

Qualitative and quantitative trace analysis on liquids and solid samples by laser-induced breakdown spectroscopy (LIBS)

Laserinduzierte Plasmaspektroskopie zur qualitativen und quantitativen Spurenanalyse an Flüssigkeiten und Feststoffen

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"In Wirklichkeit sind die Dinge ganz anders als sie wirklich sind…"

(Jersey Jetsch)

Abstract

Laser-induced breakdown spectroscopy is a reliable technique for qualitative and quantitative analysis of elements. Features like *in situ* measurement capability, simultaneous multi-elemental detection, and real-time measurements in the laboratory and in the field make LIBS in a powerful and attractive analytical tool. A further advantage is the ability to investigate samples with hardly any preparation. The necessary sample volume is negligible and therefore, the analysis is almost non-destructive.

In principle LIBS comprises the spectroscopic evaluation of an optical spectrum obtained from a plasma. The plasma is induced on or in the sample by a focused beam of a pulsed laser. A further excitation of the plasma has large potential for sensitivity enhancement. The resulting spectrum includes a signature of the chemical species in the sample. A quantitative information can be obtained from calibration curves. Improved limits of detection occur with added internal standards, because the sample and the standard material are affected in the same way of random fluctuations of emission intensity.

The detection of heavy metals in liquid samples and quantification of their concentration by spectroscopy is particularly important in fields of industrial processing and environmental monitoring. The analysis of liquid samples using LIBS is challenging in terms of limits of detection. Quenching processes in liquids depress the optical emission signal. Transferring the measurement in liquids to a gaseous environment, presented by a cavitation bubble, overcomes this restriction. Two laser pulses are focused subsequently into a liquid sample. The plasma of the first laser pulse expands and finally develops into a cavitation bubble. A further plasma is induced in the cavitation bubble at its maximum size. Those optical emissions lead to reproducible spectroscopic results.

This work shows the improvement of LIBS in aqueous solutions exemplarily of several (trace) elements with special emphasis on environmental concern, e.g., the sensitive detection of chromium, manganese, palladium. Experimental innovation in the double-pulse setup has been combined with the implementation of internal standards.

Manganese (Mn) is a marker for tidal and seasonal fluctuations in the wadden sea. Like sodium chloride its concentration is influenced by the tidal cycle but additionally by seasonal changes due to other mobilizations, e.g. reduction of organic material. Dissolved manganese in distilled water has been determined with a limit of detection of $80 \ \mu g/L$. Optical emission signals have been obtained by excitation of the liquid sample. Strontium (Sr) has been successfully added as an internal standard. The double-pulse laser is guided by an optical quartz fiber into the liquid. Therefore, a target is necessary for absorbing laser energy until a breakdown occurs. It provides the evolution of a stable cavitation bubble and a reliable plasma signal for LIBS after 80 μ s bubble life time.

The transfer of this method to other chemical elements, i.e. palladium (Pd), is possible with some restrictions. Electroless metal deposition of palladium on the target (silicon wafer) has been observed, while chromium and silicon do not influence each other.

Spectroscopic emission intensities of an element are strongly dependent on the physical properties and composition of the surrounding matrix. Complex matrices, like seawater, or elements with a high spectral density of emission lines, like iron, hide minor elements. Resonance fluorescence spectroscopy has been demonstrated as a significant technique to amplify individual optical emission. Therefore, the method has a potential for trace analysis in difficult matrices. In case of indium improved signal intensity of about 350 times has been demonstrated.

Statistical data evaluation using principal components analysis (PCA) is a methodical add-on to enhance the outcome of spectroscopic results. It allows one to differentiate between similar sample groups, e.g. microorganism or pollen. PCA has been tested at historical iron alloy samples, because the main component is iron and the sample spectra have only minor deviations. The method yields a further insight into the variance of the samples, if the data base is sufficiently large. Spectra have been recorded using LIBS and micro LIBS with a focal spot size of approx. 10 μ m. Micro LIBS has a high resolution and enables spatially defined areas like slag inclusion to be investigated.

Laser-induced breakdown spectroscopy in cavitation bubbles has been proved as a feasible method for the elemental analysis of metals in aqueous solution. Special emphasis on the temporal and spatial evolution of the cavitation bubble is therefore necessary which is strongly dependent on the laser energy, the focusing of the laser beam, etc. A novel and powerful optical method to diagnose the temporal and spatial evolution of cavitation bubbles in liquids has been developed. It enables the dynamics of laser-driven cavitation bubbles to be experimentally analyzed with the help of a HeNe laser. Various liquids, i.e. distilled water and glycerine for its high viscosity and density have been under investigation.

LIBS in cavitation bubbles is an analytical method to determine dissolved heavy metals in a concentration range down to the range of $\mu g/L$. The method has been tested on the example of chromium, manganese, palladium, and indium. Selective excitation of certain emission lines enhances signal intensities. As well the data evaluation of unspecific spectra can be investigated by chemometrics.

Kurzfassung

Laserinduzierte Plasmaspektroskopie (laser-induced breakdown spectroscopy, LIBS) ist für eine zuverlässige qualitative und quantitative Analyse chemischer Spurenelemente geeignet. Die Methode zeichnet sich durch die Möglichkeit der online und *in situ* -Messung, simultaner Multielementanalyse sowie durch die Echtzeitanalyse im Labor aber auch in Feldmessungen aus. Die Analyse kann in der Regel ohne Probenvorbereitung durchgeführt werden. Da nur eine geringe Probenmenge von wenigen Mikrogramm ablatiert wird, ist die Methode außerdem minimalinvasiv.

Das Grundprinzip von LIBS ist einfach. Die wesentlichen Elemente des Messaufbaus sind ein Pulslaser, ein Spektrometer sowie eine Datenauswertung. Der Laserstrahl wird direkt auf bzw. in die Probe fokussiert und erzeugt dort ein Plasma. Die emittierten optischen Signale sind elementspezifisch und ein Maß für die Zusammensetzung sowie die Konzentrationen. Ein quantitatives Ergebnis kann durch die Verwendung von Standardproben und mittels Kalibrationskurven erzielt werden. Das optische Signal der Probe unterliegt stark den Einflüssen der Laserleistung und Fluktuationen bei der Anregung. Die Verwendung eines internen Standards ermöglicht eine Entkopplung von solchen Effekten und führt zu besseren Nachweisgrenzen.

Die Analyse von Schwermetallen und deren Konzentrationsbestimmung in flüssigen Proben ist in der Überwachung von industriellen Produktionsprozessen und im Bereich der Umweltanalytik im Zusammenhang mit online-Monitoring von großem Interesse. Konzentrationsbestimmungen mittels LIBS sind in Flüssigkeiten oftmals weniger nachweisempfindlich als an Feststoffen in Luft. Die Fluoreszenz nimmt ab, weil eine Energieübertragung auf andere Moleküle erfolgt. Diese geringeren Emissionen haben schlechtere Nachweisgrenzen zur Folge. Das Quenching ist aber vernachlässigbar, wenn das Plasma in eine gasförmigen Atmosphäre in Form einer Kavitationsblase induziert wird. Die Kavitationsblase wird dabei ebenso wie das Plasma mit einem Laser erzeugt.

Diese Arbeit zeigt die Möglichkeiten von LIBS zur Untersuchung flüssiger Proben durch methodische Entwicklungen am Beispiel umweltrelevanter Elemente wie Chrom, Mangan und Palladium. Gelöstes Mangan kann als geochemischer Marker für mikrobiologische Aktivitäten im Sediment des Wattenmeeres verwendet werden. Ähnlich wie bei Natriumchlorid variiert die Konzentration durch Ebbe und Flut, allerdings zeigt sich eine zusätzliche Abhängigkeit von jahreszeitlichen Entwicklungen. Mangan wurde mit einer exzellenten Nachweisgrenze von 80 μ g/L unter Verwendung von Strontium als internem Standard mittels eines fasergeführten Lasers direkt in wässrigen Proben bestimmt. Um eine ausreichend hohe Leistungsdichte für einen optischen Durchbruch zu erreichen, wurde ein Target in Form eines Siliziumwafers vor der Faser platziert. Die Methode ist generell auch zur Konzentrationsbestimmung andere Elemente einsetzbar. Am Beispiel von Palladium hat sich allerdings gezeigt, dass es unter Verwendung eines Siliziumtargets zu einer stromlosen Metallabscheidung kommt. Dadurch wird Palladium in Abhängigkeit von der Zeit und der Anzahl der Laserpulse auf dem Target angereichert. Ein Einfluss auf die Konzentration von Chrom ist im Gegensatz dazu nicht nachweisbar.

Die Nachweisgrenzen einzelner Elemente können in Proben unterschiedlicher Zusammensetzung variieren. Komplexe Probenzusammensetzungen, wie in Meerwasser, oder Proben mit hoher spektraler Dichte, z.B. Eisen, überlagern Elemente geringerer Konzentrationen. Aus diesem Grunde wurde die Resonanzfluoreszenzspektroskopie in Flüssigkeiten unter Verwendung von Kavitationsblasen erprobt. Diese Technik erhöht die Fluoreszenz durch eine resonante Anregung spektraler Emissionslinien um Größenordnungen. Am Beispiel von Indium wurde eine Signalverstärkung um einen Faktor 350 gezeigt.

In dieser Arbeit wurde ebenfalls auf die Möglichkeiten der statistischen Datenauswertung eingegangen. Proben, die aus komplexen Materialien mit ähnlichen Hauptkomponenten bestehen, sind oftmals schwer voneinander zu unterscheiden. Die Hauptkomponentenanalyse ermöglicht eine Klassifizierung auf der Datenbasis spektroskopischer Untersuchungen. Am Beispiel historischer Eisenproben wurde die Methode evaluiert und als vielversprechend eingestuft. Allerdings muss ein ausreichend großer Datensatz zur Verfügung stehen, der auch die ursprünglichen Erze der Proben mit einschließt. Micro-LIBS, mit einem Ablationsbereich von ca. 10 μ m Durchmesser, ist für die Analyse von Probenmaterial geeignet, das wie z.B. Schlackeeinschlüsse in Stahlproben, eine hohe räumliche Auflösung benötigt.

Laserinduzierte Plasmaspektroskopie an Kavitationsblasen hat sich als zuverlässige Methode der Elementanalyse von Schwermetallen in Flüssigkeiten bewiesen. Die Dynamik der Blasenentwicklung muss dafür allerdings bekannt sein. Diese ist ebenso wie die Form der Kavitationsblase unmittelbar von der verwendeten Laserenergie, der Fokussierung des Laserstrahls, dem Absorptionsverhalten der Flüssigkeit und anderen Parametern beeinflusst. Die Entwicklung einer optischen Methode unter Verwendung eines HeNe-Lasers ermöglicht die räumliche und zeitliche Analyse von laserinduzierten Kavitationsblasen. Die Methode wurde an destilliertem Wasser, sowie wegen der hohen Viskosität und Dichte an Glycerin erprobt.

LIBS in Kavitationsblasen ist für die Schwermetallanalyse in wässrigen Proben je nach chemischem Element in Konzentrationen bis in den Bereich von wenigen $\mu g/L$ geeignet. Die Methode wurde exemplarisch an Chrom, Mangan, Palladium und Indium unter Einsatz verschiedener Versuchsaufbauten und der Verwendung von internen Standards getestet. Die selektive Fluoreszenzanregung von Emissionslinien führt dabei zu einer Signalverstärkung einzelner Linien, während der Einsatz chemometrischer Methoden eine Gruppierung der LIBS-Spektren ohne die Betrachtung diskreter Linien ermöglicht.

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1 Motivation

Laser-induced breakdown spectroscopy (LIBS) is a versatile analytical tool in the field of optical emission spectroscopy (OES). Samples of all states of aggregation can be investigated often without any preparation. Applications can be found in both research and industry, in many fields comprising life science to space exploration. The rather simple basic setup of a laser and a detection system can be adapted to many tasks. It can be improved by modulation of laser energy and wavelength as well as spectrometer specification, i.e. resolution, spectral band width, and sensitivity of the detector. The further application of sequential laser pulses using an ablation pulse followed by a re-excitation pulse is suitable to improve the detection limits of LIBS. However, the timing between the laser pulses and data acquisition is critical.

The main advantages of laser-induced breakdown spectroscopy are those of OES. Generally, all elements of the periodic table and fragments of molecules can be detected. Even the ability of simultaneously multi-elemental detection is given.

Additionally, LIBS is a powerful analytical tool owing to its *in situ* measurement capability and the possibility of real-time analysis in the laboratory or in the field. Several significant advantages make LIBS well applicable [SiRa11], [SaCi95], [CrRa06]:

- hardly any sample preparation is necessary
- a negligible amount of sample is needed (submicrogram)
- application to solid, liquid, and gaseous samples
- rapid method allows online analysis
- adaptability to different measurement scenarios including the use of optical fibers
- analysis of hazardous substances by remote control
- in situ measurements due to optical access to sample material
- high sensitivity on some elements, e.g monitoring of chlorine, fluorine
- reliable plasma
- sample vaporisation and excitation in one single step

Laser excitation leads to atomization and vaporization of the sample thus producing free atomic elements (ions, atoms, and electrons). Therefore, a limitation of LIBS is given in the field of analytics of molecules. The sensitivity of LIBS, hence the lower limits of detection (LOD), is confined in several cases compared to other (standard) analytical methods e.g. ICP-OES (inductively coupled plasma-optical emission spectrometry). Thus, research is taking effort in exploiting the technique's potential and minimizing the drawbacks. Nevertheless, the positive features of LIBS are outstanding for many applications. LIBS enables a detailed analytics of elements and will be presented in this thesis.

A comparison of laser-induced breakdown spectroscopy with other conventional spectroscopic methods like atomic absorption spectroscopy (AAS), ICP-OES, X-ray fluorescence (XRF) is shown in the following Table 1.1.

Method Advantage Disadvantage LIBS simultaneous multi-element analysis, greater sensitivity for the detection of portable, organic compounds are posan element in its native matrix sible AAS quite inexpensive analysis one element at a time, ashing destroys organic compounds **ICP-OES** multi-elemental spectrum, high resosample preparation lution, reduced molecular interference, higher sensitivity and LOD XRF nondestructive, portable inability to detect elements with atomic number < 12

Table 1.1: Merit of conventional atomic spectroscopic techniques compared to LIBS [SiRa11]

The aim of this work is the trace analysis of heavy metals e.g. manganese (Mn), chromium (Cr), and palladium (Pd) in liquid samples with environmental impact. The concern about heavy metals, hence elements with a higher atomic weight, is often contributed to their toxicity. In the case of manganese, the element is a marker in coastal flat tidal waters of the North Sea. Large changes in concentration of manganese appear during tides and seasons due to the binding of manganese with mineral particles in suspension or precipitation in the sediment. Primary organic particle production and microorganisms are responsible for re-mineralization. They have a specific influence on the heavy metal budget of the water and on mineral materials in suspension [WSG94], [Las195], [Sch97].

A LIBS methodology has been developed to detect the manganese concentration in a simple, rugged, and sensitive analysis. It is applicable to other heavy metals as well and shows a high potential to be instrumented for field use in a further step. The location to implement this method is a backbarrier tidal flat area close to the East Frisian island Spiekeroog in the German Wadden Sea. The research group on "BioGeoChemistry of Tidal Flats" has concentrated their work on this area, aiming to understand the fundamentals of important processes in a tidal flat system in general.

Furthermore, the detection and qualitative analysis of heavy metals in liquid samples and their quantification by spectroscopy are particularly important in fields of industrial processing, environmental monitoring, and the treatment of waste material [RaCr89]. Organometallic compounds e.g. arising from the biological conversion of inorganic metallic contaminants or from direct discharge to the aquatic system are often harmful. Various heavy metals like chromium, iron, cobalt, copper, manganese, molybdenum, nickel, vanadium, zinc, and tin are valuable micronutrients.

Metals in liquid samples like seawater or even distilled water are more difficult to analyze compared solid samples. To prevent strong quenching effects, different techniques have been employed such as e.g. analysis on flowing surfaces [OKS+04], on frozen samples [CTT+01], and on nebulized liquids [KYM+03]. If a reliable system in a rough environment like seawater containing algae and particulate matter is required, the use of nozzles, nebulizers or jets might be failure-prone.

An elegant approach to create a transient gaseous environment within the liquid sample has been introduced by creating a cavitation bubble induced by a laser pulse. A further laser pulse induces a plasma for spectroscopy within the lifetime of this cavitation bubble. The latter is filled with vaporized liquid and gas. Cavitation bubble and LIBS plasma are induced directly in the liquid or on a target. The target serves primarily as an absorber to start the optical breakdown if laser energy is guided via an optical fiber.

