Laser-Induced Breakdown Spectroscopy in Elemental Analysis

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Laser-induced breakdown spectroscopy (LIBS) has evolved considerably in recent years, particularly the application of portable devices for the elemental analysis of solids in the field. However, aqueous analysis using LIBS instruments, either in the laboratory or in the field, is rather rare, despite extensive research on the topic since 1984. To achieve this, researchers examined the literature published between 1984 and 2023, comparing various settings and parameters in a database. There are four different categories of LIBS instruments: laboratory-based, online, portable, and telescopic. Additionally, there are four main categories of sample preparation techniques: liquid bulk, liquid-to-solid conversion, liquid-to-aerosol conversion, and hydride generation. Various experimental setups are also in use, such as double-pulse. Moreover, different acquisition settings significantly influence the sensitivity and therefore the detection limits. Documentation of the different methods of sample preparation and experimental settings, along with their main advantages and disadvantages, can help new users make an informed choice for a particular desired application. In addition, the presentation of median detection limits per element in a periodic table of elements highlights possible research gaps and future research opportunities by showing which elements are rarely or not analysed and for which new approaches in sample preparation are required to lower the detection limits.

laser-induced breakdown spectroscopy (LIBS)   elemental analysis   aqueous solutions

trace elements

1. Introduction

The analysis of aqueous solutions for different elements is important for numerous reasons, such as environmental analysis [1], resource estimation [2], hydrogeochemical research questions [3], process control in nuclear fuel reprocessing plants [4], industrial control [5][6][7], food analysis [8], and medical applications [9]. Today, elemental analysis of aqueous solutions is typically performed in the laboratory using well-established methods such as ion chromatography (IC), atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry ICP-MS [10][11].

Another possible analytical technique that is capable of analysing aqueous solutions is laser-induced breakdown spectroscopy (LIBS). The atomic emission spectroscopy technique was developed shortly after the introduction of the first lasers in the 1960s [12]. It involves a low-energy, pulsed laser focused on a sample by a lens. A small volume of the sample is vaporised in a plasma which is created by the high energy density at the surface, and the

emitted light is collected and sent to a spectrometer where it is dispersed [13]. With the use of a detector, the signals are recorded and digitised. The spectrum can be evaluated with suitable software and the atoms, ions and simple molecules contained in the plasma can be determined qualitatively via the characteristic lines [13]. By using certified reference materials (CRMs), it is possible to establish a calibration that also quantifies the elements and molecules present. The advantages of LIBS are typically minimal sample preparation, low instrumentation cost, rapid analysis, simultaneous detection of multiple elements, and the possibility of in situ analysis, real-time analysis, and remote analysis [14][15]. In particular, the analysis of solids, including soils, geological samples, archaeological samples, metals, and alloys using portable LIBS (pLIBS) devices has developed enormously in the last few years [16] and the applications are hardly limited. As a result, pLIBS has established itself as a powerful competitor and companion to portable X-ray fluorescence (pXRF) in field analysis of solids, as it is theoretically capable of analysing the entire periodic table of elements [16][17].

However, the analysis of aqueous solutions with LIBS, whether in the laboratory or in the field, has since played a rather niche role among potent and widely used analytical methods such as ICP-MS, ICP-AES, AAS, and IC [11]. This may be due to the complex interactions during the formation of the plasma at the surface of the liquid [10], or simply because the other methods have become so well-established that it has been difficult for LIBS to establish itself.

