. Instrumentation

For the ablation of the samples, a J200 Tandem LA/LIBS system (Applied Spectra, Inc., Fremont, Ca) with a wavelength of 266 nm and a four ns pulse length was used. The online-LASIL cell is placed in the XYZ chamber of the laser, enabling spatially resolved sample investigations.

For the analysis of the generated particle suspension an ICP-MS (iCap Qc ThermoFisher Scientific, Germany) in standard mode was used as the detection system (see Table 1). For the sample introduction into the ICP-MS a peristaltic pump (Perimax 12, SPETEC, Erding, Germany), a PFA nebulizer, and a cyclonic spray chamber were used. The ICP-MS was tuned for maximum intensity of the ¹¹⁵In signal and CeO⁺/Ce⁺ ratio below 2% before all experiments with a solution provided by the manufacturer. The data were recorded and evaluated by the instrument software Qtegra Version 2.8.

2.3. Online-LASIL measurement setup

For the online-LASIL measurements, a cell with three drillings for the in- and outlet of the carrier solution, similar to the one described in the work of Herzig et al. [19], was used. In this work, the second inlet was used to introduce a make-up solution for stabilization of the ablation products, whereas in the current study the additional inlet is used to improve the washout and transport behavior of the online-LASIL cell. Moreover, the geometry of the flow channel formed by the PDMS-film was slightly changed, while the height was still 0.5 mm the diameter was minimized from 2 mm to 0.5 mm, resulting in an enhanced flow velocity of the carrier solution over the sample surface.

For the analysis the sample is placed inside the cavity of the PEEK body and the cell is sealed, as mentioned before. Both inlets of the LASIL cell are flushed with 2% HCl until the system is filled, the flow of the carrier solution is set to 0.28 ml/min for inlet 1 and 0.12 for inlet 2, resulting in a total flow of 0.4 ml/min. Before the analysis is started the carrier solution is segmented with Ar bubbles. To achieve a consistent frequency and length of the gas bubbles, an Arduino controller was implemented to regulate a six-port injection valve, as can be seen in Fig. 1.

One can see that in the six-port injection valve, port 1 is the inlet for the carrier solution, port 2 is the outlet for the carrier solution or the gas bubbles, port 3 is the inlet of the gas (pressure ca. 1 bar), port 4 is sealed to avoid excessive loss of gas, port 5 is not used, and port 6 is a drain for the carrier solution. In this way, either the carrier solution or gas is transported alternately to the inlet of the LASIL cell, which leads over the sample. The six-port injection valve can switch between two different positions. In the first position, the carrier solution from port 1 is transported to the LASIL cell, and the gas is stopped by the sealed one. In the second position, the carrier solution is directed to a waste bin, and the gas flow is connected with the online-LASIL cell. A segmented flow is achieved by continuous switching between the two positions.

Table 1
ICP-MS and Laser measurement parameters.

ICP-MS detection system	
RF Power	1550 W
Nebulizer gas flow	1.05 l/min
Cool gas flow	14 l/min
Auxiliary gas flow	0.65 l/min
Measured Isotopes	²⁷ Al, ²⁸ Si, ⁴⁴ Ca, ¹¹⁵ In, ¹²¹ Sb, ²⁰⁸ Pb, ²³⁸ U
Dwell time	0.01 s (0.05 s for ²⁷ Al)
J200 Tandem LA/LIBS	
Laser fluence	3.58/2.23 J/cm ²
Spot size	140 μ m
Scan speed	0.2 mm/s
Repetition rate	10 Hz
Liquid carrier solution flow	0.4/0.2 ml/min