Evaluation of spectral data with internal standards is useful to overcome the influence on experimental data in terms of variations at the plasma and cavitation bubble parameters. An approximately comparable vapor pressure of internal standard and analyte must be realized to achieve reproducible data, since fractional evaporation from the ablated droplets changes the ratio of free atoms until full dissociation.

This cumulative thesis is focused on developing the methodology of laser-induced breakdown spectroscopy in liquid samples on (heavy) metals. It comprises the results in four publications on the issue of the metals chromium, manganese, indium, and palladium (cf. Chapter 4). In respect to the fact that cavitation bubbles are the environment used for spectroscopy, the investigation of shock waves and cavitation bubbles and the development of an optical method to detect their dynamics are discussed in two publications (cf. Chapter 5). Further more, the classification of samples in categories by applying chemometrics to LIBS spectra has been under consideration (see Chapter 6).

Laser-induced breakdown spectroscopy in liquid samples on (heavy) metals

Detailed results are presented in Chapter 4 "Laser-induced breakdown spectroscopy on plasma in cavitation bubbles":

• The toxicity of chromium (Cr) compounds depends on the oxidation state of the metal. Chromium (III) is an essential nutrient that can be toxic in large doses. The World Health Organization (WHO) has classified chromium (VI) as a human carcinogen.

A simple and non failure-prone setup using laser-induced breakdown spectroscopy to detect chromium in liquid samples has been developed.

S. Koch, W. Garen, M. Müller, W. Neu, Detection of chromium in liquids by laser induced breakdown spectroscopy (LIBS), Appl. Phys. A **79** (2004) 1071-1073 [KGM+04]

• Manganese (Mn) is a marker for tidal and seasonal fluctuations in the wadden sea. Like sodium chloride it is influenced by high and low tide, but additionally it shows influences by seasonal changes due to other mobilizations, e.g. reduction of organic material.

The design and development in the methodology of LIBS in a cavitation bubble are focused on the improvement of the limit of detection. This double-pulse technique induces the cavitation bubble and the LIBS plasma by a fiber-guided laser onto a target.

S. Koch, R. Court, W. Garen, W. Neu, R. Reuter, Detection of manganese in solution in cavitation bubbles using laser induced breakdown spectroscopy, Spectrochim. Acta B 60 (2005) 1230-1235 [KCG+05]

• Indium (In) was chosen as a test element due to its excitation scheme. It enables emission lines to be acquired by spatial separation from spectral lines re-excited by a tunable laser. The developed methodology is intended for use in investigations of difficult matrices (such as salt water) or elements with interference lines (such as iron). Indium itself is not particularly interesting in the field of environmental analysis.

S. Koch, W. Garen, W. Neu, R. Reuter, Resonance fluorescence spectroscopy in laser-induced cavitation bubbles, Anal. Bioanal. Chem. **385** (2006) 312-315 [KGN+06]

• Palladium (Pd) belongs to the platinum group elements (PGE). Exhausted PGE are found in urban air and accumulate on the road surface and in roadside soil. Transport of PGE via surface drainage following strong rainfall results in contamination of aquatic environments. There is now increasing evidence that a fraction of PGE in the environment is bioavailable, and potential uptake into the biosphere is raising concerns over potential risks for humans and the environment.

A target-less LIBS method in a cavitation bubble has been developed to detect elements despite electroless deposition.

S. Koch, M. Reck, W. Neu, R. Reuter, Spectroscopy on laser induced plasma in cavitation bubbles, Proc. SPIE **7376** (2010) 73761F [KRN+10]

Cavitation bubbles and dynamics

Detailed results are presented in Chapter 5:

• LIBS experiments can be performed in a micro-environment of a laser-induced cavitation bubble to avoid quenching processes. Experiments carried out in a double-pulse mode at an appropriate time delay between the plasma and the bubble at the maximum size of the bubble ensure an intense spectra [GDC+06].

For this reason, important physical phenomena of cavitation by laser-induced optical breakdown have been analyzed and modeled. Distilled water and a retrograde fluid, isooctane, have been under investigation to identify the differences in the cavitation process and shock wave propagation. Images of the bubble and the shock waves have been recorded with an exposure time of 100 ns or a multiple exposition to estimate their temporal evolution.

M. Müller, W. Garen, S. Koch, F. Marsik, W. Neu, E. Saburov, Shock waves and cavitation bubbles in water and isooctane generated by Nd:YAG laser. Experimental and theoretical results, Proc. SPIE 5399 (2004) 275-282 [MGK+04]

• Further-more, a versatile optical method to detect the dynamic of the cavitation bubble has been developed. The maximum radius of the bubble and the collapse time, depending on several parameters like energy and composition of the liquid, can be measured. The spectroscopic analysis in a cavitation bubble needs to be carried out, before the pressure rises inside the bubble due to a collapse, hence at the maximum radius of the bubble. The novel method determines the timing for LIBS in a cavitation bubble instantly. Distilled water and glycerine regarding its high viscosity and density have been under investigation.

S. Koch, W. Garen, F. Hegedüs, W. Neu, R. Reuter, U. Teubner, Time-resolved measurements of shock-induced cavitation bubbles in liquids, Appl. Phys. B (2012) DOI: 10.1007/s00340-012-5070-1 [KGH+12]

Laser-induced breakdown spectroscopy applied to historical iron samples Detailed results are presented in Chapter 6:

LIBS in combination with chemometrics is a versatile tool for classifying samples in categories. Principal components analysis (PCA) is a widely used statistical technique in chemometrics. PCA applied to LIBS spectra improves the access to the elemental composition. This diagnostic tool allows to trace molecules and cluster as well. The combination of both methods shows potential for *in situ* online determination [DCP08]. Improved application of LIBS-based discrimination by employment of statistical methods is ongoing on chemical and biological samples. In this investigation, chemometrics have been applied to data recorded by LIBS of a collection of weapon and armor objects (16th-19th centuries). Results of LIBS and PCA of historical samples with the main component iron are presented.

S. Koch, D. Anglos, B. Meyerer, E. Peev, J. Diekhoff, W. Jahn, C. Jöhnk, M. Sohn, P. Siozos, U. Teubner, W. Neu, Laser-induced breakdown spectroscopy applied to historical iron samples, submitted to Journal of Cultural Heritage (2012) [KAM+12]

2 Fundamentals

The characteristics of laser-induced plasma have a major influence on quantitative LIBS analysis. Spectral emission of the plasma is not only related to the concentration of the elements constituents but also to a number of parameters of the laser ablation process for example fluence, pulse duration, power density, wavelength, etc., sample composition and matrix effects. The laser ablation process includes evaporation, vaporization, atomization, ejection of atoms, ions, molecular species and fragments; gas and hydrodynamic expulsion; shock waves; plasma initiation and expansion; plasma-matter interactions; etc. [Russ95].

2.1 Plasma physics

Dielectric breakdown occurs at partial or complete ionization of a solid, liquid, or gas through absorption of thermal or electromagnetic energy. The ionization results in a plasma, the fourth state of matter. A plasma is a gas mixture containing neutral particles (atoms and molecules, respectively), positive ions, and free electrons which interact with each other and photons of different energy levels and excitation states. One possibility of plasma generation is a laser-induced breakdown. The following sections describe the plasma evolution in liquids and its relevance for element spectroscopy, and the development of a cavitation bubble used as a gaseous environment for spectroscopy.

2.1.1 Plasma generation

Monochromatic, linearly polarized plane waves, as an approximation of a real laser beam, are propagating in condensed matter (solid or liquid) with an energy of $E = \hbar \omega$, where \hbar is Planck constant h divided by 2π and ω is the angular frequency.

The interaction between the electromagnetic field (\vec{E}, \vec{B}) of laser radiation and matter is related to absorption. The most crucial parameter is the absorption coefficient α of linear as well as nonlinear interaction. Basically, the absorption can be described by Lambert-Beer's law:

$$I(x) = I_0 \cdot e^{-\alpha x} \tag{2.1}$$

The absorption length is defined by $1/\alpha$ [Fran65]. Absorption coefficient and absorption length of water as a function of the wavelength are shown in Figure 2.1.



Figure 2.1: Absorption coefficient and absorption length in water in the 0.2 μ m to 200 μ m wavelength region [HaQu73]

Water does not contain free moving electrons. The electrons are bound to a particular molecule. Generation of free electrons in water needs a photon with energy corresponding to wavelengths of $\lambda \approx 190$ nm or less or a temperature $T \approx 75\,000$ K to exceed the excitation potential of water which is $E_{Ion} = 6.5$ eV for the condensed state. These electrons are "quasi-free", i.e. their kinetic energy is large enough that they can move through the liquid without being trapped by localized potential wells. Therefore thermal or linear absorption do not lead to sufficient ionization and plasma. Mainly direct ionization of the medium by multiphoton absorption or cascade ionization, also called avalanche ionization, leads to a laser-induced plasma [KHR97].

Cascade ionization

Cascade ionization is initiated through the creation of "seed" electrons. The cascade needs only a few free electrons available in the volume of the focused laser beam prior to the pulse. An impure medium allows most likely the ionization of impurities by thermal excitation hence producing "seed" electrons. The generation of seed electrons in a pure medium is related to the ionization of a few molecules in the medium through multiphoton absorption [KHR97].

Once seed electrons are available the cascade built-up to high free electron densities begins. Free electrons are accelerated by absorbing energy of laser photons during collision with heavy particles, i.e. ions or molecules. This mechanism is called inverse bremsstrahlung (IB) (absorption) and can be approximated as [Bekf76]

$$\alpha_{IB}(\text{cm}^{-1}) = 1.37 \cdot 10^{-35} \ \lambda^3 \ n_e^2 \ T_e^{1/2}, \tag{2.2}$$

where λ (µm) is the wavelength of the laser radiation, T_e (K) is the electron temperature and n_e (cm⁻³) is the electron number density. When a free electron absorbs a photon [ZeRa66], heavy particle collisions are necessary to satisfy energy and momentum conservation. A free electron, that gained an energy larger than the ionization energy, may ionize an atom or molecule by collision, therefore producing two electrons of lower energy. The nonresonant continuum absorption of the laser radiation by free electrons and plasma charges describes a cascade ionization because the electron collisions lead to further ionization and dissociation of molecules in approx. 10^{-15} s. Shockley [Shoc61] introduced the lucky electron model. It assumes that the statistic of a cascade breakdown process is driven by the probability of a seed electron gaining enough energy from the field to produce the first ionization of a bound electron. The probability P shows an exponential dependence on E, the root-mean-square optical electric field [BaBa72], [KHR97]:

$$P = A' \exp\left(\frac{-K'}{E}\right) \tag{2.3}$$

where the factor A' depends on the number of initially free electrons in the focal volume, the pulse width τ_p , the average time between collisions, the fraction of collisions that are energy absorbing and therefore "lucky", and the number of half-cycles of the field needed to reach the ionization energy E_{Ion} . The factor K' depends on the mean free path between collisions and on E_{Ion} .

Multiphoton absorption

Multiphoton absorption of the excited or of the ground state atoms leads to ionization and the generation of free electrons. As described above, the direct photo-ionization by the absorption of a single laser photon is ruled out due to $\hbar\omega_{photon} > \hbar\omega_{laser}$. The only possibility for photo-ionization absorption to occur is by simultaneous absorption of a number of photons, which is less probable because the absorption cross section decreases. As well the absorption coefficient is rapidly decreasing in a nonlinear optical process, therefore multiphoton absorption becomes significant at high irradiance only [KHR97].

Cascade and multiphoton ionization are dependent on the beam irradiance I_{rad} (photons per unit area per unit time) in the breakdown volume. The breakdown threshold for pure aqueous media is significantly higher for multiphoton-initiated breakdown as opposed to impurity-initiated cascade breakdown. This is valid at pulse widths $\tau_p \leq$ some nanoseconds. Impurities can significantly lower the cascade breakdown threshold by contributing seed electrons (cf. Fig. 2.2). Both, medium characteristics (ionization energy, impurity level) and beam characteristics (wavelength, pulse width, focal spot size) are related to the required threshold irradiance I_{rad} , e.g. $I_{rad} > 10^{10} \text{ W/cm}^2$ [VNN+98] for water.



Figure 2.2: Irradiance threshold for LIB in pure and impure water (tap water) at a wavelength of 1064 nm dependent on pulse width and laser spot size between 10 μ m and 90 μ m [KHR97]

Due to the high density of free electrons the absorption of laser radiation by the plasma is leading to high temperatures of $> 20\,000$ K in the early plasma lifetime [CrRa06]. In aqueous media 6000 - 15000 K [BaRi68] and 20 - 60 kbar [VBJ94], respectively,

are achieved. Successively, a thermal plasma expansion ($\sim 10^5$ m/s) at supersonic velocities follows which in turn creates a shock wave. The particle number rises due to dissociation in molecules, ions, atoms, and electrons. The energy for the dissociation of molecules is approx. 3-5 eV, which is the mean value of bond energy of molecules. The number of particles in liquid can be determined from the Avogadro number, the molecular weight, and the density with $3.3 \cdot 10^{22}$ molecules/cm³. The minimum ionization energy for water is $E_{Ion} = 6.5$ eV, due to a transition from a 1b₁ molecule band to an exciton band [WVH76]. The two bond electrons in this orbital are rather easy to ionize and therefore leading to a calculated electron density of $n_e = 6.6 \cdot 10^{22} \text{ cm}^{-3}$. Significant absorption and scattering of the incident laser radiation leads to a fractional ionization of $3 \cdot 10^{-3}$ in water [BaRi68] resulting in a critical free electron density of $n_e = 2 \cdot 10^{20} \text{ cm}^{-3}$. This value corresponds with data evaluation from Kennedy et al. [KHR97] with an electron density of 10^{20} cm⁻³ for the "flash" endpoint and 10^{18} cm⁻³ for the bubble endpoint while Hahn and Panne [HaPa07] estimated an electron density of typically $10^{17} - 10^{19}$ cm⁻³. The critical free electron density $n_e = 10^{18}$ cm⁻³ for the standard theoretical definition of a breakdown [HJF+97] will be considered for further assumptions.

2.1.2 Laser-induced cavitation bubbles

The plasma starts to expand from the onset of the breakdown at the focal volume in all directions until it is thermalized. However, the rate of expansion is largest towards the focusing lens, because the laser radiation enters the plasma from that direction and is strongly absorbed. The pear- or cigar-shaped expansion results from this nonisotropic absorption and is called moving breakdown [CrRa06], [DRC+88].

The plasma expands adiabatically after the termination of the laser pulse [SiNa90] with the thermodynamic relation

$$T \cdot V^{\kappa-1} = constant, \tag{2.4}$$

where κ is the ratio of specific heat capacities at constant pressure and volume V. The adiabatic expansion at supersonic speed leads to a compression of the liquid and the formation of a shock front surrounding the plasma. The high temperatures in the plasma lead to the creation of a bubble enclosing plasma volume. The bubble is a thin layer of water vapor and diffused gas at high temperature and pressure which grows into a cavitation bubble as the plasma continues to expand, to cool, and to decay [VBP96]. Fig. 2.3 shows the cavitation bubble evolution and energy conversion due to laser-induced breakdown in water.



Figure 2.3: Cavitation bubble evolution and energy conversion due to laser-induced breakdown in water [Mull07]

Here, the maximum radius of the bubble r_{max} is reached at approx. $\Delta t = 80 \ \mu s$ (according to this work). The mean expansion speed of the bubble (ca. 0.2 m/s) is much smaller than the velocity of e.g. nitrogen with $\approx 500 \text{ m/s}$ at 300 K. Therefore a homogenous local density and energy distribution in the volume of the bubble can be estimated.

The growth of the bubble leads to a decreasing pressure inside the bubble due to the increasing volume of the bubble and due to the condensing vapor at the phase boundary. As a result, the pressure is reduced to the saturated vapor pressure of the liquid. The bubble reaches its maximum radius when the evaporation of liquid into the bubble equals the condensation of vapor out of the bubble.

At this stage where $r_b = r_{max}$, the cavitation bubble is supporting a gaseous environment for spectroscopy. The index *b* refers to the bubble. If the temperature, *T*, is uniform and the bubble contains only vapor, the internal pressure p_b will be the saturated vapor pressure $p_v(T)$ [ALT+01]. The system has reached a thermodynamic equilibrium but not a dynamic equilibrium. $T_b(t)$ is not necessarily to determine at maximum radius, because the difference between the unknown temperature T_b and the known temperature T_{∞} in the surrounding liquid is negligible [Bren95].