In the meantime, numerous sample preparation techniques and experimental setups that circumvent the problems mentioned have been developed and presented in the literature [15][18]. These enable detection limits for several elements that compete with ICP-MS. **Figure 1** illustrates the constant increase in publications on the topic of aqueous solution analysis by LIBS since the first application in 1984 by Cremers et al. [19]. Harun and Zainal already gave a comprehensive overview of different sample preparation techniques in liquid analysis [15]. However, the diversity and variety of different instrument types, sample preparation techniques, LIBS experimental setups, and acquisition settings can be confusing to new users. This may hinder the more widespread use of LIBS in laboratories for aqueous analysis.
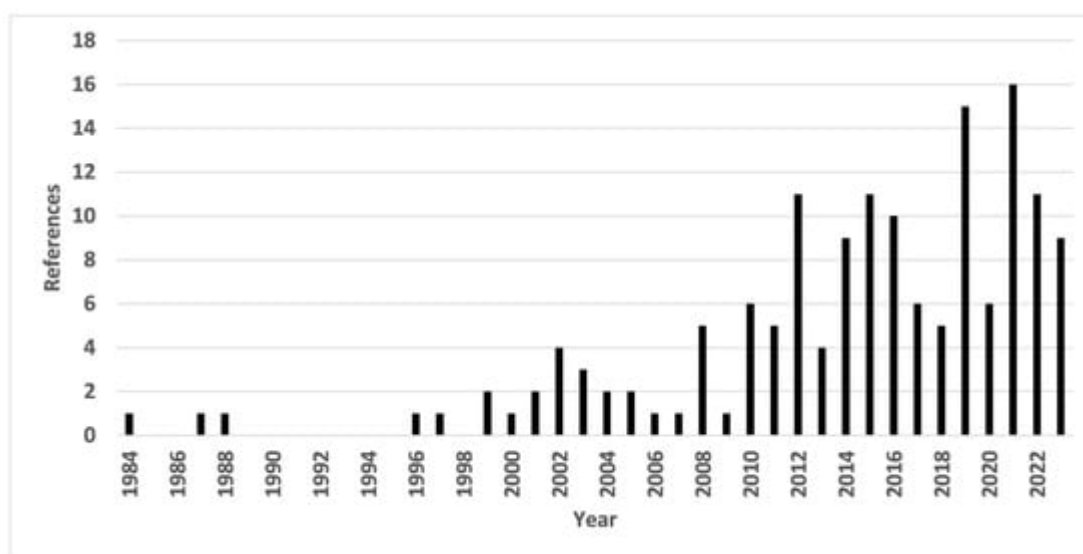
Figure 1. Number of references reporting one or more detection limits for the analysis of aqueous solutions by LIBS from 1984 to date. Data based on the literature reviewed.

Firstly, historical and spatial aspects of research into elemental analysis in aqueous solutions using LIBS are discussed. Sample types and sample preparation techniques to overcome the physical issues are then elaborated on. It is highlighted which sample preparations have given surpassing results and which are not recommended. The focus is less on a comprehensive discussion of the various methods of sample preparation, but rather on which methods are more commonly used and give better results for a specific application. The different types of instruments and their main advantages and disadvantages are also presented. For signal enhancement, different experimental setups are used and their main advantages and disadvantages are discussed. In addition, the most important acquisition settings are presented, as they strongly influence the analysis results. The analysis of the frequency of the different acquisition settings and the different sample preparation techniques used may help scientists who want to use LIBS for their research to make an informed choice for a particular application.

2. Sample Preparation Techniques

It has been shown that there is no standard approach to aqueous LIBS analysis in terms of sample preparation, LIBS experimental setup, or acquisition settings. Several very different techniques are used, each with its own advantages and disadvantages. This is due to the variety of possible applications, ranging from basic research in laboratory analysis, typically using standoff or self-arranged LIBS [20], to remote analysis for hazardous substances, using telescopic systems [21], and to in situ analysis for environmental concerns using online [22] or portable instruments [11]. Therefore, both the LIBS setup and the sample preparation technique should be selected according to the desired application.

However, one of the sample preparation methods can be excluded in the choice of sample preparation. Surface analysis of bulk liquids has many limitations, such as high laser energy requirements and low sensitivity, which have been extensively described in the literature (e.g., [23]), and is therefore not recommended. Splashing and liquid evaporation compensation methods should be used instead. Analysis inside the liquid is a bit more promising but is subject to shot-to-shot variability [24].