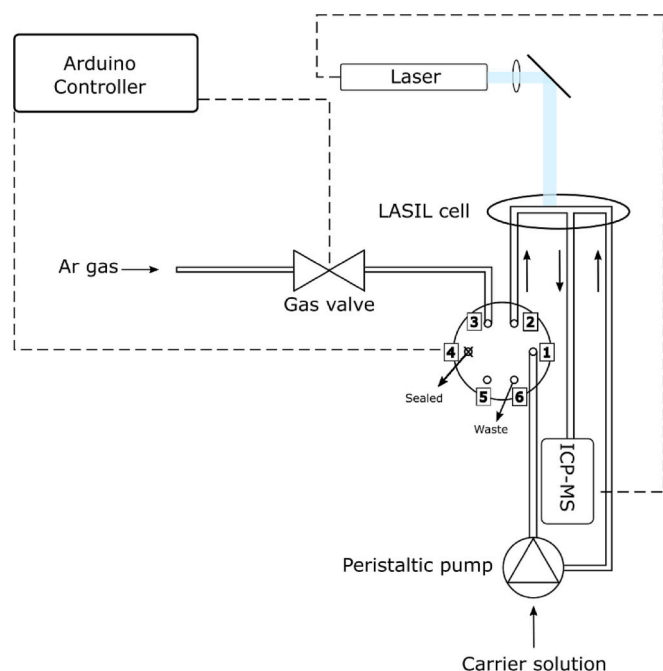


Fig. 1. Schematic representation of the complete online-LASIL measurement setup utilizing the controlled segmented flow of the carrier solution.

With this instrumental setup, the length of the liquid and gas segments can be adjusted to the desired laser pattern. The length of the liquid segments is regulated by the overall flow of the carrier solution and the time the six-port injection valve dwells in position 1. Whereas the length of the gas segments is affected by the pressure of the gas at the inlet and the time the six-port injection valve resides in position 2.

3. Results and discussion

3.1. Improved washout behavior

As already demonstrated in the work of C. Herzig [20], the segmentation of the carrier flow with gas bubbles significantly improves the washout behavior. In this study, introducing air bubbles was conducted using a simple T-piece connected to a peristaltic pump tubing. Therefore, resulting air bubbles showed significant variations in size and time of occurrence. For this reason, no uniform ablation behavior could be achieved, as sample ablation occurred either in the presence or in the absence of the gas bubbles. Resulting differences in the ablation rate are of minor importance if intensity ratios of main sample components were measured, as in the case of the determination of sample stoichiometry, but prevent the accurate analysis of trace constituents.

For this purpose, synchronizing the ablation process with the appearance of liquid carrier segments is an essential precondition for constant ablation conditions. Therefore, this work focuses on the control of the occurrence and duration of the introduced gas bubbles, resulting in a highly reproducible and stable segmentation of the carrier flow.

To illustrate the improvements achieved with the segmented flow of the online-LASIL method, the signal intensity of the trace element Pb in the NIST612 standard material ($38.57 \pm 0.02 \mu\text{g/g}$) was monitored. Therefore, five line scans measured with the proposed procedure are compared with the conventional approach using only a liquid carrier stream. The results can be seen in Fig. 2, which indicates that introducing the Ar-gas bubbles leads to a fast decrease and increase of the Pb-signal intensity. At the same time, the signal stays stable when the liquid segments reach the detector. Herein the reproducibility of the gas bubble generation can be seen as the change in the Pb-signal caused by the Ar-bubbles, which occur in regular time intervals.

Having a look at the peaks, which indicate the ablation event on the NIST612, one can see that the Pb-signal intensity only increases during one liquid segment. On the one hand, this demonstrates that there are no mixing effects of the nanoparticles between neighboring liquid segments during the transport to the nebulizer. On the other hand, this shows the