In this stage, quenching effects will be reduced and another excitation provides species for spectroscopy. Spectral lines are estimated to show a reduced line width than in air at atmospheric pressure due to the low pressure side in the cavitation bubble [Nyga93]. The further development of the cavitation bubble is of interest only in respect to cavitation bubble dynamics and does not influence spectroscopic approaches.

"Cavitation and bubble dynamics" by Brennen [Bren95] and "Fundamentals of cavitation" by Franc and Michel [Fran04] are standard literature with detailed explanations of cavitation bubbles and related phenomena. A brief overview according to Kennedy *et al.* [KHR97] is given in the following passage.

After it's maximum expansion the bubble starts to shrink because the pressure of the surrounding liquid exceeds the saturated vapor pressure $p_{H_20} \approx 20$ mbar inside. The bubble collapses when the rate of condensation cannot off set the volumetric reduction. The rising temperature and pressure may release a second shock wave and heat the gas sufficiently to cause the bubble to re-expand, if enough energy is stored in the bubble. The diversion into an acoustic transient and further processes, such as heating the surrounding liquid, is responsible for the loss in the bubble's internal energy. Depending on the amount of energy the bubble oscillation may continue for several cycles of expansion and collapse, although the generation of an acoustic transient occurs in typically only the first few cycles. Typically, smaller residual bubbles are observable in the initial area after the end of oscillation of the cavitation bubble. In presence of a solid boundary a liquid formation jet occurs during the collapse [KHR97]. Mainly cavitation bubbles in liquids are under investigation by several research groups because of the thermal and mechanical effects including the destructive action.

2.2 Plasma properties and spectroscopy

Quantitative analyses of the elemental composition of a sample by means of laserinduced plasma requires the measurement of intensities of those spectral lines that are characteristic for the individual species present in the specimen. The intensities must then be related to the number densities of the species. Plasma dynamics can be described when the system achieves a thermodynamic equilibrium after a certain relaxation time τ .

Thermodynamic equilibrium

A thermodynamic equilibrium describes a plasma characterized by the same temperature for a system composed of electrons, atoms, ions, and radiation by statistical mechanics [Mull89]. The Boltzmann distribution function describes the relative population distribution n_u^s having excitation energy E_u e.g. of atoms or ions at thermal equilibrium [Grie63], [Thor88]

$$n_u^s = n^s \frac{g_u}{U^s(T)} \exp\left(-\frac{E_u}{kT}\right) \tag{2.5}$$

where n_u^s indicates the population density of the excited level u of species s,

 g_u is the statistical weight,

 E_u is the excitation energy of the level u,

 n^s is the total number density of the species s in the plasma,

 \boldsymbol{k} is the Boltzmann constant, and

 $U^{s}(T)$ is the internal partition function of the species at temperature T.

The internal partition function

$$U^{s}(T) = \sum_{u} g_{u} \cdot \exp\left(-\frac{E_{u}}{kT}\right)$$
(2.6)

describes the summation over all allowed electronic energy level E_u with the statistical weight g_u . At low temperatures, the partition function may be approximated by the degeneracy of the ground state if the first excited state energy is very large compared with $E_{therm} = kT$.

Local thermodynamic equilibrium (LTE)

In fact, thermodynamic equilibrium would either require an unbound, spatially and homogenous plasma or a plasma enclosed in a ideal blackbody hohlraum (cavity) [Grie97]. A useful approximation is a local thermodynamic equilibrium. In LIBS plasmas, where the ionization degree is sufficiently high, LTE allows the use of thermal equilibrium relations for level populations and particle velocity distributions.

In such a maximum entropy configuration where the system can be described by the scalar magnitude "temperature", indeed also for the electrons (Boltzmann energy distribution function with Maxwellian velocity distribution), this temperature is governing - amongst others - the excitation of energy levels excitation for radiative transition in atoms and molecules. For thermal equilibrium conditions at this very temperature, the concentration of particular species, like neutrals, dissociated, ionized, and excited atoms and molecules is described by the Saha equation which bases on the law of mass action.

For the characterization of the behavior of the plasma after the second excitation laser pulse collisional processes must be much more dominant than radiative ones, to make sure that the deficit of radiative energy is negligible. This means that the probability of de-excitation by inelastic collision for an excited state must be very large compared to that of spontaneous emission to fulfill the criterion for the LTE.

Zel'dovich and Raizer [ZeRa66] estimated the thermalization described by the relaxation time τ of energy exchange between heavy particles (ions and neutrals, τ_{I-N}) during collision from the relation

$$\tau = \frac{M^{1/2} T^{3/2}}{8.8 \cdot 10^{-2} n^s Z^4 \ln\Lambda}$$
(2.7)

and for electron-electron collisions

$$\tau_{e-e} = \frac{T^{3/2}}{3.8 \ n_e \ln\Lambda} \tag{2.8}$$

with

$$\Lambda = \frac{3(kT)^{3/2}}{2(4\pi)^{1/2} Z^3 e^3 n^{1/2}}$$
(2.9)

where Z is the charge of the particles, M is the atomic weight, and $\ln \Lambda$ stands for the Coulomb logarithm which involves dynamical information about particle collisions. Λ is on the order of 10.

Figure 2.4 demonstrates the relaxation time τ_{e-e} for electron-electron collisions. The thermalization is achieved within picoseconds with an estimated electron density n_e of 10^{18} cm⁻³. Therefore an uniform temperature distribution in the plasma and a local thermodynamic equilibrium can be expected because the relaxation time is much smaller than the plasma expansion time and pulse width of the laser radiation both of the order of several nanoseconds. The relaxation time τ depends on the velocity of the particles which is in turn proportional to the square root of the mass with $\tau \sim 1/\bar{\nu} \sim m^{1/2}$ where $\bar{\nu}$ is mean thermal speed. Therefore the relaxation time for electrons is ca. 100 times smaller than for ions at the same temperature [ZeRa66]. The validity of the LTE can be verified with the McWhirter criterion [Whir65] by the relation:

$$n_e \ge 1.6 \cdot 10^{12} T^{1/2} (\Delta E_{ul})^3 \tag{2.10}$$



Figure 2.4: Relaxation time τ for electron-electron collisions with $\Lambda = 35$ for temperatures T_e in steps of 2500 K

where ΔE_{ul} is the highest energy transition for which the condition holds. It was derived for homogeneous, stationary, and optically thin plasmas. Cristoforetti *et al.* [CGA+10] show that this mostly used criterion is a necessary but not essentially a sufficient condition. The criterion, originally introduced by Griem [Grie63], gives a minimum electron number density in the plasma which is necessary to warrant the existence of the LTE. Collisional depopulation rates for all electron levels of the atom need to be at least ten times higher than the radiative depopulation rate to neglect deviations from LTE.

Plasma temperatures

Plasma temperatures can be calculated by ratios of line intensities, in case of LTE. According to Boltzmann's distribution at plasma temperature T one obtains for each species at a given ionization stage

$$\frac{I_1}{I_2} = \frac{g_1 A_1}{g_2 A_2} \cdot \frac{\lambda_2}{\lambda_2} exp\left(-\frac{|E_1 - E_2|}{kT}\right),\tag{2.11}$$

where A is the Einstein coefficient of spontaneous radiative emission. The individual line pair is describes with 1 and 2 [SBK+00].

Several relative line intensities of different elements and ionization states lead to accurate temperatures diagramed by the Boltzmann plot method. Selecting lines from successive ionization stages of the same element does considerably improve the sensitivity. The effective energy difference is enlarged by the ionization energy, which is much higher than the thermal energy. In LTE, the ratio of such line intensities is given by

$$\frac{I'}{I} = \left(\frac{f'_O g' \lambda^3}{f_O g \lambda'^3}\right) \left(4 \pi^{3/2} a_0^3 n_e\right)^{-1} \left(\frac{kT}{E_H}\right)^{3/2} \cdot exp\left(-\frac{E' + E_\infty - E - \Delta E_\infty}{kT}\right), \quad (2.12)$$

where the primed symbols represent the line of the element with higher ionization stage, f_O is the oscillator strength, g is the statistical weight, a_0 is the Bohr radius, E_H is the ionization energy of the hydrogen atom, E the excitation energy. ΔE_{∞} is the correction to the ionization energy E_{∞} of the lower ionization stage due to plasma interactions given by

$$\Delta E_{\infty} = 3z \frac{e^2}{4\pi\epsilon_0} \left(\frac{4\pi n_e}{3}\right)^{1/3}, \qquad (2.13)$$

where z = 1 for neutral atoms, z = 2 for singly ionized species, etc. [Grie64].

Electron density

The intensity distribution within the natural line width is given by a frequency-dependent Lorentzian profile in the ideal case of a free atom

$$I(\nu) = \frac{I_0(\gamma/4\pi)^2}{\left[\left(\nu - \nu_o\right)^2 + \left(\gamma/4\pi\right)^2\right]}$$
(2.14)

where I_0 is the intensity at the resonance frequency ν_o and γ the radiation damping constant. The inverse of the damping constant is the lifetime of a classical oscillator which is about 10^{-8} s for emission in the visible region. The intensity spread over a range of frequencies is called natural line broadening. It is hardly observable due to Doppler broadening and caused by random thermal motions of the emitting atoms. This dominates the line shape near the center and results in a Gaussian profile $\Delta \nu_D$ with full width at half maximum (FWHM) of

$$\Delta \nu_D = \frac{2\nu_0}{c} \sqrt{\frac{RT \ln 2}{M}} = 7.16 \cdot 10^{-7} \nu_0 \sqrt{\frac{T}{M}}$$
(2.15)

where ν_0 is the frequency of the line center and R is the ideal gas constant [Demt07].

Both broadening mechanisms are negligible, if the radiating atom is surrounded by a dense plasma. The charged particles produce an electric field which interacts with the atom, hence leading to line broadening called Stark broadening and Stark shift. Balmer line H_{β} at 486.1 nm natural line width is $\Delta \nu_{nat} = 1.25 \cdot 10^{-5}$ nm. Doppler broadening line width $\Delta \nu_D = 0.035$ nm at $T = 10\,000$ K is comparable low to Stark broadened $\Delta \nu_{Stark} \approx 1$ nm [Bekf76].

This line broadening is suitable for determining the electron density. Because of the Lorentzian shape of the (Stark) broadened spectral line $\Delta \lambda_{line}$ and the spectrometer resolution $\Delta \lambda_{spectrometer}$, the following calculation is applicable: $\Delta \lambda_{total} = \Delta \lambda_{line} + \Delta \lambda_{spectrometer}$ [SBK+00]. The following formula can be applied for plasma diagnostics using H-like atoms to determine the electron density

$$n_e = C(n_e, T) \ \Delta \lambda_{FWHM}^{3/2} \tag{2.16}$$

where the constant $C(n_e, T)$, which only weakly depends on n_e and T, has been taken from the literature [Grie64] for the H_{β} line of the Balmer series. Griem [Grie64] has graphically interpolated line profiles of hydrogen to determine $C(n_e, T)$. Samek *et al.* [SBK+00] conclude that H_{β} and H_{γ} lines are the first choice to determine the electron density in a LIBS plasma. These lines are not influenced by additional line broadening from self-absorption and/or self-reversal like the H_{α} line while H_{δ} line is masked by a strong nitrogen line.

Optical thickness of the plasma

Quantitative analysis by spectroscopic methods relies on: LTE, optically thin plasma, and a stoichiometric ablation, i.e. the plasma content matter is representative for the sample composition [ChRu91].

The optical thickness τ_o of a plasma is described by $d\tau_o = -\alpha dx$ [ZeRa66]. The plasma needs to be optically thin, i.e. the emitted radiation to traverse and escape from the plasma without significant absorption or scattering. Otherwise, a high density plasma absorbs its own emission known as self-absorption. This is mainly true for resonance lines connected to the ground state. The absorption leads to a distortion in the spectral line profile showing a broadened line. The plasma temperature also tends to drop down towards the outer parts of the plasma-plume. Self-reversal can occur when light passes through these colder sections. It results in lines with a dip at their center and therefore misleadingly interpreted as two lines. Gaseous samples and liquid samples analyzed on the surface [SBK+00] are less effected by self-reversal and self-absorption in comparison to solid ones. Also higher species concentrations or higher laser intensities lead to stronger distortion of the spectral line shape [RaTh07].

In the low concentration limit where the plasma becomes optically thin, the integrated intensity I grows with the number density [AnMi06]

$$I = \frac{h \nu_0 n^s}{8\pi^2} \frac{A_{ul} g_u}{U^s(T)} \cdot \exp\left(-\frac{E_n}{kT}\right).$$
(2.17)

2.3 Spectrochemical quantitative analysis

Plasmas may emit photons broadband from the ultraviolet to the infrared due to bremsstrahlung from free electrons and transitions resulting from electron-ion recombination. As shown in Figure 2.5, for a transient excitation unspecific emission decays rapidly and is followed by atomic lines, both ionic and neutral, and molecular bands. Insertion of a delay time allows to record LIBS spectra when signal to background rises and atomic emission lines become much sharper [CrRa06].



Figure 2.5: Laser-induced plasma initiation and the recombination and relaxation of emission lines [SiRa11]

The signal of an atomic or ionic line S is the product of the excited state number density n_u , the spontaneous transition probability A_{ul} , and the detection function f_{det}

$$S = n_u A_{ul} f_{det}.$$
 (2.18)

The detection function

$$f_{det} = V_{exc} f_{cal} \eta_{det} \Delta \Omega \tag{2.19}$$

includes the excitation volume V_{exc} (cm³), seen by the detector, and the overall detection efficiency η_{det} (counts photon⁻¹ s) including parameters like optical transmission, detector gain and integration time, the solid angle $\Delta\Omega$, and a calibration function f_{cal} . The function f_{cal} includes self-absorption (and self-reversal) effects and therefore plasma characteristics like optical thickness, hence, the probability that photons reach the detector after being emitted inside the plasma.

The excitation/ionization mechanism leading to atomic (ionic) emission is comprised as f_{exc} . This function multiplied by the number density in the gas phase of the plasma plume describes the total number of excited atoms (ions) of the excited volume. The number density in the gas phase equals the number density in the sample times ablation/vaporization function. This product includes the parameter weight fraction χ , a stoichiometric factor f_{st} , and the ratio of ablated sample mass times Avogadros number divided by the molar mass.

Including these factors which have been described by Tognoni *et al.* [TPC+06], the signal S can be expressed by

$$S = A_{ul} \left(m(N_A/M) \chi f_{st} \right) f_{exc} \left(f_{cal} \eta_{det} \right) = A_{ul} f_{int} f_{exc} f_{det}.$$
(2.20)

The function f_{int} is related to the initial interaction between the sample and the laser which leads to the ablation/vaporization of the material.

2.3.1 Methods based on internal standards

Precise knowledge of plasma parameters is difficult to obtain. Therefore the application of internal standards is an approach to neglect plasma influences.

A weak line of the element which is the major constituent of the sample whose intensity remains constant for all standard samples could be used as a standard. Concentrations will be determined in relation to the chosen line intensity [Thak07].

A further method of Kim *et al.* [Kim89] is the most practical to extract quantitative information of sample composition. An element which is known not to be present in either the unknown or the standard samples is added as internal standard at a known concentration. The line intensity of the standard $I_{standard}$ needs to be proportional to its concentration. Sample concentration can be calculated by multiplying the concentration of the standard times the ratio $I_{sample}/I_{standard}$. This method has been used throughout this work. However, variations in the matrix between the unknown sample and the standard must be minimal due to the fact that laser material interaction with the sample is highly matrix dependent. The use of matrix-matched standards overcomes the restriction, since both the known standard and the unknown sample are affected [TPC+06].

2.3.2 LIBS of aqueous solutions

Measurements in liquids show a lack of signal intensity compared to analyses of samples in air. Compared to gases the density differs by an order of 10^3 leading to stronger quenching. This process includes a variety of different interactions, i.e. excited state reactions, energy transfer, complex-formation and collisional quenching. Giacomo *et al.* [GDC+04], [GDC+05] determined higher excitation temperatures of plasma in cavitation bubbles created on submerged samples compared to plasma in vacuum according to ablation time. Comparing temperatures at similar electron densities leads to similar values.