Furthermore, in situ applications require sample preparation techniques that are easy to use in the field. Therefore, methods such as LB soaked on FP, SE LSC, and LSC FP are recommended. However, when selecting a sample preparation technique, it should be noted that several sample preparations also pre-concentrate the sample solution and thus can lower the LoDs significantly (e.g., most LSC techniques). This can help to achieve LoDs significantly below 1 mg/L. As portable instruments are typically less sensitive than laboratory devices using higher energies, sample preparation should include preconcentration steps. For online or laboratory analysis, more complex LIBS setups with more complicated sample preparation techniques can be chosen (e.g., LJ, LAC). Here, preconcentration may be helpful but not imperative. Some LJ analysis already reached sensitivities comparable to commercial ICP-AES devices without any preconcentration [7] and could also be used in online and real-time analysis. For Na, cylindrical jets showed lower sensitivity compared to sheet jets [7]. The special form of an LJ

capillary effectively reduces splashing [25] but brings along a more complicated experimental setup and costly consumables.

When only hydride-generating elements (e.g., As or Se) are to be analysed, HG is a good choice as it significantly improves sensitivity by eliminating spectral and chemical interference [26]. However, this method is limited to a small group of elements, which can form hydrides (e.g., As, Sn, Sb, Se, Ge, Pb, Bi, Te), and it requires a complicated measurement setup.

Coupling LIBS with ion exchange techniques can also be a good option to improve sensitivity and reduce matrix effects in LIBS liquid analysis [27]. However, this also requires a complicated setup, which reduces the advantage of simple and fast sample preparation over other methods such as IC. The same is true for the isolated droplet technique. An easy way to avoid splashing is the LSC technique of freezing the sample [28][29]. This sample preparation does not require much expertise or a complicated setup and could also be performed in situ using liquid nitrogen [29]. However, no preconcentration is achieved this way.

ESD achieves preconcentration, but many chemicals are required, as well as additional parts and experimental knowledge. ED also pre-concentrates the samples and therefore has improved sensitivity [30][31]. The main drawback is the comparatively long time required for analysis due to the deposition process (>>10 min). Ad/ab on wood chips [32] or graphene oxide [33] is also quite time consuming but can be realised cost-effectively and improves sensitivity as well. Chelating (e.g., [34]) is even more time-consuming, requires more chemicals, and is usually not possible for multi-element analysis. However, it can be more efficient in enrichment than FP [34]. MeGe, as described by [35], is very similar to chelating, but requires even more time in sample preparation due to the long drying process. This makes the method less favourable in comparison to the other presented methods.

Analysis in ID, either with an isolated droplet generator (IDG) or by acoustic levitation [36], adds complexity in the experimental setup, which minimises its advantages over conventional analytical techniques. NPs have the potential to improve the sensitivity as well [37][38] and are easier to introduce in sample preparation.

When using LSC of a droplet on a surface with no adsorption/absorption step, some form of SE is recommended to improve the homogeneous distribution and shape of the evaporation residue (EvR). Without any SE, an effect typically referred to as the coffee ring effect (CRE) occurs, leading to lowered repeatability due to inhomogeneous distribution of the EvR [39][40]. SE can be implemented by making the surface more hydrophobic to improve the distribution of the EvR [39] to introduce a geometric constraint (GC) technique [41][42] or to combine both [38].

3. Instrument Types, Experimental Setups, and Acquisition Settings

Furthermore, it is also possible to improve the various sample preparations with a special LIBS setup. These include, e.g., double-pulse (DP), laser-induced fluorescence (LIF), resonance-enhanced (RE), resonant (R), and microwave enhancement (MW) LIBS. Depending on the design of the LIBS, such setups may not be possible or

lead to complexity that diminishes the main advantage of LIBS over other laboratory methods in being simple in sample preparation [43]. The simplest method to use is DP, which typically enhances the signal ten times and for some elements up to 50 times [43]. The other experimental setups are more complicated, require more experienced staff, and do not all allow multi-elemental detection, but can improve sensitivity.

The acquisition settings also affect sensitivity and should likewise be adapted to the method. For example, the gate delay should be long enough to minimise the influence of continuum radiation, which typically occurs at the very beginning of the breakdown and provides no useful information, in addition to degrading the signal-to-noise ratio [44]. However, with overly long gate delays, the signal becomes weaker. Although it is possible to set the optimum delay time for each element individually, using different delay times for different elements prevents simultaneous detection. For this reason, when analysing multiple elements, a gate delay should be selected that is suitable for all the elements to be detected.