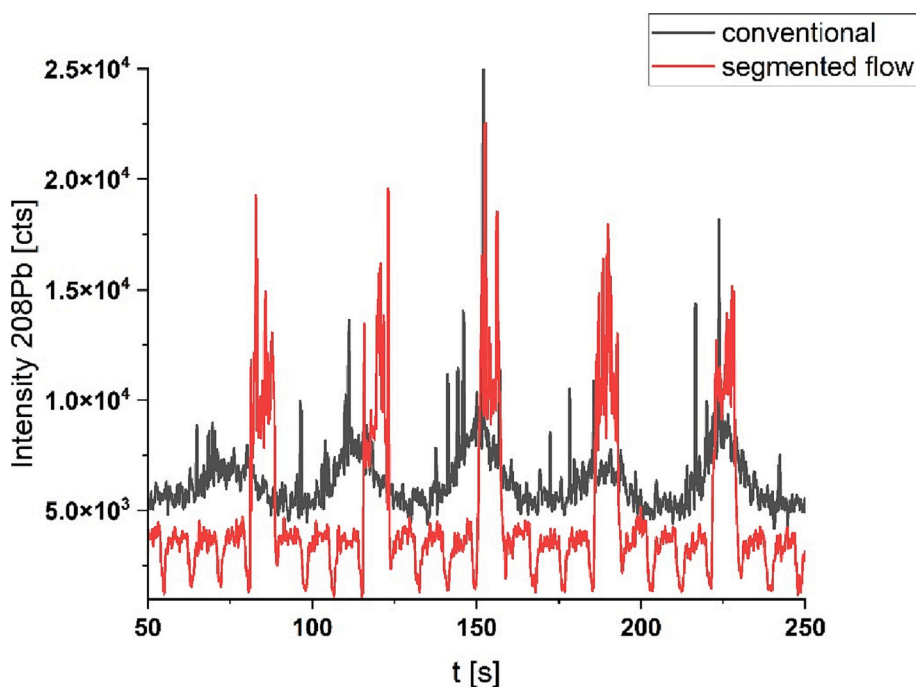


Fig. 2. Comparison of the Pb signal-over-time profile of the conventional online-LASIL method (gray) and the one utilizing the segmented flow (red). The bubbles were introduced every 7 s for 0.3 s with a pressure of ca. 0.8 bar. Ablation patterns started 1–2 s after the bubble passed the sample and lasted for 2.5 s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reproducibility of the alignment of the laser pattern and the liquid segments, assuring that the laser only ablates material while the sample is covered with one liquid segment.

The benefits of this method can be seen by comparing the findings obtained with the conventional method and the method utilizing the segmented flow, indicating that the improved washout behavior leads to a better signal-to-background ratio and thereby to a reduced limit of detection. In addition, the signal of the ablated nanoparticles becomes more constant and, therefore, more reproducible. This can be seen in the relative standard deviation of the integrated signal of the ablation event, which decreases from 49% for the conventional procedure to 12% for the approach using the segmented carrier flow. This outcome is further confirmed by the absence of spikes between the ablation events, which have been frequently observed with the conventional approach. These spikes result from nanoparticles that were not simultaneously washed out with the nanoparticle collective resulting in delayed transport and introduction into the ICP-MS.

To further show this method's possibilities, the carrier solution's flow was halved to 0.2 ml/min (0.14 ml/min for inlet 1 and 0.06 ml/min for inlet 2) in a second experiment (see Fig. 3). This leads to a longer transport time of the nanoparticles from the LASIL cell to the ICP-MS. In the case of the conventional method, significant broadening of the nanoparticle peaks from approximately 25 s to 36 s was observed, thereby causing a higher dilution of the analytes. This can be seen by the averaged signal intensity, which stays the same, although the use of a reduced carrier flow rate should result in a more concentrated particle suspension. Moreover, an enhanced occurrence of spikes between the ablation events for the conventional method can be observed, indicating a less efficient transport of the nanoparticles. The same trend could be observed for all the measured analytes.

On the other hand, the online-LASIL method with the segmented flow doesn't show a peak broadening of the signal. The peak width of approximately 7 s is still determined by the length of the liquid carrier segment produced with the synchronized segmented flow. Moreover, an improvement of the Pb-signal can be observed by a factor of 1.5. This can be explained by the decrease of the liquid carrier flow, which results in a reduction of the liquid volume while the amount of ablated material

stays the same, resulting in more concentrated nanoparticle suspensions. Considering the analysis of trace elements, this fact can be utilized to keep the dilution of the ablated nanoparticles to a minimum and further decrease the limit of detection.

3.2. Online-LASIL quantification strategy

For the online-LASIL-ICP-MS measurements, an adoption of the standard addition method similar to that described by C. Herzig [13] was used. Therefore, the carrier solution is spiked with a known amount of analyte. During the sample's ablation, the concentration of the carrier solution is further increased with an unknown amount of nanoparticles. In this way, the concentration of the ablated material $c_{ablation}$ can be calculated by the concentration c_{spike} and signal intensity I_{spike} of the spiked carrier solution and the signal intensity of the ablated material and the spike I_{total} :

$$c_{ablation} = \frac{c_{spike}}{I_{spike}} (I_{total} - I_{spike}) \quad (1)$$

As already mentioned, this method avoids the subsequent measurement of standards and the carrier solution, making it time-saving. Moreover, this quantification approach compensates for instrumental drifts and is thus applicable for long measurement times.