Sample preparation

An advantage of LIBS is the capability to analyze samples with no or little preparation. The small spot size of a focused laser beam and therefore the little amount of vaporized sample mass leads to an accuracy depending on the homogeneity of the sample. At the same time it allows measurements of small sample sites for example on paintings or slag inclusions. Generation of depth profiles is a further potential of the negligible amount of sample. The lack of sample preparation includes that analyses on solids may be influenced by small amounts of surface contaminants. Application of several pre-pulses is adequate to clean surfaces. Reproducibility of the plasma strongly depends on changes in surface properties. However, a spark in a pulsed mode yields a lower total emission signal and less reproducible sample excitation than a continuous excitation, i.e., in inductively coupled plasma (ICP) spectroscopy [Crem87]. Dissolved samples are therefore homogenized and better reproducibly to investigate but chemical digestion is often time consuming and expensive.

Gases and liquids containing dissolved materials tend to be well-mixed and therefore may be assumed to be homogeneous so that every plasma interrogates a small volume having a composition representative of the bulk sample. Averaging a number of laser shots minimizes the influence of sampling factors, i.e. the laser pulses interrogate the same sample volume.

Matrix effects

The sample composition and physical properties may affect the element's signal. Changes in concentration of one or more of the matrix elements modifies an elemental signal even though the element's concentration remains constant. Physical and chemical matrix effects are known. The physical matrix effects are related to the laser-induced ablation according to the physical properties of the sample, including differences in specific heat, latent heat of vaporization, thermal conductivity, absorption, etc. of different matrices. The chemical effects arise when the presence of one element alters the emission characteristics of another element.

Both effects complicate the calibration procedure and have to be taken into account [CrRa06]. Elements captured by a chemical reaction and therefore implemented into a molecule cannot be measured quantitatively. Chemical analysis both in liquids or of samples in liquids need further consideration. Investigation of submerged samples often show a lack of sensitivity. Having liquids as a sample all standards need to be adopted to the matrix influencing in the same way the plasma as the original sample. Several standard matrices are available but are still limited compared to real samples. The analysis of liquids presented in this work refers also to investigations on an immersed target (silicon wafer or aluminum). The target serves only as an efficient absorber of energy mostly used in case of fiber-guided laser systems. Investigated elements and targets employed have shown surface interaction that may change the concentration of the analyte in the liquid and therefore resulting misleadingly in altered concentration values.

2.4 Statistical data evaluation by chemometrics

Chemometrics includes mathematical and statistical operations on data of analytical measurements. Standard literature "Chemometrics in Spectroscopy" by Mark and Workman [MaWo07] and "Chemometrics: a textbook" by Massart *et al.* [MVD+03] explain the variety of methods, their mathematical background, and application in detail.

Chemometrics in LIBS is a recently explored ongoing research field comprising a number of statistical methods, i.e. principal components analysis (PCA), principal components regression (PCR), or multiple linear least squares regression (MLLSR), also known as multiple linear regression (MLR), and partial least squares regression (PLS). These treatments of data are used to gauge the overall discrimination ability of spectroscopy. Hence, they are also dedicated to samples which have been challenging for LIBS. This includes multiple elements in complex matrices and organic compounds. In general, analysis of samples containing carbon, hydrogen, oxygen, and nitrogen is possible with LIBS. Problematic are those samples whose main constituents show little variation and no additional elements for tracing. This occurs in the field of explosive and biological materials. Especially hazardous compounds are highly interesting because of the remote sensing potential of LIBS. Hybl *et al.* [HLB03] have demonstrated that biological aerosols, e.g. pollen and fungal spores, show a finger print in broadband measurements of organic material which are associated with several non-organic elemental lines. The application of PCA allows samples to be categorized within particular classes.

PCA has the potential to structure data. Results are typically presented graphically and allow one to identify outliers and groupings of data, etc. The principal components represent n-dimensional data in a reduced number of dimensions, usually two or three.

The mathematical evaluation of data sets includes the following procedure: (1) data acquisition; (2) to work with normalized values; the mean value has to be subtracted from each data dimension; (3) calculation of the covariance matrix; (4) determination of the eigenvectors and eigenvalues of the covariance matrix; (5) data compression and dimensionality reduction by choosing components and forming a feature vector (the eigenvector with the highest eigenvalue is the principle component of the data set); (6) deriving a new data set [Smit03].

PCA refers to definitions in statistics, which are described briefly. The variance is the squared deviation of a vector from its expected mean value, hence the deviation of x to \bar{x} . The covariance is similar but in terms of two vectors. It compares the difference of the variance of two vectors. The difference is the variance from x to \bar{x} to the variance y to \bar{y} . The definition can be transferred to get a quadratic and symmetric covariance matrix and the related correlation coefficient with values between [-1, 1]. The calculation of the correlation of measured data is defined in a correlation matrix.

An example of the transformation of a three-dimensional database in terms of PCA and the reduction to two dimensions are shown in Figure 2.6:

(a) A number of multidimensional measurements are depicted as a scatter plot (red volume). (b) The origin of the coordinate system is transferred to the balance point of the scatter plot. (c) The coordinate system is turned until the x axis shows into the same direction as the largest variance (blue arrow). (d) The y axis is turned in the direction with the highest possible variance which is not correlated to the x axis

(green arrow). The x axis remains unchanged; therefore, the system is turned around the x axis. (e) The procedure is going on until k axes are aligned in the direction of the largest variance but not correlated to the other k-1 axes. Further on, the ratio of each principal components variance and the complete variance needs to be calculated. Information about weighting of the principal components allows to chose the required dimension, e.g. for components with highest or lowest variance.



Figure 2.6: Transformation of three-dimensional database and the reduction to two dimensions by PCA [Sieg12]

PCA gives an interpretation of a database by determining the components with the largest/smallest influence. If the components are known, the reduced number of basic vectors can be determined. This is a reduction of dimensions with the smallest possible loss of data information.

3 Experimental setup

Figure 3.1 shows a typical LIBS setup for the analysis of aqueous samples within this thesis. Specific variations in design and parameters within each experiment are explained in detail in the related publications [KCG+05], [KGN+06], [KRN+10], [KGH+12]. Double-pulse experiments in liquids are carried out by making use of a target or directly in liquids. A breakdown in liquid samples is induced by a fiber guided Nd:YAG laser (Laser 1 / bubble laser) onto a target where it generates a cavitation bubble. At its maximum size a second Nd:YAG laser (Laser 2 / plasma laser) suitable for spectroscopy is guided through the same fiber. This method is as well described as targetless mode. For LIBS without a target, at first a plasma is induced by a Nd:YAG laser @ 532 nm wavelength (Laser 1). It evolves into a cavitation bubble with a maximum size. A plasma, suitable for spectroscopy, is induced by a second Nd:YAG laser @ 1064 nm wavelength (Laser 2) focused with an off-axis mirror.



Figure 3.1: Typical setup for LIBS on liquid samples
Breakdown inside the cavitation bubble occurs in experiments when tight focused laser energy exceeds the necessary energy of a breakdown in air. The laser beam focused by an off-axis mirror from below through the bottom into the cuvette is leading to reliable plasma ignition inside a cavitation bubble. Inducing the plasma this way prevents perturbation from rising residual bubbles and splashing on the surface. The advantage of an off-axis mirror is the large diameter of 30 mm combined with a short focal length of f = 25 mm at the same time.

Focal spot size can be calculated as [Noll06], [RaTh07]:

$$d_2 = \frac{4f\lambda}{\pi d_1} M^2; \ d_2 \approx 2.44\lambda \frac{f}{d_1}$$
 (3.1)

where d_2 is the diameter of the focus, f is the focal length, d_1 is the diameter of the illuminated aperture of the focusing lens, and M^2 is the beam propagation ratio. M^2 has values in the range of 2 to 10 for typical Nd:YAG lasers. Laser spots are calculated with a diameter of $d_{Laser1} \approx 6 \,\mu\text{m}$ and $d_{Laser2} \approx 4 \,\mu\text{m}$.

Plasma emission is collected by a multimode quartz fiber and guided to a spectrometer. A CCD camera attached to a microscope is used to monitor bubble expansion and plasma evolution recorded as shadow images. Camera and illumination are perpendicularly oriented to the lasers. Illumination is not shown in the schematic overview.

Figure 3.2 sketches the temporal evolution of different species and timing in singlepulse and double-pulse LIBS.

The analogous setup is used for data acquisition to evaluate plasma temperatures and electron densities and described in detail in [KRN+10]. To obtain time resolved fluorescence intensities the gate pulse width Δt_b has been changed and set to 50 ns. The measured line profiles are a convolution of the line width and the spectrograph's resolution. All measured intensities have to be corrected by the response factor of the spectrograph, includes parameters, like slit width, grating dispersion, and quantum efficiency of ICCD camera. The instrumental response factor is determined by the use of two supplemental light sources. A standard quartz tungsten halogen lamp of black body like spectral irradiance (Model No: 63358, LOT Oriel) was used for intensity calibration. A mercury argon calibration source (CAL-2000, Mikropack) produces low-pressure Hg and Ar emission lines serving as narrow band line source to determine the spectrographic resolution.



Figure 3.2: a) Time periods after plasma formation and temporal evolution of different species. The measuring gate window Δt_b for spectroscopy starts after delay time t_d . b) Timing scheme for double-pulse LIBS with varying Δt between the laser pulses shorter than collapse time t_c [CrRa06]

4 Laser-induced breakdown spectroscopy on plasma in cavitation bubbles

This chapter includes four publications on spectroscopy of heavy metals in liquids.

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The sensitivity in detecting traces of heavy metals in liquids by laser-induced breakdown spectroscopy has been methodically enhanced. The limit of detection (LOD) is greatly improved by using laser-induced plasma excitation of sample material inside a cavitation bubble [KCG+05] in contrast to single pulse excitation [KGM+04]. LOD's are element and matrix dependent values, have to be thoroughly determined experimentally. The spectroscopic LIBS methods applied in the frame of this work are mainly carried out within cavitation bubbles. Double-pulse LIBS requires a time-resolved detection of atomic and ionic emission lines pretty much comparable to single-pulse experiments. But in addition a further laser pulse is indispensable to induce a cavitation bubble. The

gaseous low-pressure environment of the cavitation bubble is suitable for sensitive spectroscopic analysis [Nyga93]. Strong variations of pressure and temperature, respectively, occur inside the cavitation bubble. Therefore, a time delay Δt between the laser pulse inducing the cavitation bubble (Laser 1) and the laser pulse inducing the plasma inside the cavitation bubble (Laser 2) needs to be adjusted carefully. Further enhancement is possible by using resonant excitation of selected atomic or ionic transitions.

A quantitative analysis includes the calibration of the measuring system with standard samples of known concentrations. The use of an internal standard is a versatile method for further improvement ruling out the influence of plasma conditions [KGN+06]. Thereby ratio of normalized spectral line intensities of atomic and ionic species under investigation and an added well known concentration of a further element (internal standard) leads to excellent correlations.

Optical fibers are able to transport the laser photons as well as fluorescence emission to or from non accessible sample sites, therefore allowing remote LIBS. However, the generation of an optical breakdown requires either an absorbing liquid or a fluence in excess of the breakdown threshold. The latter is not feasible due to high divergence output beam characteristics of fiber guided radiation. Therefore, a target at a certain distance from the fiber tip is needed to absorb the pulse energy leading to laser-induced breakdown. Size and cavitation bubble and plasma evolution inside the bubble is easy to control. The implementation of a target for plasma excitation can be a powerful method to improve the LOD.

The analysis by use of a target has several drawbacks, e.g. contamination by target ablation, durability of target material, interference of emission lines. The method is not applicable to each heavy metal because electroless deposition, e.g. of palladium, leads to cumulated concentrations over time [KRN+10]. Therefore LIBS without a target is tested.

Table 4.1 summarizes investigated metals in aqueous solutions including used lasers, targets, internal standards, and the resulting LOD.

Element	Wavelength $/ nm$	Laser pulses	Target	Standard	Wavelength / nm	LOD mgL ⁻¹
single pulse						
Cr I	357.9,	Nd:YAG	_	_	_	200
	359.3,	(1064 nm)				
	360.5					
double-pulse						
Mn I	403.1,	$2 \times \text{Nd:YAG}$	Si	Sr II	407.8	0.08
	403.3,	(532 nm)				
	403.5					
Mn I	403.1,	Nd:YAG	_	Sr II	407.8	0.3
	403.3,	(532 nm),				
	403.5	Nd:YAG				
		$(1064~\rm{nm})$				
Pd I	351.7	Nd:YAG	Si	Cr I	357.9	5
		(532 nm),				
		Nd:YAG				
		$(1064~\rm{nm})$				
double-pulse plus resonant excitation						
In I	410.2	$2 \times \text{Nd:YAG}$	Al	_	_	10
		(532 nm),				
		Dye Laser				
		$(451.1~\mathrm{nm})$				

Table 4.1: LODs and parameters for LIBS analysis of dissolved metals in aqueous solutions

4.1 Detection of chromium

Appl. Phys. A 79, 1071–1073 (2004) DOI: 10.1007/s00339-004-2633-y Applied Physics A Materials Science & Processing

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Detection of chromium in liquids by laser induced breakdown spectroscopy (LIBS)

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ABSTRACT Environmental concerns about the amount of dissolved heavy metals in coastal tidal waters have led to investigations into possible ways to detect chromium dissolved in water. A method using fluorescence spectroscopy in solution has been proposed. However, such optical emission spectroscopic methods tend to suffer from a lack of sensitivity caused by the strong quenching processes in liquids. In this investigation, Nd : YAG Q-switched laser pulses were utilised to generate a plasma filled bubble in a chromium solution. Fluorescence in the plasma was detected using an optical fibre tip placed adjacent to the bubble. Light wavelengths characteristic of chromium were detected and spectral images recorded using an optical multi-channel analyzer.

PACS 39.30.+w; 42.62 Fi; 52.38 Mf; 92.20 Ny

1 Introduction

Laser induced breakdown spectroscopy (LIBS) has been used for the analysis of liquids [1]. Different experimental approaches have been used, such as laser sparks on the surface of a solution [2] contained in a cylindrical glass vial [3] or beams focused into a stream of sample solution [4]. Cáceres et al. used a quick-freeze method for the precise quantitative analysis of elemental traces in water, down to concentrations of a few ppm [5]. Use of a Meinhard Nebulizer facilitates detection limits of down to 160 ppb chromium [6]. Knopp et al. investigated various elements using plasma within liquids in a rectangular cell [7]. However, the use of double-pulse laser methods has shown improved results [8-10]. Rai et al. have shown that the limit for chromium detection was found to be 120 ppb using the double-pulse method compared to 1300 ppb in single excitation mode [11]. Standard analysis methods for chromium in surface, ground, and drinking water using inductively-coupled plasma atomic emission spectrometry (ICP-AES) can be found in EN ISO 11885 1998-03. Pollution limit values for chromium concentration range from 0.05 mg/l to 0.1 mg/l according to WHO [12] and US EPA [13].

The aim of this investigation is to find a simple, rugged detection method suitable for field use. The site objective for

using such a method was taken as being the Wadden Sea, a tidal flat close to the East Frisian island Spiekeroog. A stable running portable system is required, which prohibits the use of nozzles, nebulizers or jets that may be affected by seawater or its contents, such as algae and sand.

2 Experimental

A diagram of the experimental set-up using a single pulse mode is shown in Fig. 1. A Q-switched Nd : YAG laser (New Wave Research, Tempest) provides 5 ns pulses at 1 Hz repetition rate and up to 18 mJ pulse energy. The fundamental Nd : YAG laser wavelength at 1064 nm is used to induce breakdown within a chromium solution. The laser beam is focused by two plano-convex BK-7 lenses placed at a total focal length of about 21 mm from the target. The laser energy level is reduced to obtain a plasma source smaller in cross-section than that of the fibre [14]. The sample cell consists of a fused silica cuvette of dimensions $20 \times 20 \times$ 10 mm³ including one lens. Plasma emission is collected directly by a quartz fibre (core diameter: $600 \,\mu m$) perpendicular to the laser beam path. The numerical aperture of the sampling fibre is matched to the Czerny-Turner Spectrograph (Acton Research, Spectra Pro 275; grating: 300 lines/mm; 300 nm blaze) by means of a biconvex lens. An intensified CCDcamera (Sony CCD Video Camera Module XC-77RR-CE, 756×581 pixels, $11 \times 11 \,\mu\text{m}^2$ with a Hamamatsu V3063U Image Intensifier) records the signal. Triggering of the gated ICCD is set to record time-lapsed after plasma ignition to minimize detection of background emission. The measurement gate is set to 10 µs. Sampling and data acquisition are controlled by a PC-based frame grabber card. The system is synchronized by a digital delay/pulse generator (Stanford Research Systems, DG 535), which also delivers the master trigger.