Another enhancement possibility, which is often easy to implement, is to use a purge gas such as Ar, which also amplifies the signal intensity significantly [45]. Even some portable LIBS units are already equipped with Ar cartridges for signal amplification [39].

A change in pulse duration, pulse energy, wavelength, or repetition rate essentially influences the energy that is supplied to the sample and is thus available for the formation of the plasma. Moreover, increasing the repetition rate reduces analysis time and improves averaging [13]. Typical lasers used in LIBS liquid analysis are Nd:YAG lasers with a fundamental wavelength of 1064 nm. Using different wavelengths can improve detection. For example, the CO_2 wavelength of 10,600 nm is particularly suitable for the analysis of water, as it absorbs in the infrared range [13]. However, the wavelengths used were between 266 and 1064 nm. The wavelengths 532, 355, (352), and 266 nm are the second to fourth harmonics of the Nd:YAG laser, with a fundamental wavelength at 1064 nm.

According to [13], typical pulse energies for LIBS are between 10 and 500 mJ. In the literature reviewed, pulse energies between 0.2 and 800 mJ were found, with most in the range 0.2 to 100 mJ. Energies below 10 and around 100 mJ are the most common. The pulse energy must be high enough to ablate enough material to produce a strong signal. However, a low energy pulse combined with a shorter pulse width and higher repetition rate will also result in a higher power density [13]. Handheld devices generally operate with lower pulse energies. For example, the SciAps Z300 uses a pulse energy of 5–6 mJ, a frequency of 50 Hz (10 Hz), and a pulse width of 1 ns [46].

4. Elements and Their Reported Detection Limits

Looking at the elements analysed, several areas of interest stand out. The frequent testing of potentially toxic elements [47] such as Cr (N = 87) or Pb (N = 76) is particularly striking. There is a very strong interest in the detection of these elements because they are problematic elements in drinking water [48]. Also, Cu and Cd are analysed very frequently, which are also potentially toxic elements [48]. Furthermore, there is a second group of

elements that are often analysed: Na, (Mn), Ca, Mg, Sr, K, and Li. These are typical cations in natural waters and therefore of interest in natural water analysis.

It is striking that arsenic (As) is less often analysed then Cr, Pb, Cu, Cd, and Zn, although it is a very problematic element in drinking water [49]. This may be because As is not as well analysed by LIBS as other elements such as Li and Cr. According to Cremers and Radziemski, the most common and useful spectral range for LIBS analysis is 200–900 nm [13]. Unfortunately, there are few strong lines for As in this range that can be used for quantification. Therefore, for As quantification, it is recommended to use pre-concentration methods or to choose HG.

S, N, F, Br, and P (and to a lesser extent Cl) are also relatively rarely analysed, although they are typically present as anions in natural water. This is also due to the fact that these elements are not analysed as well by LIBS as other elements such as Li and Cr. These six elements have among the highest ionisation energies of the 56 elements for which detection limits have been found. The ionisation energy plays a major role for these elements, since the lines typically chosen for quantification lie in or near to the infrared range (except for P) and are difficult to excite due to the high ionisation energy [50]. The intensities are therefore usually so weak that low concentrations cannot be detected [50][51]. For example, the strongest lines for F and Cl are below 200 nm, below the range of typical CCD detectors and in a range where a vacuum is required in the light path [52]. Therefore, a detour via indirect analysis is usually used (for example, molecular emission, as compounds such as CaF and CaCl show higher intensities) [14]. Another option is to analyse the excess of a more easily analysable element (e.g., Ag or Ba) that reacts with the anions by precipitation [50].

It is also interesting to note that some atypical elements such as Tc were analysed in water. The reason for this is the possibility of remote LIBS analysis. Samek et al. analysed Tc with a telescopic LIBS system over a distance of 3 m [21]. Also, the catastrophe of the Fukushima nuclear disaster has led to development of LIBS aqueous analysis for elements like Cs, Sr, and Zr [53][54][55][56].

References

1. Hartzler, D.A.; Bhatt, C.R.; McIntyre, D.L. Design, Construction, and Validation of an in-Situ Groundwater Trace Element Analyzer with Applications in Carbon Storage. Sci. Rep. 2023, 13, 7516.