Derived knowledge about the elemental concentrations in the carrier solution after sample ablation allows the calculation of elemental ratios, which has been used for the assessment of sample stoichiometry in previous studies. The direct determination of the solids composition is not possible with this approach. For this purpose information about the ablated sample volume is needed, moreover, information about the transport and detection efficiency of the measured analytes is mandatory. A frequently used strategy to overcome these difficulties is to correlate the findings obtained for the target elements with the outcome derived for a simultaneously measured major sample constituent with known content, which allows the determination of the trace element contents in the investigated solid sample.

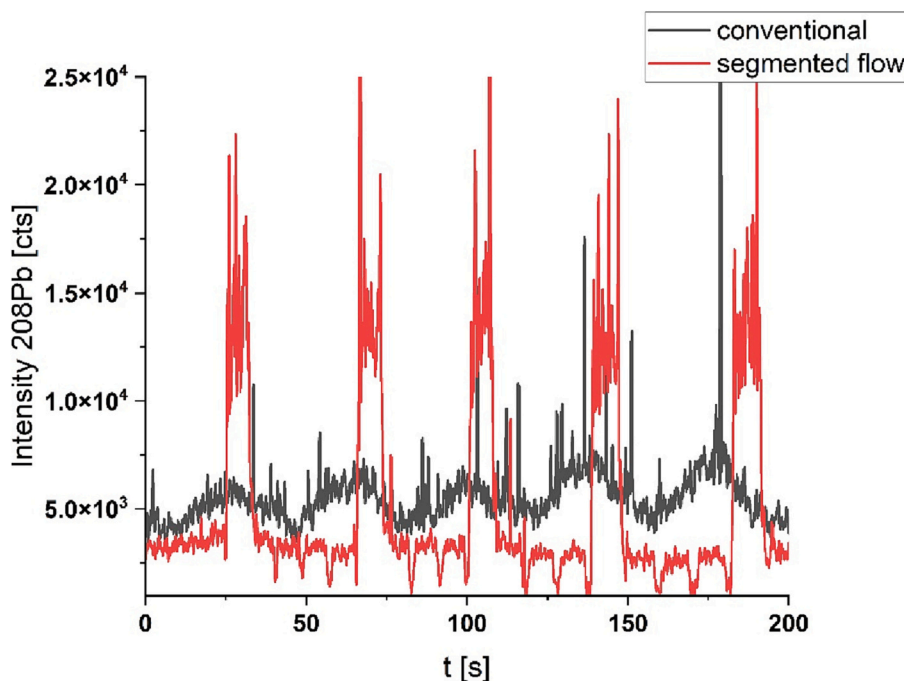


Fig. 3. Comparison of the Pb signal-over-time profile of the conventional online-LASIL method (gray) and the one utilizing the segmented flow (red) with a halved speed of the carrier solution (0.2 ml/min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Quantification of the trace elements in the NIST612

For the validation of the new measurement setup for quantitative investigations, the trace elements uranium, antimony, and lead were analyzed in the SRM NIST612. Application of the concept for quantitative online-LASIL analysis discussed in the previous chapter requires at least one measurable major sample component and a sufficient sensitivity for the trace elements of interest. For this reason, the selection of monitored isotopes (^{121}Sb , ^{208}Pb , and ^{238}U) has been extended with ^{44}Ca , a major constituent of SRM NIST612 with a certified content of 8.8%.

By quantifying the concentrations of Ca and the elements of interest in the nanoparticle suspension generated during sample ablation, the content of the trace elements in SRM NIST612 can be inferred as the analyte to calcium concentration ratio in the carrier solution resembles the composition prevailing in NIST612. For this purpose, the concentration ratio obtained from the online-LASIL measurement was multiplied with the known Ca content of NIST 612. It should be mentioned, that the In-signal was not used for normalization of the analyte signals. It was only used as a quality control for the segmentation of the carrier solution, since it indicates the frequency and the stability of the gas bubble introduction.

Application of this approach resulted in concentrations of 41.3 ± 7.9 $\mu\text{g/g}$ for U, 41.0 ± 6.0 $\mu\text{g/g}$ for Sb, and 37.3 ± 6.5 $\mu\text{g/g}$ for Pb in SRM NIST612 (see Fig. 4). The uncertainty was calculated using the student t-distribution for a confidence interval of 95% ($n = 8$, $t = 2.36$). Based on the overlapping of the uncertainty interval of the online-LASIL and the certified value or the preferred values of the GeoRem database [21], the obtained results are in good agreement. This outcome demonstrates that using this method trace elements down to the low ppm range can be accurately measured with a relative standard deviation between 6 and 8%.