Solutions of chrome-alaun ($KCr(SO_4)_2 \cdot 12H_2O$) in double distilled water, with concentrations between 40 ppm and 2200 ppm, were used as samples.

Results

Low plasma-inducing laser energy with less than 1.3 GW/cm^2 helps to protect the fibre tip, which can be damaged due to the short distance of ca. 450 µm between plume and fibre. A spatially confined plasma field with approximately 400–500 µm length and 300 µm height emits suffi-

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cient light for fibre-guided detection. Direct fibre coupling leads to about the same solid angle as lens coupling systems but avoids any subsequent optical losses. Also, the relation of the spherical surface of the solid angle section between plasma and fibre is 40 times better than between plasma and lens. The quality of the spectra captured depends on the shape and position of the plasma and its distance to the fibre tip. This is affected by laser jitter, causing spatial fluctuations in laser-induced breakdown. Use of a target to reduce this phenomenon could increase reproducibility but increases com-

plexity of such a set-up. Different concentrations of chrome-alaun in water were investigated. Different delay times have been used (Figs. 3 and 4) to optimize the S/N-ratio. During each series of measurements peak intensities increased with the concentration of chromium solution. Care was taken to ensure that the positioning of the spectroscopic fibre in relation to the plasma, the laser energy level, and the time delay values were faithfully reproduced. Fichet et al. [15] found the best results at maximum intensity divided by the background spectrum. The peak value was calculated by averaging the values after background correction for each single sample data point. The atomic spectral lines (shown in Fig. 2) of two triplet bands at 357.9 nm, 359.3 nm and 360.5 nm and 425.4 nm, 427.5 nm and 429.0 nm identify chromium. Higher sensitivity at the triplet with lower wavelengths was observed due to the 300 nm blazing of the spectrometer grating. Calibration

of chromium concentrations over a wider range proved difficult. As can be seen in Fig. 3, the relation between concentrations from 80-2200 ppm and ensuing intensity is not linear for similar conditions. Delay times suiting low and high concentrations are not generally attainable. Limited range tests do indicate a linear relation. Shorter delay times for lower concentrations improved the measured peak intensity. Published calibration values for chromium investigations indicate a small range of 5 ppm [11]. If a range from 20-100 ppm is used, a linear dependence becomes evident (Fig. 4). The data measured appear to be in good agreement with results from Yueh et al. [16], who found a linear relationship between 0.4-5 ppm. The limit of detection was set by them to 0.4 mg/l with a liquid jet system at 425.4 nm. In other earlier investigations, chromium was detected in water down to a limit of 10 mg/l by Vogel et al. [14] at 425.43 nm wavelength and 0.1 mg/l [17] at 283.563 nm. Although reproducibility may be questioned, this suggests that chromium should be detectable at 357.9 nm down to a concentration of 40 mg/l. This system was found to be unsuitable for the determination of unknown concentrations whilst requiring a number of different calibration steps. The advantage of such a system, however, is the improved setup conditions for measurements over long distances.

An optimum experimental system for the detection of chromium with LIBS requires a built-in calibrative function to allow a reliable quantitative analysis with necessary continuous calibration at each single measurement. It is also intended



FIGURE 2 Spectrum of chromium with LIBS in chromealaun solution, 1330 ppm concentration, 3.5 µs delay time



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FIGURE 4 LIBS calibration obtained from Nd : YAG measurements

Peak intensity versus concentration range of

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to generate a cavitation bubble in which a secondary plasma will be excited. The detection fibre will be placed in the cavitation bubble. Spectroscopic detection in gaseous bubbles may improve the limits of detection by avoiding the strong quenching processes that occur in liquids [10]. The investigation has indicated that the detection of plasma emission may be used to quantify chromium contaminant levels in water.

4 Conclusion

The feasibility of the use of LIBS for the detection of chromium in aqueous solutions at a wavelength of 357.9 nm has been demonstrated. Although promising, the methods proposed do not as yet yield the desired accuracies required for a quantitative analysis of chromium concentration in water. An online analysis system in a measurement tower situated in the North Sea will be equipped with a fibre-guided system suitable for distances of up to 50 m between measurement system and detection sensor. The limit of detection was given as 200 ppm as detected by single pulse excitation, and down to 40 ppm with a signal to noise ratio of 2:1. Calibration of such a system using an internal reference may lead to improved results. Research is currently being focused on this specific point. Spectroscopy in cavitation bubbles is expected to increase limits of detection.

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FIGURE 3

chromium

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4.2 Detection of manganese



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SPECTROCHIMICA ACTA **Part B**

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Analytical note

Detection of manganese in solution in cavitation bubbles using laser induced breakdown spectroscopy $\stackrel{\approx}{\sim}$

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Abstract

Levels of dissolved manganese in water samples down to 80 µg/l are measured using emission spectroscopy. Optical emission spectroscopic methods tend to be insensitive in liquids due to strong quenching processes. Laser induced breakdown spectroscopy (LIBS) within a cavitation bubble overcomes this restriction. The output of a double pulsed Q-switched Nd:YAG laser, operated at 532 nm, is coupled to an optical fibre. The fibre guides the laser pulses to a silicon target immersed in a water sample contaminated with manganese. The cavitation process is initiated with the first laser pulse. At maximum bubble expansion, the second laser pulse ignites the plasma in the vapour/gas-filled cavitation bubble. Emission is collected by an additional optical fibre located near the bubble. Characteristic spectral line intensities of manganese are recorded and correlated to an internal calibration standard. Spectral analysis and data acquisition are carried out using an image-intensified optical multi-channel analyser. © 2005 Elsevier B.V. All rights reserved.

PACS: 39.30.+w; 42.62 Fi; 52.38 Mf; 92.20 Ny Keywords: Emission spectroscopy; LIBS; Nd:YAG; Manganese; Cavitation bubble; OES

1. Introduction

Laser induced breakdown spectroscopy (LIBS) has been used for analytical purposes in aqueous solution [1,2], on the surfaces of liquid [3,4], and frozen samples [5]. Doublepulse laser methods provide better results as compared to single spark methods [6–8]. A detection limit (LOD) for manganese (at the wavelengths of 403.08, 403.31, and 403.45 nm) on the surface of the liquid was found to be 10 mg/l [9], while 700 μ g/l was reported for a Liquid Jet System is determined at a wavelength of 403.076 nm [10]. The use of a Meinhard nebulizer resulted in an LOD down to 0.6 ppm [11].

It is known that LIBS in liquids is plagued with difficulties due to the inherent strong quenching processes. To overcome this, one takes advantage of the formation of cavitation bubbles. The absorption of laser energy in water generates a violent gas bubble seeded at a micro-bubble or another foreign body in suspension. The shock wave generated, moving ahead of the bubble surface, causes the formation of a low pressure wave which increases the bubble volume. This process occurs until the pressure inside the bubble is reduced below the surrounding fluid pressure, as a result of the increased volume and the decreasing temperature. This in turn reduces the bubble volume while increasing again the inner pressure, thus leading to further expansion. All this processes lead to a number of oscillatory volume changes until the exhaustion of the bubble energy [25-27]. The maximum expansion, which occurs with the first cavitation bubble, provides a gaseous environment for

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Table 1 Compilation of experimentally determined manganese concentrations,

Reference	Mn _{diss:} -concentration	Mn _{diss:} -concentration/ µmol/l	
LIBS LOD			
Samek et al. [9]	10 mg/l	182.02	
Yueh et al. [10]	700 μg/l	12.74	
Kumar et al. [11]	0.6 ppm	10.92	
This paper	80 µg/l	1.46	
Pollution limits in di	rinking water		
WHO [19]	0.5 mg/l	9.10	
EPA [20]	0.05 mg/l	0.91	
Concentration in the	Wadden sea		
Summer [18]	88 μg/l	1.60	
Winter [18]	0.5 μg/l	0.01	

All concentrations are also given in micromoles per liter.

optical emission spectroscopy. A second laser pulse directed onto the silicon target leads to a laser induced breakdown and subsequent plasma and subsequent atomic line emission within the gas atmosphere of the cavitation bubble [12]. The laser beam is guided into the liquid by means of an optical fibre and without using lenses. Preliminary studies [13] have shown that optically focussed laser beams in liquids causes spatial fluctuations of the laser induced breakdown. Abandoning the lenses prevents focusing, thus making the use of a target necessary. Due to its numerical aperture, the fibre tip needs to be positioned close to the target in order to be able to induce optical breakdown. The plasma has to be placed under the spectroscopic fibre. This has to be ensured with the use of a fibre guided laser.

The aim of this investigation is the development of a LIBS methodology to determine the manganese concentration in coastal flat tidal waters of the North Sea. There are several reasons why this determination is important. Large changes in concentration of this element appear during tides and seasons due to the binding of manganese with mineral particle in suspension or precipitation in sediment (see Schonfeld et al. [14]). Primary organic

particle production and micro-organisms are responsible for re-mineralisation. They have a specific influence on the heavy metal budget of the water and on mineral material in suspension. Wulffraat et al. [15] have shown that the whole North Sea is being encumbered by heavy metal and nutrient input from the Atlantic Ocean, the English Channel, and large rivers [16]. The relatively high manganese concentration [17] compared to surface water of the Atlantic and the continental shelf region may also be influenced by seasonal and other mobilisations e.g. reduction of organic material. Supply of freshwater through creeks via flood gates may also have a strong influence on tidal flat conditions. The tidal flats between the terrestrial (freshwater) and the marine (North Sea) realm contain between 88 and 0.5 µg/l manganese, measured with inductively coupled plasma mass spectrometry (ICP-MS) [18]. Finally, according to WHO [19] and EN ISO 11885 1998-03/EPA [20], the pollution limit values for manganese concentration in drinking water range from 0.5 to 0.05 mg/l (see Table 1).

2. Experimental setup

A double pulse, Q-switched Nd:YAG laser beam (New Wave Research, Solo III PIV) is coupled by a biconvex BK7 lens with a focal length of f=40 mm to a quartz fibre with core diameter $d=600 \ \mu\text{m}$. The laser is set to provide 6 ns pulses at the second harmonic wavelength of 532 nm with a repetition rate of 5 Hz. The laser peak irradiance at the fibre tip is 7 MW/cm² for the first laser pulse and 6.2 MW/cm² for the second. A sketch of the experimental setup is shown in Fig. 1. The fibre is guided to a silicon target and ensures that plasma emission occurs at a fixed location. The silicon target is fixed on an aluminium support, held by an x-yadjustment to allow horizontal movement of the target, necessary after every sample measurement. The first laser pulse induces a cavitation bubble in the solution containing manganese and strontium as an internal standard (cf. Sample preparation). The second laser pulse induces a breakdown



Fig. 1. Schematic dual-pulse LIBS setup

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Fig. 2. Shadow image of cavitation bubble showing the laser ablation fibre (left) and the spectroscopic fibre (top).

within the maximum expansion of the cavitation bubble, i.e., after approx. 80 µs.

Plasma emission is collected directly by a 1.2 mm quartz fibre perpendicular to the target. The sample cell is a glass cuvette $(20 \times 20 \times 10 \text{ mm}^3)$. A magnetic stirrer avoids the deposition of the ablated silicon on the target surface. During the experiments, the positioning of the fibre with regard to the target is kept constant. The cuvette itself is moved only to allow changing of sample fluid. A microscope fitted with CCD camera (PCO SensiCam, VGA, 640×480 Pixel, $9 \times 9 \ \mu m^2$) is used to observe both the bubble expansion and plasma [22]. The camera was used to detect shadow images at an exposure time of 20 µs. The fast photography illumination necessary for observation of the positioning of fibre to target relation is provided by a lamp which is focussed on the target using two BK7 lenses $(f_1=100, f_2=50)$. The spectroscopic fibre is adjusted to approx. 1 mm above the surface of the cavitation bubble. This allows to protect the analysis fibre from any damage due to ablation pulse, debris and shock wave effects. Fig. 2 shows the shadow image of the cavitation bubble and plasma emission induced by the Nd:YAG double pulse.

The numerical aperture of the sampling fibre is matched by a biconvex lens, f=16 mm, and a cylindrical lens, f=10mm, to an Acton Research SpectraPro spectrograph. This Czerny–Turner spectrograph with a focal length of 275 mm is used with a grating of 1200 lines/mm blazed at 500 nm. An intensified CCD detector (Andor i-star DH734, 1024 × 1024 Pixel, $13 \times 13 \mu m^2$, Gen II intensifier) records the signal. Triggering of the gated ICCD camera is set with a delay of 450 and 600 ns, respectively. The longer delay times improve the signal, especially for lower concentrations. The measuring gate width varies between 1 and 10 μ s. Continuous background plasma emission is reduced effectively by the given delay times. Control of delay and synchronisation is performed by a delay/gate generator (Stanford Research Systems DG 535).

3. Sample preparation

Sample ablation and atomisation are complex processes that depend upon many experimental parameters such as the

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amount of ablated sample material and the related plasma temperature [23]. The varying parameters are difficult to control and to measure during an analysis. To overcome this drawback, the use of an internal standard is advisable. In our case, the internal standard is a known concentration of strontium added to the unknown concentration of manganese. For the analysis, the background corrected peak area of the manganese intensity is normalised to the peak area of strontium. A dilution series of manganese solutions resulted in concentrations between 0.02 and 100 mg/l. In the low concentration range, a stock solution of 1000 µg/ml Mn from Mn(NO₃)₂*4 H₂O in 5% HNO₃ was used, while samples with concentrations higher than 6 mg/l are prepared from MnCl2*2 H2O. A constant amount of strontium is added to each sample of the dilution series as an internal standard. Stock solution is 1000 µg/ml Sr for AAS from SrCl₂*6 H₂O. All samples are diluted in doubly distilled water. Part of a silicon wafer was used as target material.

4. Results and discussion

The quantitative analysis of manganese in pure water is carried out using the spectral line triplet at 403.075, 403.306 and 403.448 nm of Mn I. Fig. 3 shows the ionic line of strontium at 407.77 nm chosen as internal standard (see below) and an atomic line of the target material silicon (410.29 nm).

4.1. Internal standard

The behavior of the Mn emission signal versus concentration shown in Fig. 4 can be significantly improved by normalizing the signal to an internal standard. If the choice



Fig. 3. LIBS spectrum of a liquid sample containing 40 mg/l Mn^{2+} and 10 mg/l Sr^{2+} . Background corrected peak areas are shaded.

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Fig. 4. Calibration graph obtained by plotting the Mn emission peak area versus concentration.

is correctly made, the variation of parameters like plasma temperature, amount of ablated material, bubble size and also the phase of bubble oscillation have almost no influence as the internal standard as well as the manganese concentration are effected identically (Fig. 5A).

The positive effect on the signal intensity using cavitation bubbles has been shown in earlier investigations by Nyga and Neu [12] and Nyga [21]. The double pulse technique has improved the peak intensities in water in comparison to the single pulse technique; however, different materials than the elements investigated here are used. The Si target itself has been tested as an internal standard by using its line at 410.29 nm. Because of the high intensity, this emission and that occurring at longer wavelengths have to be attenuated in order to avoid overloading the ICCD detector. Ko et al. [23] pointed out that the behavior of elements having different vapour pressures is not correlated within short delay times. Fractional evaporation from the ablated droplets will change the ratio of free atoms until all material is atomised. The vapour pressure of manganese (121 Pa at 1517 K) is 25 times higher than that of silicon (4.8 Pa at 1683 K). Moreover, because of the different state of aggregation between the trace and the target elements, different times of ablation, excitation and emission are expected, therefore resulting in a poor correlation.

As shown in Fig. 5A, the use of silicon as an internal standard is not suitable because the correlation between the peak area of manganese divided by the peak area of silicon is poor (R=0.837). In addition, the high intensity of the line implies that a change of the absolute concentration of silicon would be rather insensitive compared to the absolute concentration, silicon is not a good choice for this method because of the largely different natural concentrations of this element in sea water.

An element with spectral lines close to the relevant peaks of Mn within the spectral region investigated with our Czerny–Turner monochromator was chosen. Strontium has spectral lines similar in wavelength compared to manganese. The lines have also similar intensities, allowing comparable signal amplification and accumulation for both elements. The vapour pressures of manganese (121 Pa at 1517 K) and strontium (246 Pa at 1042 K) are only marginally different. Sr concentration in sea water (8 μ g/l) is strongly correlated with salinity and therefore easily accessible [24].