2. Zuber, A.; Bachhuka, A.; Tassios, S.; Tiddy, C.; Vasilev, K.; Ebendorff-Heidepriem, H. Field Deployable Method for Gold Detection Using Gold Pre-Concentration on Functionalized Surfaces. Sensors 2020, 20, 492.

3. Koch, S.; Court, R.; Garen, W.; Neu, W.; Reuter, R. Detection of Manganese in Solution in Cavitation Bubbles Using Laser Induced Breakdown Spectroscopy. Spectrochim. Acta Part B At. Spectrosc. 2005, 60, 1230–1235.

4. Wachter, J.R.; Cremers, D.A. Determination of Uranium in Solution Using Laser-Induced Breakdown Spectroscopy. Appl. Spectrosc. 1987, 41, 1042–1048.

5. Kuwako, A.; Uchida, Y.; Maeda, K. Supersensitive Detection of Sodium in Water with Use of Dual-Pulse Laser-Induced Breakdown Spectroscopy. Appl. Opt. 2003, 42, 6052.

6. He, Y.; Wang, X.; Guo, S.; Li, A.; Xu, X.; Wazir, N.; Ding, C.; Lu, T.; Xie, L.; Zhang, M.; et al. Lithium Ion Detection in Liquid with Low Detection Limit by Laser-Induced Breakdown Spectroscopy. Appl. Opt. 2019, 58, 422.

7. Nakanishi, R.; Ohba, H.; Saeki, M.; Wakaida, I.; Tanabe-Yamagishi, R.; Ito, Y. Highly Sensitive Detection of Sodium in Aqueous Solutions Using Laser-Induced Breakdown Spectroscopy with Liquid Sheet Jets. Opt. Express 2021, 29, 5205.

8. Bocková, J.; Marín Roldán, A.; Yu, J.; Veis, P. Potential Use of Surface-Assisted LIBS for Determination of Strontium in Wines. Appl. Opt. 2018, 57, 8272.

9. St-Onge, L.; Kwong, E.; Sabsabi, M.; Vadas, E.B. Rapid Analysis of Liquid Formulations Containing Sodium Chloride Using Laser-Induced Breakdown Spectroscopy. J. Pharm. Biomed. Anal. 2004, 36, 277–284.

10. Bhatt, C.R.; Goueguel, C.L.; Jain, J.C.; McIntyre, D.L.; Singh, J.P. LIBS Application to Liquid Samples. In Laser-Induced Breakdown Spectroscopy; Elsevier: Amsterdam, The Netherlands, 2020; pp. 231–246. ISBN 978-0-12-818829-3.

11. Schlatter, N.; Lottermoser, B.G.; Illgner, S.; Schmidt, S. Utilising Portable Laser-Induced Breakdown Spectroscopy for Quantitative Inorganic Water Testing. Chemosensors 2023, 11, 479.

12. Baudelet, M.; Smith, B.W. The First Years of Laser-Induced Breakdown Spectroscopy. J. Anal. At. Spectrom. 2013, 28, 624.

13. Cremers, D.A.; Radziemski, L.J. Handbook of Laser-Induced Breakdown Spectroscopy, 2nd ed.; Wiley, A John Wiley & Sons, Ltd., Publication: Chichester, UK, 2013; ISBN 978-1-118-56736-4.

14. Tang, Z.; Hao, Z.; Zhou, R.; Li, Q.; Liu, K.; Zhang, W.; Yan, J.; Wei, K.; Li, X. Sensitive Analysis of Fluorine and Chlorine Elements in Water Solution Using Laser-Induced Breakdown Spectroscopy Assisted with Molecular Synthesis. Talanta 2021, 224, 121784.

15. Harun, H.A.; Zainal, R. Laser-Induced Breakdown Spectroscopy Measurement for Liquids: Experimental Configurations and Sample Preparations. J. Nonlinear Optic. Phys. Mat. 2018, 27, 1850023.

16. Senesi, G.S.; Harmon, R.S.; Hark, R.R. Field-Portable and Handheld Laser-Induced Breakdown Spectroscopy: Historical Review, Current Status and Future Prospects. Spectrochim. Acta Part B At. Spectrosc. 2021, 175, 106013.