Instrumental limits of detection, which were obtained via the standard deviation of the response of the calibration curve and the slope for the measured trace elements, multiplied with a factor of 3.3 are in the

ng/l range (U: 2.6 ng/l; Sb: 2.1 ng/l and Pb: 2.3 ng/l). The concentrations measured in the carrier solution after sample ablation are a factor of 10 higher for U, respectively 6 higher for Sb and Pb. For the analyzed solid material, this results in a method detection limit of around 5 $\mu\text{g/g}$ for the solid sample. These limits of detection indicate that even lower concentrations could have been quantified. Moreover, further improvements are possible by using a reduced flow rate for the carrier solution (see chapter 3.1) or by utilizing larger spot sizes or higher laser repetition rates. This reflects how easily this method can be adapted to optimize the analysis for specific applications.

3.4. Application example silicon carbide

The new powerhouse of the semiconductor industry is wide-bandgap semiconductor materials, like SiC, which, particularly in power applications, outperform silicon-based devices [22,23]. For semiconductors the distribution of dopants is crucial to obtain the desired electronic conductivity for specific devices [24]. This work proposes the improved online-LASIL setup as a fast and reliable method to quantify dopants in SiC. For this reason, the concentration of four different Al-implanted SiC samples was quantified. Those samples were prepared by ion implantation [25], while only the upper 250 nm had a homogeneous dopant distribution.

For this investigation, the laser parameters had to be optimized to achieve an ablation depth lower than 200 nm. Line scans were measured using laser energy of 2.23 J/cm^2 and a beam diameter of 140 μm ; repetition rate and scan speed were not changed. These conditions resulted in a mean ablation rate between 190 nm and 200 nm per ablated line, measured at three positions with a "DektakXT" profilometer stylus (Bruker).

To compare the online-LASIL results with the implanted Al concentrations, the measurement results had to be converted to particle density in the solid SiC sample, which is the specified unit of the Al-implantation. For this purpose, the Si concentration of the carrier solution was also determined, besides the Al concentration (intensities

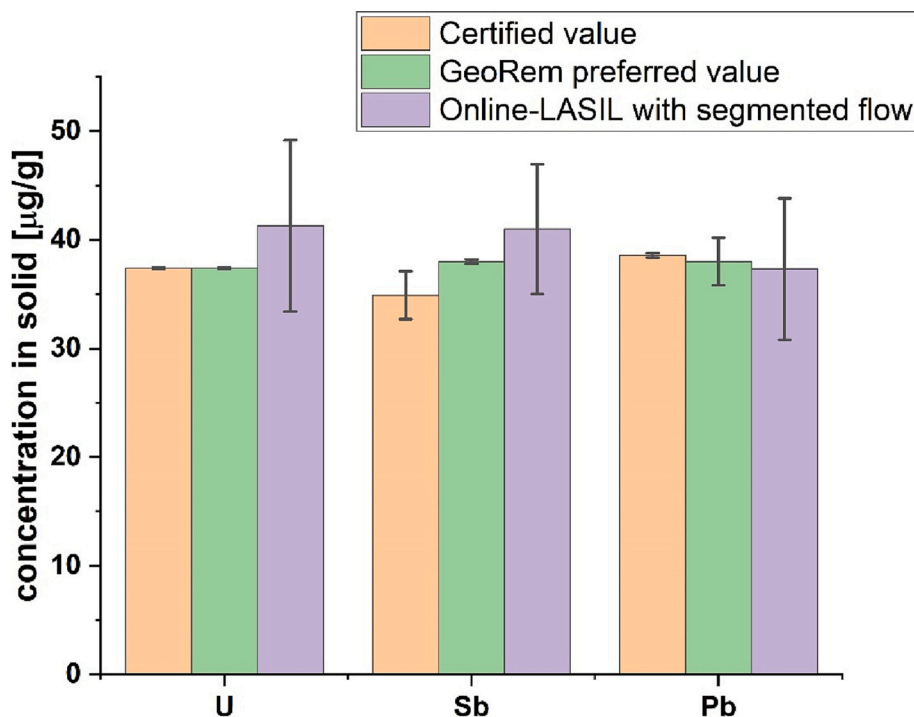


Fig. 4. Quantitative results of the online-LASIL measurement with the segmented flow of the NIST612 (violet) compared to the preferred values of the GeoRem database (green) and the certified values (orange). Error bars of the measurement results depict the uncertainty calculated according to student t-distribution ($\alpha = 0.05$; $n = 8$; $t = 2.36$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were normalized to ^{115}In). For both concentrations, the substance amount fraction X_i was calculated with the concentration measured in the carrier solution and the molecular weight M_i , thereby the particle density of Al C_{Al} could be calculated as follows:

$$C_{Al} = \frac{X_{Al}\rho_{SiC}N_A}{\sum_{i=1}^n (X_i * M_i)} \quad (2)$$

In this formula ρ_{SiC} is the density of silicon carbide (3.21 g/cm³), and N_A is the

Avogadro constant (6.022*10²³ mol⁻¹). Based on the stoichiometry of SiC, the substance amount fraction of carbon was assumed to be the same as that of Si.

The results of the Al atom density of the four measured samples can be seen in Table 2. For comparison also the calculated implantation level is presented in this graph. The relative standard deviation depends on the implantation concentration and varies from 4% for the highest Al-level to 13% for the sample with the lowest particle density, showing excellent comparability to the data derived from analysis of the NIST612. The results of the quantitative analysis are in good agreement with the calculations of the ion implantation.

In contrast to the bulk measurement of the NIST612, the analysis of the SiC shows another advantage of this method since spatially resolved analysis with a constant ablation rate is possible. Preliminary attempts to use a segmented flow didn't achieve such a constant ablation behavior, since the interaction of the laser beam is different in the presence and absence of gas bubbles, thus a perfect synchronization between the appearance of gas bubbles and the laser shots is a prerequisite for investigations with constant ablation rate. Moreover, one has to consider that the investigation was limited by the depth of the homogeneous doped region of around 250 nm. Therefore the amount of ablated material is restricted, necessitating sufficient sensitivity for successful measurements. This precondition could be flexibly addressed by adjusting the dilution of the ablation products with the carrier solution to achieve the desired limits of quantification.

4. Conclusion

This work focuses on the quantitative determination of trace elements using online-LASIL in technological materials with no matrix-matched standards available. Since previous applications of this technique focused on determining main components, optimization of the washout behavior and transport of the suspended nanoparticles was mandatory to achieve sufficient sensitivity for analyzing elements in dopant concentrations. Therefore, the controlled segmentation of the carrier solution was introduced by a six-port injection valve, which is regulated by an Arduino controller. In this way, the ablated material could be trapped inside one liquid segment, and the washout time and thereby the dilution within the carrier solution could be minimized. The improvements achieved by those adaptations could be demonstrated by the quantitative analysis of selected trace elements in SRM NIST612, showing good agreement between measured and certified values for trace constituents with contents in the low µg/g range.

Moreover, the adaptation of the frequency and length of the introduced air bubbles makes it easy to align the laser pattern with the liquid segments. This ensures that the material is only ablated in the presence of a carrier solution, which is a prerequisite for quantitative and spatially resolved analysis. Considering the comparatively small doping depth of the SiC samples, this study wouldn't have been possible without a constant ablation rate.

Another crucial factor of this measurement method is the ability to choose the gas used to segment the carrier solution. In previous studies, the segmented flow could only be realized using air, causing the risk of interferences induced by polyatomic ions containing the elements nitrogen, oxygen, and carbon. In the case of SiC, the introduction of air bubbles would result in massive interferences on the isotopes used for

Table 2

Comparison of the particle density of Al in SiC of the improved online-LASIL method and the implanted concentrations.

Expected implantation values	online-LASIL measurement
Al atom density (cm ⁻³)	Al atom density (cm ⁻³)
3*10 ²⁰	3.01 ± 0.13*10 ²⁰
1*10 ²⁰	1.01 ± 0.06*10 ²⁰
3*10 ¹⁹	3.12 ± 0.22*10 ¹⁹
1*10 ¹⁹	1.33 ± 0.17*10 ¹⁹

the analysis of Si. By the use of Ar for the segmentation of the carrier flow, those interferences could be avoided.

Declaration of Competing 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.

Data availability

Data will be made available on request.

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