A possible disadvantage of using Sr as internal standard is the fact that an ionised Sr line is compared to a neutral line of Mn. Due to the delay times used, a similar population



Fig. 5. A: Calibration curve between 6 and 100 mg/l Mn, 10 mg/l Sr and Si as internal standards; B: Calibration curve between 0.02 and 6 mg/l Mn, 1 mg/l Sr as internal standard. The inset shows a magnification of the values down to 0.6 mg/l.

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of the ionic and atomic state is expected. Assuming a given population of neutrals and ions in the plasma, both elements are excited from the ground state to an equivalent upper energy level of approx. 24,800 cm¹⁻; for Mn and of approx. 24,500 cm¹⁻; for Sr. The positive arguments above and the excellent correlation experimentally found (see below) support strontium.

The results for a medium and a small dilution series of manganese are shown in Fig. 5. The correlation has been established between the ratio of the peak areas to the manganese concentration in milligrams per liter. The results for a higher manganese concentration (between 6 and 100 mg/l) compared to silicon and strontium are shown in Fig 5A. Strontium concentration was kept constant at 10 mg/l. The correlation with strontium is excellent (R = 0.99969), with a Relative Standard Deviation (RSD) of 11%. The result for lower manganese concentration (between 20 µg/l and 6 mg/l) is shown in Fig. 5B. The correlation is again excellent (R = 0.99969), although the linear equation differ. The Relative Standard Deviation is very poor for the lower concentrations. The single RSD is around 14% for concentration between 6 and 0.4 mg/l, 22% down to 80 µg/l and up to 52% for concentration of 20 µg/l. An RSD of 22% is reasonable for our measurement. A value higher than 22% shows an unreliable LOD, even if the calibration curve has a good correlation.

These relatively high RSD values also indicate that this method is not comparable to a standard chemical analysis of Mn in sea water by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), characterized by an RSD of 3%. The best detection limit achieved is not satisfactory for the investigation of sea water yet. In addition, in order to improve the reliability of the measurement, it will be necessary to use the Standard Addition Method, especially in the case of field measurements. This method is more practicable and has a smaller error than the calibration shown here.

Finally, since the method will be eventually applied in field, an integrated system, including the sample cuvette, the target and the laser-guiding and measuring fibres together, will be designed.

5. Conclusion

Our results show the feasibility of successfully carrying out LIBS in water within a cavitation bubble. The experimentally obtained LOD of dissolved manganese in distilled water was 80 μ g/l. Measurements for smaller concentrations down to 20 μ g/l are possible but lead to an unsatisfactory RSD. Strontium has been successfully used as internal standard. More effort needs to be directed towards improving the limit of detection and the RSD. In the planned work, a resonant excitation scheme will be tested to further enhance the sensitivity for manganese. Investigation of matrix effects, namely caused by sea salt, are in progress. Finally, several modifications for field measurements will be also necessary.

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4.3 Resonance fluorescence spectroscopy

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SPECIAL ISSUE PAPER

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Resonance fluorescence spectroscopy in laser-induced cavitation bubbles

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Abstract Laser-induced breakdown spectroscopy (LIBS) in liquids using a double-pulse Q-switched Nd:YAG laser system has provided reliable results that give trace detection limits in water. Resonant laser excitation has been added to enhance detection sensitivity. A primary laser pulse (at 532 nm), transmitted via an optical fiber, induces a cavitation bubble and shockwave at a target immersed in a 10 mg l^{-1} -100 mg l^{-1} indium (In) water suspension. The low-pressure rear of the shockwave induces bubble expansion and a resulting reduction in cavity pressure as it extends away from the target. Shortly before the maximum diameter is expected, a secondary laser pulse (also at 532 nm) is fed into the bubble in order to reduce quenching processes. The plasma field generated is then resonantly excited by a fiber-guided dye laser beam to increase detection selectivity. The resulting resonance fluorescence emission is optically detected and processed by an intensified optical multichannel analyzer system.

Keywords Resonance fluorescence spectroscopy · Cavitation bubble · LIBS · Indium

Introduction

Resonance fluorescence spectroscopy (RFS) has been shown to be one of the most sensitive atomic spectroscopic techniques. It is also referred to in some of the literature as resonance-enhanced laser-induced plasma spectroscopy

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[1], laser-excited atomic fluorescence spectrometry [2] or trace analyzer based on laser ablation and selectively excited radiation (TABLASER) [3]. The aim of this investigation is the development of a RFS-based cavitation bubbles methodology for determining the concentrations of elements in liquids. This methodology is intended for use in investigations of difficult matrices (such as salt water), or elements with interference lines (such as iron). The experimental method itself was chosen to demonstrate its ability to provide the lowest detection limits for indium. Indium itself is, however, not particularly interesting in, for example, the field of environmental analysis. Indium has not been investigated with LIBS or RFS up until now, but it is regularly used as an internal standard for inductively coupled plasma mass spectrometry (ICP-MS). It was chosen as test element due to its excitation scheme which exhibits a variety of spectral excitation and emission lines, as shown in Fig. 1. The LIBS technique has been applied successfully to a variety of different elements from a number of groups [4-8]. An advantage of using laserinduced cavitation bubbles is its ability to stop strong quenching processes, which tend to be prominent in liquids and which inhibit sensitive measurements [10, 11].

Laser pulse generation of a shockwave initiated at the target will cause an initial bubble in suspension to expand due to the low-pressure rear of the expanding pressure transient. This macroscopic cavitation bubble will therefore temporarily display reduced internal pressures during the experiment [9]. RFS can also be applied to elements that do not display different spectral lines for excitation and detection, such as manganese [8]. This experiment is part of a preliminary study of the application of RFS in laser-induced cavitation bubbles. The usage of this methodology is intended to provide in situ online analysis for both environmental purposes and in the food industry.

Indium belongs to the third group of the periodic table of elements. A sketch of its scheme of atomic levels is shown in Fig. 1. Of interest here are the two different energy levels of the $4d^{10}5s^25p$ electron configuration which share a higher 6s level. The excitation of an electron from the metastable $5p^2P_{3/2}$ ($E_{\text{metastable}}=0.274$ eV) level to the



Fig. 1 Indium atomic energy levels and spectral assignments. Excitation energies are given in eV; optical transition wavelengths in nm; corresponding transition probabilities in 10^8 s^{-1} are included in parentheses [12]

resonant $6s^2S_{1/2}$ state ($E_{resonant}=3.02 \text{ eV}$) can be driven by a dye laser tuned to 451.1 nm. The fluorescence from the $6s^2S_{1/2}$ state to the ground-level $5p^2P_{1/2}$ state gives an atomic line at 410.2 nm. Excitation and detection wavelengths are both detectable seperately. This allows the ICCD camera to be triggered just before the start of resonant excitation, thereby reducing the time constraints. Exact delay time constraints are crucial when analyzing elements with resonant excitation and detection spectra at the same wavelength.

Experimental

A double-pulse Q-switched Nd:YAG laser beam (Solo III PIV, New Wave Research, Fremont, CA, USA) is coupled to a quartz fiber, with a core diameter of d=600 µm, using a biconvex BK7 lens, focal length f=40 mm. The laser provides 6 ns pulses at the second harmonic wavelength of 532 nm with a repetition rate of 1 Hz. The laser peak irradiance at the fiber tip is 540 mJ cm⁻² for the primary and 490 mJ cm⁻² for the secondary laser pulse. A sketch of the experimental set-up is shown in Fig. 2. The fiber is



guided to an aluminum target and positioned so as to ensure that plasma is generated at a given position. The aluminum target is mounted on an x-y-z adjustment table to allow horizontal movement of the target, which is required after each sample measurement. The first laser pulse generates a cavitation bubble in the indium solution (see the Sample preparation section). The second laser pulse is timed to induce a plasma breakdown just before the maximum expansion of the cavitation bubble is expected (after ~100 µs). A Lambda Physik (Göttingen, Germany) ScanMate LPY150 dye laser using coumarin 450 (peak at 448 nm, tuning range 434–463 nm [13]) is pumped by a Nd:YAG laser at a wavelength of 355 nm. The output of the narrow-band tunable dye is coupled by a BK7 lens (f=25 mm) to a quartz fiber with core diameter $d=300 \mu m$. The fluence at a wavelength of 451.1 nm at the fiber tip is \sim 4.5 mJ cm⁻². Plasma emission is collected directly by a fiber bundle (90 fibers with 100 μ m core diameter) perpendicular to the target. The fiber used to transmit the excitation emission is placed inside the detection fiber bundle. This arrangement is shown in Fig. 3.

The sample cell is a glass cuvette $(20 \times 20 \times 10 \text{ mm}^3)$. A magnetic stirrer stops the deposition of ablated aluminum on the target surface. The position of the fiber with respect to the target is held constant during the experiments. After a complete measurement sequence, the cuvette is removed, rinsed and filled with an increased concentration of suspension. It is then readjusted to the target. A microscope fitted with a CCD camera (SensiCam, VGA, 640×480 pixel, 9×9 µm² pixel area, PCO, Kelheim, Germany) is used to observe bubble expansion and plasma emission [14]. The camera is used to detect shadow images at an exposure time of 30 µs. The fast photography illumination required to observe the position of the fiber in relation to the target is provided by a cold-light lamp focused on the target using two BK7 lenses (f_1 =100 mm, f_2 =50 mm). The spectroscopic fiber is adjusted to be ~ 1 mm above the surface of the cavitation bubble. This protects the analysis fiber from any damage due to the ablation pulse, debris and shockwave effects. Figure 3 shows a shadow image of the cavitation bubble and the plasma emission induced by the Nd:YAG double pulse.





Fig. 3 Shadow image of a cavitation bubble showing the laser ablation fiber (*left*), the spectroscopic fiber bundle (*top*) and the dye fiber (*top*, *inside fiber bundle*)

The numerical aperture of the sampling fiber bundle is matched with a spot-to-line converter to the Acton Research (Acton, MA, USA) SpectraPro spectrograph. A Czerny-Turner spectrograph with a focal length of 275 mm and a grating of 1200 lines/mm blazed at 500 nm is used. An intensified CCD detector (i-star DH734, Andor, Belfast, UK, 1024×1024 pixels, 13×13 μ m² pixel area, Gen II intensifier) records the signal. The gated ICCD camera is set to trigger 1 µs after plasma ignition and 0.2 µs before the dye laser pulse. The measuring gate width is 10 µs. The delay and synchronization is controlled by a delay/gate generator (DG 535, Stanford Research Systems, Sunnyvale, CA, USA). Sample preparation

The ICP-OES standard solution of indium was obtained from a stock solution of 1000 μ g ml⁻¹ In from In(NO₃)₃ in 3% HNO₃. Different concentrations are yielded using a dilution series from 10 mg l⁻¹ to 100 mg l⁻¹. All samples are diluted in deionized water. An aluminum band (Merck, Darmstadt, Germany) was used as target material.

The background-corrected normalized intensity of the peak at 410.2 nm is correlated with the indium concentration. Each sample was measured ten times, each with ten accumulated pulses.

Results and discussion

The quantitative analysis of indium in pure water is carried out by detecting and measuring the spectral line at 410.2 nm (6s ${}^{2}S_{1/2} \rightarrow 5p {}^{2}P_{1/2}$). The 6s level is resonantly excitated by the 451.1 nm line (5p ${}_{2}P_{3/2} \rightarrow 6s {}^{2}S_{1/2}$). Figure 4 shows the intensities of single pulses result from combinations of different lasers. The line widths for the excitation spectra are similar to that of the emission line shown, which is attributed to deficiencies in the dye laser system. The resonant excitation of plasma inside a cavitation bubble in order to induce an atomic line of In only requires that a dye and two Nd:YAG lasers are used. Other combinations yield either no signal (one Nd:YAG to induce the plasma or bubble) or a higher background (combination of two lasers). The timing (100 µs: ignition of the plasma in the cavitation bubble, plus 1 µs: open the measuring window of the gated spectroscopy camera, plus 0.2 µs: resonant irradiation of the dye laser) was calculated to provide the best results. It was expected that resonant excitation without laser-induced plasma inside the cavitation bubble would also show a peak. Transitions with a



Fig. 4 Optical emission signal due to combined excitation by different lasers



Fig. 5 Correlation coefficient of normalized intensity of peak area at 410.2 nm in relation to indium concentration

total angular momentum J=0, however, have a lower intensity. Due to the delay time of $\sim 1 \mu s$, no optical emission signal was detected. This time delay is relatively long compared to that used by other experimenters, and the emission was therefore reduced to below detectable levels. De Giacomo et al. [5] have shown spectra with a delay time of 200 ns, although a long-lasting emission (for about $4 \mu s$) was also mentioned. The weak OES signal was observed with a time delay of 400 ns.

The correlation between the background-corrected normalized peak at 410.2 nm and the indium concentration is shown in Fig. 5. The correlation for a concentration range of 10 mg Γ^{-1} to 100 mg 1^{-1} is excellent (*R*=0.9976) even without using internal standards.

The influence of a variety of parameters such as plasma temperature, amount of ablated material, bubble size and phase of bubble oscillation on the peak signal could be reduced if internal standards were used. However, although the use of such an internal standard would yield more reliable results, it would also lead to more sophisticated measurements. The relative standard deviation is less than 5%, except in the case of 10 mg l^{-1} (15%). The limits of detection achieved by LIBS or RFS are not particularly satisfying, but earlier results from using LIBS in cavitation bubbles have shown the possibilities of this technique. Earlier investigations using emission spectroscopy with an identical set-up apart from the use of a dye laser have shown excellent results for levels of dissolved manganese in water samples down to 80 μ g l⁻¹ [8]. The limit of detection also depends on the element. De Giacomo et al. [5] have shown that even using identical set-ups can lead to different detection limits, such as 1.4 mg l^{-1} for magnesium (Mg) and 0.4 mg l^{-1} for sodium (Na). Due to the fact that In was chosen as the test element, no further work into enhancing this limit of detection is planned.

Up to now the excitation wavelength of the dye laser and the fluorescence of In have been separated using a spectrograph. Further work is planned where one of the atomic lines of indium (for example, the line at 410.2 nm) will be re-excited and the subsequent fluorescence will be detected at the same wavelength. However, to make sure that the detected peak originates solely from the fluorescence of In, the timing must be exact. By initially investigating the timing using different wavelengths for excitation and detection, it is possible to avoid wrong source interpretation or damaging the spectroscopic camera. The next step is then to transfer this method to atomic or ionic lines of other elements, which may not have the ability to be excited and detected at different wavelengths.

Conclusions

Results have shown the feasibility of successfully carrying out resonance fluorescence spectroscopy within laserinduced cavitation bubbles. The correlation coefficient between the intensity and the indium concentration is excellent. The limit of detection in the case of 10 mg l^{-1} of indium needs to be improved, but the correlation observed without internal standard use is promising. Further work into excitation and detection at the same wavelengths is planned, but with the risk of wrong source interpretation reduced. This requires a careful preliminary study of the timing requirements for the lasers and optical detection. The timing required for resonant excitation of an indium line has been determined by using different types of laser to induce cavitation bubbles, plasma, and resonant excitation.

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4.4 Spectroscopy on laser induced plasma

Spectroscopy on laser induced plasma in cavitation bubbles

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ABSTRACT

Spectroscopic results with laser induced breakdown spectroscopy (LIBS) in liquids have shown a signal improvement using double pulse experiments compared to single pulse measurements. A setup of two Q-switched Nd:YAG lasers in an orthogonal arrangement have led to bright illuminated plasma inside cavitation bubbles. A Nd:YAG laser pulse focussed by a lens (6 ns@532 nm, $2.9*10^{19}$ W/m²) into the center of a water filled cuvette gives rise to a cavitation bubble. A second tightly focused Nd:YAG laser pulse (5 ns@1064 nm, $3.1*10^{19}$ W/m²) induces a plasma at approximately 70 µs delay within the cavitation bubble. These absolutely reliable processes allow to capture image sequences of plasma filled cavitation bubbles with an ultrafast camera. The optical emission is guided via a quartz fibre to a Czerny-Turner spectrograph and recorded by an intensified CCD camera. A delay time of more than 1.7 µs between plasma ignition and spectroscopic data taking is necessary to avoid inverse bremsstrahlung and residual lines arising from bright plasma emission. Characteristic spectral line intensities of manganese (Mn) and Palladium (Pd) are recorded and correlated with an internal calibration standard using strontium (Sr) and chromium (Cr) respectively. The LOD of manganese is 0.3 mg/L.