17. Harmon, R.S.; Senesi, G.S. Laser-Induced Breakdown Spectroscopy—A Geochemical Tool for the 21st Century. Appl. Geochem. 2021, 128, 104929.

18. Keerthi, K.; George, S.D.; Sebastian, J.G.; Warrier, A.K.; Chidangil, S.; Unnikrishnan, V.K. Optimization of Different Sampling Approaches in Liquid LIBS Analysis for Environmental Applications. J. Anal. At. Spectrom. 2022, 37, 2625–2636.

19. Cremers, D.A.; Radziemski, L.J.; Loree, T.R. Spectrochemical Analysis of Liquids Using the Laser Spark. Appl. Spectrosc. 1984, 38, 721–729.

20. Shao, Y.; Ma, S.; Zhao, X.; Tian, H.; Chen, S.; Dong, D.; Zhou, J. Determination of Phosphorus in Water Using Iron Hydroxide Assisted Laser-Induced Breakdown Spectroscopy. J. Anal. At. Spectrom. 2023, 38, 638–641.

21. Samek, O.; Beddows, D.C.S.; Kaiser, J.; Kukhlevsky, S.V.; Liska, M.; Telle, H.H.; Whitehouse, A.J. Application of Laser-Induced Breakdown Spectroscopy to In Situ Analysis of Liquid Samples. Opt. Eng. 2000, 39, 2248.

22. Sui, M.; Fan, Y.; Jiang, L.; Xue, Y.; Zhou, J.; Zhong, S. Online Ultrasonic Nebulizer Assisted Laser Induced Breakdown Spectroscopy (OUN-LIBS): An Online Metal Elements Sensor for Marine Water Analysis. Spectrochim. Acta Part B At. Spectrosc. 2021, 180, 106201.

23. Contreras, V.; Valencia, R.; Peralta, J.; Sobral, H.; Meneses-Nava, M.A.; Martinez, H. Chemical Elemental Analysis of Single Acoustic-Levitated Water Droplets by Laser-Induced Breakdown Spectroscopy. Opt. Lett. 2018, 43, 2260.

24. Goueguel, C.; McIntyre, D.L.; Jain, J.; Karamalidis, A.K.; Carson, C. Matrix Effect of Sodium Compounds on the Determination of Metal Ions in Aqueous Solutions by Underwater Laser-Induced Breakdown Spectroscopy. Appl. Opt. 2015, 54, 6071.

25. Zhang, D.C.; Hu, Z.Q.; Su, Y.B.; Hai, B.; Zhu, X.L.; Zhu, J.F.; Ma, X. Simple Method for Liquid Analysis by Laser-Induced Breakdown Spectroscopy (LIBS). Opt. Express 2018, 26, 18794.

26. Ünal, S.; Yalçın, Ş. Development of a Continuous Flow Hydride Generation Laser-Induced Breakdown Spectroscopic System: Determination of Tin in Aqueous Environments. Spectrochim. Acta Part B At. Spectrosc. 2010, 65, 750–757.

27. Kim, T.; Ricchia, M.L.; Lin, C.-T. Analysis of Copper in an Aqueous Solution by Ion-Exchange Concentrator and Laser-Induced Breakdown Spectroscopy. JNL Chin. Chem. Soc. 2010, 57, 829–835.

28. Harun, H.A.; Zainal, R. Improvement of Laser Induced Breakdown Spectroscopy Signal for Sodium Chloride Solution. Mal. J. Fund. Appl. Sci. 2018, 14, 429–433.

29. Sobral, H.; Sanginés, R.; Trujillo-Vázquez, A. Detection of Trace Elements in Ice and Water by Laser-Induced Breakdown Spectroscopy. Spectrochim. Acta Part B At. Spectrosc. 2012, 78, 62–

66.

30. Chen, Z.; Li, H.; Zhao, F.; Li, R. Ultra-Sensitive Trace Metal Analysis of Water by Laser-Induced Breakdown Spectroscopy after Electrical-Deposition of the Analytes on an Aluminium Surface. J. Anal. At. Spectrom. 2008, 23, 871.

31. Kurniawan, K.H.; Pardede, M.; Hedwig, R.; Abdulmadjid, S.N.; Lahna, K.; Idris, N.; Jobiliong, E.; Suyanto, H.; Suliyanti, M.M.; Tjia, M.O.; et al. Practical and Highly Sensitive Elemental Analysis for Aqueous Samples Containing Metal Impurities Employing Electrodeposition on Indium-Tin Oxide Film Samples and Laser-Induced Shock Wave Plasma in Low-Pressure Helium Gas. Appl. Opt. 2015, 54, 7592.

32. Chen, Z.; Godwal, Y.; Tsui, Y.Y.; Fedosejevs, R. Sensitive Detection of Metals in Water Using Laser-Induced Breakdown Spectroscopy on Wood Sample Substrates. Appl. Opt. 2010, 49, C87.

33. Ruiz, F.J.; Ripoll, L.; Hidalgo, M.; Canals, A. Dispersive Micro Solid-Phase Extraction (DμSPE) with Graphene Oxide as Adsorbent for Sensitive Elemental Analysis of Aqueous Samples by Laser Induced Breakdown Spectroscopy (LIBS). Talanta 2019, 191, 162–170.

34. Tian, H.; Jiao, L.; Dong, D. Rapid Determination of Trace Cadmium in Drinking Water Using Laser-Induced Breakdown Spectroscopy Coupled with Chelating Resin Enrichment. Sci. Rep. 2019, 9, 10443.

35. Lin, Q.; Han, X.; Wang, J.; Wei, Z.; Liu, K.; Duan, Y. Ultra-Trace Metallic Element Detection in Liquid Samples Using Laser Induced Breakdown Spectroscopy Based on Matrix Conversion and Crosslinked PVA Polymer Membrane. J. Anal. At. Spectrom. 2016, 31, 1622–1630.

36. Meneses-Nava, M.A.; Pichardo, J.; Rodriguez, M.; Rosas-Roman, I.; Maldonado, J.L. Detection Enhancement at Parts per Billion Level of Aluminum in Water Droplets by a Combination of Acoustic Levitation and Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy. Spectrochim. Acta Part B At. Spectrosc. 2021, 184, 106280.

37. De Giacomo, A.; Koral, C.; Valenza, G.; Gaudiuso, R.; Dell'Aglio, M. Nanoparticle Enhanced Laser-Induced Breakdown Spectroscopy for Microdrop Analysis at Subppm Level. Anal. Chem. 2016, 88, 5251–5257.

38. Wu, M.; Wang, X.; Niu, G.; Zhao, Z.; Zheng, R.; Liu, Z.; Zhao, Z.; Duan, Y. Ultrasensitive and Simultaneous Detection of Multielements in Aqueous Samples Based on Biomimetic Array Combined with Laser-Induced Breakdown Spectroscopy. Anal. Chem. 2021, 93, 10196–10203.

39. Schlatter, N.; Lottermoser, B.G. Quantitative Analysis of Li, Na, and K in Single Element Standard Solutions Using Portable Laser-Induced Breakdown Spectroscopy (pLIBS). GEEA 2023, 23, geochem2023-019.

40. Liu, K.; Tang, Z.; Zhou, R.; Zhang, W.; Li, Q.; Zhu, C.; He, C.; Liu, K.; Li, X. Determination of Lead in Aqueous Solutions Using Resonant Surface-Enhanced LIBS. J. Anal. At. Spectrom. 2021, 36,

2480–2484.

41. Ma, S.; Tang, Y.; Ma, Y.; Chen, F.; Zhang, D.; Dong, D.; Wang, Z.; Guo, L. Stability and Accuracy Improvement of Elements in Water Using LIBS with Geometric Constraint Liquid-to-Solid Conversion. J. Anal. At. Spectrom. 2020, 35, 967–971.

42. Ahlawat, S.; Mukhopadhyay, P.K.; Singh, R.; Dixit, S.K.; Bindra, K.S. Laser Textured Superhydrophilic Silicon for Uniform Solidification and Sensitive Detection of Water Based Samples Using Laser Induced Breakdown Spectroscopy. J. Anal. At. Spectrom. 2023, 38, 883–892.

43. Cremers, D.A.; Chinni, R.C. Laser-Induced Breakdown Spectroscopy—Capabilities and Limitations. Appl. Spectrosc. Rev. 2009, 44, 457–506.