Keywords: LIBS, cavitation bubble, manganese, palladium

1. INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) has shown to be a powerful tool for the investigation of solid, liquid, and gaseous samples¹. The limit of detection (LOD) in the case of manganese in different solid samples ranges from 0.11 ppm to 470 ppm (cfs. Handbook of LIBS², Compilation^{3, 4}). Industrial applications like scrap material recycling⁵ and homeland security⁶ appliances start to get implemented relying on a variety of ready-to-use equipment being available on the market. Experiments with double-pulse LIBS have shown a 10 to 100-fold increase in emission line intensities².

Elemental analysis in liquids is more difficult to investigate, but has also shown reasonable results⁷. To prevent strong quenching effects of the fluid matrix different techniques have been employed like e.g. analysis on flowing surfaces⁸, on frozen samples⁹, and on nebulized liquids¹⁰. Recently more often a double pulse setup using different geometrical designs and different time delays have been reported. Arrangements are collinear multiple pulses or an orthogonal intersection (Lui et.al.¹¹ and ref. therein), typically one beam perpendicular and one parallel to the surface. The second pulse serves either to enhance the ablation efficiency or to reheat the plasma plume. Double pulse LIBS in bulk water and on submerged samples has been investigated as well^{12,13, 14}.

An elegant approach to create a transient gaseous environment within the liquid sample was introduced by creating a laser induced cavitation bubble^{14, 15}. A second laser pulse induces the spectroscopic plasma within the lifetime of this cavitation bubble. The latter is filled with vaporized liquid and the ingredients. Cavitation bubble and LIBS plasma were produced via optical fibre guiding on a target, which serves primarily as an absorber to start the optical breakdown¹⁶.

Evaluation of spectral data with internal standards is useful to overcome the shortcome of experimental data in terms of varying plasma and cavitation bubble parameters. An approximately comparable vapour pressure of internal standard and analyte must be realised to achieve reproducible data, since fractional evaporation from the ablated droplets changes the ratio of free atoms until all material is atomized^{2,9}.

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Manganese is a good marker for tidal and seasonal fluctuations in the wadden sea. Large changes in concentration of this element appear due to the binding of manganese to mineral particles in suspension or in the sediment. Primary organic particle production and micro-organisms give rise to re-mineralization of manganese. Dissolved Mn has been measured for example with ICP-MS¹⁷. In-situ or on board measurements would lead to a better screening. Contaminations of palladium, a platinum group element (PGE), started to come into focus due to airborne particulate matter emission of catalytic converters¹⁸. Emitted PGE are found in urban air and accumulate on the road surface and in roadside soil. Transport of PGE via surface drainage following strong rainfall is resulting in contamination of aquatic environments. There is now increasing evidence that a fraction of PGE in the environment is bio available, and potential uptake into the biosphere is raising concern over potential risks for humans and the environment¹⁹.

2. MATERIALS AND METHODS

2.1 Samples and Preparation

Several liquid samples containing elements palladium/chromium and manganese/strontium are analyzed.

Palladium samples have been prepared from standard solution for Atomic Absorption Spectroscopy (AAS), 1 g/L Pd in 10 % HCl (Acros Organics). The internal standard chromium origins from a stock solution of 1 ± 0.002 g/l in 0.5 mol/L HNO₃ (Merck). Sample concentrations range from 1 mg/L to 80 mg/L Pd while the concentration of the internal standard chromium (Cr) is kept constant at 100 mg/L. Liquids under investigation have been prepared by dilution in 1% HNO₃.

The manganese measurements made use of the addition method. Starting from pure water manganese is added from a 1.001 ± 0.002 g/L standard solution (Merck). The concentration varies from 0.7 mg/L to 24 mg/L. Strontium (Sr) serves as an internal standard at 1.3 mg/L and 2.6 mg/L. Stock is standard solution for AAS, 1 g/L in 2 % HCl (Acros Organics).

Care has been taken to avoid cross contamination. Samples were investigated immediately after preparation to avoid any deposition effects on wetted surfaces.

2.2 Methods

Extending the experiment with a target¹⁶ to a platinum group element, palladium, gives on one hand a good correlation between the concentration of palladium and spectral data and also a high standard derivation. On the other hand an electroless metal deposition²⁰ of palladium on the silicon surface leads to enrichment of the investigated element at the target. A modified setup without target has been tested with water samples containing manganese and strontium.

First step is the production of a gaseous surrounding inside the liquid sample, provided by a reliable laser induced cavitation bubble in term of stability of the bubble position and diameter. To avoid multiple breakdowns before or after the planned bubble position it is necessary to expanded and focus the laser beam into the liquid. The environment of the bubble contains a representative vaporized sample of the liquid. Second step is the ignition of a plasma by a suitable delayed second laser pulse within the cavitation bubble. The optical plasma emission is guided via a fibre to the spectrograph. The interaction region is observed simultaneously by a camera to check successfully merged dynamics of plasma and bubble.

The advantages of using a target in liquid samples is a localized excitation of plasma and cavitation bubble with fibre guided lasers.

With the set-up described, laser pulses can be guided at negligible transmission losses; and moreover, it allows experiments on samples with low or dangerous accessibility.

Emission lines of a solid target might interfere with the signal of the analyte. Intensity differences between broadened emissions lines and higher background radiation of solid targets compared to liquid samples occur. We would like to point out that an accumulation of material on the target can create systematically deviating results. This is a possible source of error should thus be avoided.

Different requirements have to be taken in account if plasma and cavitation bubble were excited both directly in liquids. The spatial "jitter" of the bubble has to be minimized to provide a maximum number of plasma filled bubbles. To exceed the breakdown threshold within the bubble a tighter focusing of the plasma ignition pulse as well as a higher energy compared to the target setup are necessary. The necessary high energy input may lead to hydrogen gamma, beta and epsilon line transitions and strong background signals in optical emission spectroscopy (OES). Longer delay times to

allow for a decay of continuous plasma emission are advisable to record spectra in targetfree mode. Hydrogen lines might interfere with atomic lines of the investigated element or even impede the appropriate use of an image intensifier of the spectroscopic camera.

2.3 Experimental setup

Fig. 1 shows the experimental setup for the analysis of different liquid samples containing manganese and strontium as well as palladium and chromium in varying concentrations. An image of a plasma filled cavitation bubble, taken by a ultrafast camera, and a picture of the setup have been implemented in the sketch.

Cavitation bubbles are produced by a Q-switched Nd:YAG laser, $\Delta \tau = 6$ ns @ $\lambda = 532$ nm (Solo III PIV, New Wave Research, Fremont, CA, USA). The laser beam is expanded by a Galilean telescope (f_1 = -40 mm, f_2 = 100 mm) in order to allow for a minimum beam waist (f_3 = 40 mm) inside the cuvette. The estimated focal spot size of ca. 4,3 µm corresponds to a peak power density of 2*10¹⁹ W/m². The glass cuvette has a size of 3 x 3 x 3 cm³ and is filled with the liquid under investigation.

A CCD camera (SensiCam, VGA, 640×480 pixel, 9×9 μ m² pixel area, PCO, Kelheim, Germany) fitted to a microscope (Leica MZ9.5, Leica Microsystems, Wetzlar, Germany) is used to monitor bubble expansion and plasma evolution²¹. The setup is designed to record shadow images of the cavitation bubbles at an exposure time of 2 μ s with variable delay times. Shadow images visualize the rate of change of density gradient by projecting parallel light through the sample. Illumination of the cavitation bubbles in the cuvette is provided by a halogen lamp collimated via two BK7 lenses (f₇=40 mm, f₈=100 mm). Optical filters (BG 38, OG 570) block undesired laser irradiation of the SensiCam. Fast photography is required to observe the position of the fibre in respect to the cavitation bubble and the plasma position inside the cavitation bubble, respectively.

Plasma inside the gaseous environment of the bubble is ignited by a further Q-switched Nd:YAG laser, $\Delta \tau = 5$ ns (a) $\lambda = 1064$ nm (Tempest, New Wave Research, Fremont, CA, USA). The laser beam is expanded and focused with a set of two lenses (f₄=-16 mm, f₅=60 mm) and a 90° off-axis parabolic mirror (f₆=25 mm). This yields a focal spot size of ca. 2,8 µm and a peak power density of 3.1*10¹⁹ W/m². An xyz- adjustment of the so called bubble laser allows to precisely and reproducibly superimpose cavitation bubble and LIBS plasma.

Plasma emission is collected by a multimode quartz fibre with 945 μ m core diameter and guided to an Acton Research (Acton, MA, USA) SpectraPro spectrograph equipped with an intensified CCD detector (i-star DH734, Andor, Belfast, UK, 1024×1024 pixels, 13×13 μ m² pixel area, Gen II intensifier). The Czerny-Turner spectrograph has a focal length of 275 mm and interchangeable gratings of 1200 lines/mm blazed at 500 nm, 3600 lines/mm blazed at 230nm, and a grating of 300 lines/mm blazed at 300 nm, respectively.

Triggering and timing of the experiment is sketched in Fig. 2. Once the cavitation bubble has reached its maximum size (approx. 70 μ s after the bubble laser pulse) plasma ignition for LIBS is triggered. The temporal evolution of the size of the cavitation bubble has been investigated earlier²² and is adequate for the experiments presented. The measuring gate of the spectroscopic camera is set after decay of inverse bremsstrahlung. In target mode optimum delay times of 0.3 μ s have been observed. This time is too short for a targetfree mode experiment because of necessarily higher amount of delivered pulse energy and therefore stronger optical emission intensities. This leads to a minimum delay time of 1.7 μ s for atomic line detection; even up to 7 μ s line signals are observable. The gate width of the spectroscopic camera is set to 1 μ s in target mode and 10-40 μ s in targetfree mode.

Triggering rate is set to 1-5 Hz by an electronic trigger box and two delay gate generators (DG 535, Stanford Research Systems, Sunnyvale, CA, USA).



Figure 1: Experimental LIBS setup on liquid samples: sketch with implemented images of a plasma filled cavitation bubble and the setup. Focal lengths f are given in mm.



Figure 2: Timing scheme for double pulse LIBS on liquid samples to visualize bubble laser intensity versus time (a); bubble radius evolution versus time taken from Müller et.al.²² (b); plasma laser intensity versus time (c); decay of emission lines versus time (d). The dashed line connecting Fig. 2a and b marks the creation of the bubble. The dashed line connecting Fig. 2b, c, and d marks the plasma ignition in relation to the cavitation bubble and the plasma decay influencing the delay for recording emission spectra.

3. RESULTS AND DISCUSSION

The data of experiments with and without targets have been evaluated by comparing background corrected and normalized peak areas of investigated elements at various concentrations to the peak area of the internal standard. Since both standard and investigated element are affected similarly by fluctuating parameters like plasma temperature, plasma pressure, collision rates etc., correlating peak area ratios allows direct conclusions about the concentration without an actual determination of these parameters².

3.1 Palladium, target mode, OES

Palladium measurements with an internal standard of chromium and a silicon target have been performed by the experimental setup described previously in Koch et. al.²³. Data evaluation has shown a promising result with a linear regression correlation coefficient of R = 0.9978 but with a high standard derivation between 3 % and 30 %. The correlation of the peak area of palladium at 351.7 nm compared with the internal standard chromium at 357.9 nm is shown in Fig. 3. Concentrations between 5 mg/L and 80 mg/L palladium were tested while the concentration of internal standard chromium is constantly kept at 100 mg/L. In the course of the experiments it became obvious that at a constant concentration of 1 mg/l palladium and 100 mg/L chromium a time dependent enrichment of palladium on the silicon

target takes place. Measurements have been repeated each 30 seconds and all recorded signals of chromium stayed stable. In contrast all palladium lines rose over time. The force of attraction between palladium and silicon due to electroless metal deposition misleads to seemingly rising concentrations of palladium. This enrichment on the target might be useful for measurements of low concentrations. Unknown factors of the amount of elemental depletion in the solution may depend on concentration, matrix effects, elemental composition, and target material. Especially the unknown dependence of enrichment versus time led to the conclusion to proceed with a targetless setup. At least the metal target would have to be replaced by a non metal target

However, ablation of the target generally resulted in readjustments of the fibre position. Ablation products in the liquid sample led to increased turbidity and absorption effects on all optical signals. Moreover, potentially emission lines of the target material may disturb or overlap the analytes fluorescence. Therefore further investigations have been carried out on manganese in targetless mode to prevent any possible interference due to the problems mentioned above.



Figure 3: Correlation between palladium concentration (5 mg/L to 80 mg/L) and signal intensity ratio of peak area from palladium (351.7 nm)/chromium (357.9 nm) with internal standard Cr constantly kept at 100 mg/L.

3.2 Manganese, targetless mode, OES

The change to a targetless mode implied the delivery of higher pulse energies which necessitate a free beam focusing of the bubble and LIBS plasma lasers. The cavitation bubble extends up to a diameter of ca. 1.5 mm. The LIBS plasma is induced inside the cavitation bubble by an off-axis parabolic mirror; an additional increase of the cavitation bubble size was observed. The manganese triplet lines at 403.1 nm, 430.3 nm, and 403.4 nm are not resolved. Nevertheless the resulting peak area was compared to the internal standard strontium @407.8 nm. Correlation for 100 accumulated spectra is shown in Fig. 4 for concentrations between 0 mg/L and 7 mg/L Mn with 2 mg/L Sr as internal standard. The linear correlation is excellent (R = 0.9982) yielding 2% relative standard deviation (RSD, 3 sigma). Based on 3σ criterion, the limit of detection (LOD) was determined as 0.3 mg/L. The lowest measured manganese concentration was 0.7 mg/L. Higher manganese concentrations from 1.3 mg/L to 23 mg/L have been tested with 1.3 mg/L internal standard concentration for a range of 1.3 mg/L - 10.2 mg/L Mn and 2.6 mg/L internal standard concentration for a range of 16,7mg/L – 23.1 mg/L Mn. 150 accumulated spectra result in a linear correlation coefficient of R= 0.9985, RSD = 9 %. The sensitivity regarding manganese is yet not that high as with a target mode setup. Former results¹⁶ have shown a limit of detection of 80 µg/L manganese in bi-distilled water. Lazic et. al.¹⁵ proved a manganese concentration of 390 µg/L by applying spectra filtering procedure²⁴. Manganese in liquid samples is described with different LOD's ranging from 0.7 ppm - 320 ppm (cfs. Handbook of LIBS², Compilation^{25, 26}).



Figure 4: Signal intensity ratio of manganese and internal standard chromium with concentration of 0 - 7 mg/L Mn and 2 mg/L Sr, 100 accumulated spectra

Optical emission spectra included disturbing hydrogen gamma, beta and epsilon line transitions occurring like residual lines (Fig. 5b2). These lines occur normally at simultaneously bright plasma emission as can be visualised by shadow images (Fig. 5b1). Different brightness of plasmas showed different spectral signals. No plasma signal inside the cavitation bubble resulted in no spectra. Hydrogen signals can also be depressed by longer delay times between plasma and signal recording. Measurements on manganese samples showed no interference but in the case of other elements, lines shows up on top of those line. A delay time longer than 1.7 μ s was required to suppress the residual signal. Shorter delay times overloaded the CCD intensifier. Since an on-site jitter either of the bubble laser or of the plasma laser influenced the line emission intensity very strongly, a correlation with internal standards was necessary.



Figure 5: Plasma formation inside a cavitation bubble (a/b 1) with related Mn spectra (a/b 2) (concentration = 100 mg/L, grating 1200 l/mm, 500 nm blaze, gate delay = 0.3μ s, gate width = 1 μ s, accumulation = 1). Residual broadened lines of hydrogen (H delta (410.2nm) and H gamma (434.0nm)) are in correlation with intensive plasma illumination.

4. CONCLUSION AND OUTLOOK

Experiments with laser induced breakdown spectroscopy on liquid samples yield reasonably good results in both targetand targetless mode. Palladium in a concentration range from 5 mg/L to 80 mg/L has been measured with a good linear correlation coefficient. A possible accumulation on the target, depending on the combination of analyte and target is a major disadvantage of the target mode method. Electroless metal deposition of palladium on silicon was observed while chromium and silicon are not influencing each other. Appropriate plastic targets may overcome this restriction. A modified setup without the use of targets lead to an excellent linear correlation (R = 0.9982) of manganese concentrations evaluated by strontium as an internal standard. The LOD is 0.3 mg/L. In order to meet trace analysis requirements the method still needs some improvement to be comparable with standard methods like ICP-MS. Resonance fluorescence spectroscopy is a possible technique to amplify signal intensities. A targetless setup is an advantage concerning attraction forces onto surfaces by the analyte. On the other hand spectra are directly related to the development of the plasma and resulting emission line intensities inside the cavitation bubble. More intense plasma emission does result in a stronger signal but also may show interfering hydrogen gamma, beta and epsilon line transitions as a drawback. The amount of energy to excite a plasma inside a cavitation bubble needs to be reduced. Up to now the impact of the plasma inside the bubble is only controllable at the applied energy level. Further developments on the setup with a dichroic mirror for a better adjustment and laser beam overlap inside the cavitation bubble might be a solution. The use of increasing accumulation numbers is also possible. Comprehensive work on plasma expansion in cavitation bubbles is in progress.