44. Zhang, D.; Chen, A.; Chen, Y.; Wang, Q.; Li, S.; Jiang, Y.; Jin, M. Influence of Substrate Temperature on the Detection Sensitivity of Surface-Enhanced LIBS for Analysis of Heavy Metal Elements in Water. J. Anal. At. Spectrom. 2021, 36, 1280–1286.

45. Scott, J.R.; Effenberger, A.J.; Hatch, J.J. Influence of Atmospheric Pressure and Composition on LIBS. In Laser-Induced Breakdown Spectroscopy; Musazzi, S., Perini, U., Eds.; Springer Series in Optical Sciences; Springer: Berlin/Heidelberg, Germany, 2014; pp. 91–116. ISBN 978-3-642-45084-6.

46. Wise, M.A.; Harmon, R.S.; Curry, A.; Jennings, M.; Grimac, Z.; Khashchevskaya, D. Handheld LIBS for Li Exploration: An Example from the Carolina Tin-Spodumene Belt, USA. Minerals 2022, 12, 77.

47. Pourret, O.; Hursthouse, A. It's Time to Replace the Term "Heavy Metals" with "Potentially Toxic Elements" When Reporting Environmental Research. Int. J. Environ. Res. Public Health 2019, 16, 4446.

48. Rai, N.K.; Rai, A.K.; Kumar, A.; Thakur, S.N. Detection Sensitivity of Laser-Induced Breakdown Spectroscopy for Cr II in Liquid Samples. Appl. Opt. 2008, 47, G105.

49. Haider, A.F.M.Y.; Parvin, M.; Khan, Z.H.; Wahadoszamen, M. Highly Sensitive Detection of Lead in Aqueous Solution Using Laser-Induced Breakdown Spectroscopy Coupled with Adsorption Technique. J. Appl. Spectrosc. 2021, 87, 1163–1170.

50. Ma, S.; Tang, Y.; Zhang, S.; Ma, Y.; Sheng, Z.; Wang, Z.; Guo, L.; Yao, J.; Lu, Y. Chlorine and Sulfur Determination in Water Using Indirect Laser-Induced Breakdown Spectroscopy. Talanta 2020, 214, 120849.

51. Ma, S.; Guo, L.; Dong, D. A Molecular Laser-Induced Breakdown Spectroscopy Technique for the Detection of Nitrogen in Water. J. Anal. At. Spectrom. 2022, 37, 663–667.

52. Asimellis, G.; Hamilton, S.; Giannoudakos, A.; Kompitsas, M. Controlled Inert Gas Environment for Enhanced Chlorine and Fluorine Detection in the Visible and Near-Infrared by Laser-Induced Breakdown Spectroscopy. Spectrochim. Acta Part B At. Spectrosc. 2005, 60, 1132–1139.

53. Matsumoto, A.; Shimazu, Y.; Nakano, H.; Murakami, K.; Yae, S. Signal Stability of Surface-Enhanced Laser-Induced Breakdown Spectroscopy for Microdroplet Analysis Using a Porous Silicon Substrate. Spectrochim. Acta Part B At. Spectrosc. 2021, 178, 106143.

54. Ramli, M.; Khumaeni, A.; Kurniawan, K.H.; Tjia, M.O.; Kagawa, K. Spectrochemical Analysis of Cs in Water and Soil Using Low Pressure Laser Induced Breakdown Spectroscopy. Spectrochim. Acta Part B At. Spectrosc. 2017, 132, 8–12.

55. Ruas, A.; Matsumoto, A.; Ohba, H.; Akaoka, K.; Wakaida, I. Application of Laser-Induced Breakdown Spectroscopy to Zirconium in Aqueous Solution. Spectrochim. Acta Part B At. Spectrosc. 2017, 131, 99–106.

56. Shimazu, Y.; Matsumoto, A.; Nakano, H.; Yae, S. Sensitive Quantitative Analysis of Strontium in Microdroplet by Surfaceenhanced Laser-Induced Breakdown Spectroscopy Using Porous Silicon 2021. Anal. Sci. 2021, 37, 1839–1841.