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5 Cavitation bubbles and dynamics

This chapter comprises the work on cavitation bubbles including the dynamic of cavitation bubbles, measurement methods of the bubble radius, and an estimation of the collapse temperature from the bubble size.

- M. Müller, W. Garen, S. Koch, F. Marsik, W. Neu, E. Saburov, Shock Waves and Cavitation Bubbles in Water and Isooctane generated by Nd:YAG Laser. Experimental and Theoretical Results, Proc. SPIE 5399 (2004) 275-282 [MGK+04]
- S. Koch, W. Garen, F. Hegedüs, W. Neu, R. Reuter, U. Teubner, Time resolved measurements of shock induced cavitation bubbles in liquids, Appl. Phys. B (2012) DOI: 10.1007/s00340-012-5070-1 [KGH+12]

The spectroscopic LIBS methods evaluated in this work are mainly carried out in cavitation bubbles. The gaseous low-pressure environment of the cavitation bubble is suitable for sensitive spectroscopic analysis [Nyga93]. The size of the bubble and the maximal radius are depending on e.g. fluence, viscosity and, temperature. The bubble dynamic of distilled water, isooctane, as an example for retrograde fluids, and glycerine for its high viscosity and density, are investigated.

Bubble size, collapse time, and oscillation behavior are largely different in water and isooctane [MGK+04]. Second maximal radius in isooctane is more than two times larger than in water. After the first compression, the bubble shape is slightly deformed and resembles the initial plasma shape. Experimental values are determined by single and multi exposure images and compared with Gilmore's model which is used for numerical simulation of bubble dynamics.

Inside the cavitation bubble high changes of pressure and temperature, respectively, occur during one life cycle. Only the bubble at its maximum extension provides a suitable environment for LIBS. For this reason, a time delay Δt between the laser pulse inducing the cavitation bubble (Laser 1) and the laser pulse for inducing the plasma inside the cavitation bubble (Laser 2) needs to be adjusted carefully to allow the bubble

to have evolved to its maximum size. A measurement method using a HeNe laser for investigating bubble evolution was developed ([KGH+12]). High temporal ($\Delta t = 20$ ns) and spatial ($\Delta r_b = 3 \ \mu m$) resolution from the onset to the collapse of a single cavitation bubble as well as the detection of the combined shock waves generated by a single shot of a high power laser are determined. Differences in bubble dynamics in distilled water and glycerine are experimentally analyzed. The method is easy to assemble and indicates presence of shock waves and temporal evolution of the cavitation bubble immediately.

Temperature estimation from bubble size

An estimation of the collapse temperature related to the maximum size of the cavitation bubble is possible under the assumption of a gaseous bubble in a mainly adiabatic process.

An adiabatic process is characterized by

$$p_i \cdot V_i^\kappa = p_f \cdot V_f^\kappa \tag{5.1}$$

where κ is the heat capacity ratio C_p/C_V or adiabatic index with the indices *i* for the initial conditions at the maximum bubble radius at the collapse time t_c and *f* for the final condition at the collapse.

The ideal gas law describes a classical ideal gas with

$$p \cdot V = n \cdot R \cdot T \tag{5.2}$$

where n is the amount of substance of the gas in terms of mole number and R is the gas constant.

The combination of Equation 5.1 and Equation 5.2 leads to

$$T_f = T_i \left(\frac{r_i}{r_f}\right)^{3(\kappa-1)} \tag{5.3}$$

with $\kappa = 1.4$ for an adiabatic change of condition of a two atomic gas and $\kappa = 1.33$ for water vapor as a three atomic molecule. The process of compression until the collapse is not completely adiabatic. The beginning of the bubble compression includes an isothermal change of condition. Hence, the polytropic exponent $n_p = 1$, where the adiabatic index κ is a special case of $n_p = \kappa$. Therefore calculations with $\kappa = 1.3$ are preferable. This value is introduced by Crum [Crum83], proved from measurements on the effective polytropic exponent for bubbles of various gases in water. Typical values of a maximum bubble radius of about $r_i \approx 1 \text{ mm}$ and a minimum bubble radius at the collapse of about $r_f \approx 0.02 \text{ mm}$, have been obtained from the the experiment [KGH+12]. A temperature of approx. 9900 K is estimated from Equation 5.3 at water temperature $T_i = 293$ K and $\kappa = 1.3$.

5.1 Shock waves and cavitation bubbles

Shock Waves and Cavitations Bubbles in Water and Isooctane generated by Nd:YAG Laser. Experimental and Theoretical Results

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ABSTRACT

Temporal evolution of laser generated cavitation bubbles and shock waves were studied. Q-switched Nd-YAG laser pulses at 1064 nm are focused into the liquid. An Imager 3 CCD camera with multi exposure mode allows recording of 10 images with minimal exposure delay of 100 ns and minimal exposure time of 100 ns. Illumination is provided by xenon flash lamp for single exposure (shock wave recording) and by halogen lamp for multi exposure mode (bubble recording). Distilled water and a retrograde fluid, isooctane, have been under investigation to identify the differences in the cavitation process and shock wave propagation. The calculation of the shock wave velocities in water and isooctane are based on image recording at constant exposure time of 100 ns and using laser differential interferometry. Strong differences of bubble oscillation were observed in water and isooctane. Gilmore's model is used for numerical simulation of bubble dynamics.

Keywords: laser, ultra fast imaging, shock waves, bubble dynamics, cavitation

1. INTRODUCTION

Optical breakdown generated by laser represents excellent possibility of the laboratory modelling of such important physical phenomena as cavitation. The major complication in the investigation of these phenomena is the time duration of the whole process. The most important events happen in microsecond time intervals for the cavitation bubble and in nanoseconds time intervals for the shock waves. By the application the single exposure record are the problems different terms for every single event. These differences can be caused by unequal plasma size and different bubble nucleus. In this paper we presented a possibility to estimate temporal evolution of a cavitation bubble and shock wave with using multi exposure record. This method allows to detect the temporal evolution rather then the single record and reduces the time of measurement. We used the single exposure record to predict the time evolution of the bubble radius. These results were instrumental to set the time delay between exposure for the multi exposure record.

The physical properties of liquids can play in many cases a dominate role in the cavitation bubble and shock waves behavior. To attach this differences we investigated distilled water and a retrograde fluid, isooctane. The majority of investigations has been carried out for water by Vogel³ and his coauthors.

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2. EXPERIMENTAL SET-UP

2.1. Experimental setup for the measurement of cavitation bubbles

The experimental arrangements for the bubble dynamic investigations is showed in Fig.1. and Fig.2. A Nd:YAG laser (New Wave Research, Tempest) in Q-switch mode was used to emit pulse signals at wavelength of 1064 nm. The laser pulses were focused trough the lens into the glass cuvette. The lens was built into the cuvette wall. The beam diameter was approximately 8 mm. The cavitation process was observed in the focus of the laser beam. Shock waves and cavitation bubbles were investigated by time resolve photography. Images were taken with CCD Imager 3 camera mounted on a microscope (Leica MZ6). For the photography of cavitation bubbles was used, multi exposure and single exposure camera record. By the multi exposure record are the individual frames stored over themselves in one picture. The continual lighting (Fig.1.) for the multi exposure was provided by halogen lamp (KL 1500 Electronic) focused through lens to microscope. The illumination for the single exposure was provided by xenon flash lamp (Drelo BAL 1507A) with the pulse duration up to 400 ns (Fig.2.). The exposure time was set constantly at 100 ns.



Figure 1. Experimental setup for the measurement of cavitation bubbles (Continual lighting).

2.2. Experimental setup for the measurement of shock waves

The basic setup for the shock wave measurement was identical to adjustment for the cavitation bubble measurement, as evidently in Fig.2. For the shock wave photography was used single exposure record. A diffusion plate was used for the light homogenization. The camera exposure time was set constantly at 100 ns. The multi exposure mode was limited up to three exposures because of the flash duration. The laser, camera recording and illumination were triggered with a Delay/Pulse generator (STANFORD RESEARCH DG 535). The laser pulse energy was measured with using internal laser sensors and with energy meter for each measurement. The energy meter was calibrated before and after each measurement in front of the laser beam. A ultra fast diode (ALPHALAS UPD) with risetime < 300 ps was used to confirm the time delay between trigger signal and laser beam initiation. For the comparison were used only results with energy abbreviation up to 3%. The water temperature was measured with digital thermometer. The laser differential interferometer⁶ was based on He-Ne laser. The interference signal was scanned with diode couple, displayed, and saved by oscilloscope. The distance between the beams was 1 mm.

3. NUMERICAL MODEL

For the calculation of temporal development of the bubble radius was used Gilmore's cavitation bubble model. The one-dimensional model considerers compressibility, viscosity and surface tension. It neglects evaporation, condensation, gas diffusion and heat transfer. The mixture of gas and vapor inside the bubble was assumed to be an ideal gas. The numerical simulation started at the maximal bubble radius after first expansion. This



Figure 2. Experimental setup for the measurement of cavitation bubbles and shock waves (Flash lighting).

initial radius for the simulation was obtained from the experiment. Start pressure of the gas inside the bubble was found by test to reach the second maximal radius.

The equation for the Gilmore's model^{2 4} is

$$\ddot{R} = \left[-\frac{3}{2} \left(1 - \frac{\dot{R}}{3C} \right) \dot{R}^2 + \left(1 + \frac{\dot{R}}{C} \right) H + \frac{\dot{R}}{C} \left(1 - \frac{\dot{R}}{C} \right) R \frac{dH}{dR} \right] \cdot \left[R \left(1 - \frac{\dot{R}}{C} \right) \right]^{-1}.$$
(1)

Where, R(t) is the bubble radius in time, \dot{R} the bubble radius velocity, C is the speed of sound in the liquid near the bubble wall and H the enthalpy difference between the liquid at pressure P(t) and at pressure p_{∞} :

$$H = \int_{p_{\infty}}^{P(R)} \frac{dp}{\rho}.$$
 (2)

The relation between pressure at the bubble wall P and liquid density is expressed by following equation

$$\frac{P+B}{p_{\infty}+B} = \left(\frac{\rho}{\rho_0}\right)^n.$$
(3)

Where B and n are experimental values. For isooctane these coefficients were evaluated from calculation of density - pressure dependence based on critical properties.¹ Pressure at the bubble wall is expressed by equation

$$P = \left(p_{\infty} + \frac{2\sigma}{R_0} - p_v\right) \left(\frac{R_0}{R}\right)^{3\kappa} - \frac{2\sigma}{R} - \frac{4\mu}{R}\dot{R}$$

$$\tag{4}$$

where σ denotes the surface tension, μ the dynamic viscosity, κ the ratio of the specific heat at the constant pressure and at the constant volume, p_v the vapor pressure and R_0 the equilibrium bubble radius. The combination between the enthalpy equation (2) and equation of state of the liquid (3) leads to following expression of speed of sound in liquid

$$C = (c_0^2 + (n-1)H)^{1/2}$$
(5)

and the enthalpy H(t) at the bubble wall

$$H = \frac{n(p_{\infty} + B)}{(n-1)\rho_0} \left[\left(\frac{P+B}{p_{\infty} + B} \right)^{(n-1)/n} - 1 \right].$$
 (6)

For the numerical simulation were used following constants:

water: $\rho = 989 \text{ kg} \cdot m^{-3}$, $\mu = 0.001004 \text{ Pa·s}$, $\sigma = 0.07274 \text{ N·m}$, $c_0 = 1480 \text{ m} \cdot s^{-1}$, $\mathbf{p}_{\infty} = 1.10^5 \text{ Pa}$, $\mathbf{B} = 314 \text{ MPa}$, $\mathbf{n} = 7$, $\kappa = 1.4$.

isooctane: $\rho = 700 \text{ kg} \cdot m^{-3}$, $\mu = 0.00048 \text{ Pa·s}$, $\sigma = 0.021 \text{ N·m}$, $c_0 = 1050 \text{ m} \cdot s^{-1}$, $\mathbf{p}_{\infty} = 1.10^5 \text{ Pa}$, $\mathbf{B} = 250 \text{ MPa}$, $\mathbf{n} = 11$, $\kappa = 1$.

4. EVALUATION OF BUBBLE ENERGY

4.1. Cavitation bubble energy

The work done during the vapor bubble expansion from the initial radius R_0 to the maximum radius R_{max} against constant pressure in liquid p_{∞} can be calculated from the following form

$$E_B = \int_{R_0}^{R_{max}} 4\pi R^2 (p_\infty - p_v) dR = \frac{4\pi (p_\infty - p_v)}{3} [R_{max}^3 - R_0^3] \doteq \frac{4\pi}{3} R_{max}^3 (p_\infty - p_v).$$
(7)

The initial bubble radius R_0 was supposed to be equal plasma radius and neglected in comparison with R_{max} .

4.2. Rayleighs formula

The work of pressure in liquid p_{∞} is used to compression of the bubble content and to increasing the kinetic energy of liquid. From this balance and by solving of a differential equation, by the bubble collapse (R = 0), we will get a relation known as Rayleighs formula⁵

$$\frac{R_0}{t_{collapse}} = \frac{1}{0.91468\sqrt{\frac{\rho}{p_{\infty} - p_v}}}.$$
(8)

From this equation follows that the rate depends only on the liquid properties. The values calculated from formula (8) for water and isooctane are given in Tab.1.



Figure 3. Temporary evolution of cavitation bubble in water with multi exposure and single exposure record after a 1-mJ, 6-ns Nd:Yag pulse. Time delays for the multi exposure are bottom-up 2, 3, 4, 4, 6, 10 and 10μ s.

5. EXPERIMENTS AND MEASUREMENT

5.1. The measurement of cavitation bubbles

To determinate bubble temporary evolution, experiments were provided in distilled water and isooctane. The laser supply axis and reference fiber was placed in one plane perpendicularly to optical axis. The halogen lamp provided continual lightening during each of exposition series. At the beginning, the bubble was recorded with single exposure to estimate preliminary the time evolution. From this measurement were deducted the delay times between each of exposition in multi exposure mode. For the better identification, the time history of the bubble had been divided into parts (expansions and compressions) and for these parts was used the multi exposition recording. The images of bubble in single exposure mode and in multi exposure mode are showed in Fig. 3.

5.2. The measurement of shock waves

The measurements of velocity and temporal and spatial distribution of the shock waves were provided in distilled water and isooctane. The laser supply axis and reference fiber was placed in one plane perpendicularly to optical axis. The lightening was provided by xenon flash lamp. The camera exposure time was set constantly at 100 ns. The lamp flash duration 400 ns provided a continual lightening during whole exposure time. The camera and flash lamp were first triggered 186 μ s after laser trigger due to a laser delay. The first measurement value was taken if it was possible to define a shock wave ring. Shock wave velocity was calculated from established exposition time and path of the shock wave far of the plasma center and flash, exposition time had been moved for acquisition of a temporal and spatial distribution of the shock wave velocity. The changes of the thickness of the shock wave ring are evidently in Fig. 4. The examination of the sound velocity with using LDI was provided after the measurements under the same laser energy level. The He-Ne was placed perpendicular to optical axis. Laser beams were located 2mm from plasma center. In this position, the shock wave velocity was proposed to be equal to speed of sound in liquid.



Figure 4. The rings circumscribed by the shock waves in water and isooctane

6. RESULTS

6.1. Cavitation bubbles

The multi exposition recording of the cavitation bubbles in liquid using a Nd:YAG laser was found to be good repeatable process for the investigation of cavitation phenomena. This method of a fast photography is appropriate for an examination of parts of the bubble live (expansions and compressions). Bubble shape depended strongly on the laser energy and optical focusing of the laser beam. Largely differences between the bubble behavior in water and isooctane are evidently in Fig.5. Second maximal radius in isooctane was more then two times bigger then in water. After the first compression was the bubble shape slightly deformated and imitated the initial plasma shape. The shock waves were produced by every compression in water and in isooctane. The calculated values of the cavitation bubble energy for water and isooctane are given in Tab.1.


Figure 5. Temporary evolution of cavitation bubble radius in water (square line) and in isooctane (ring line) after 1-mJ 6-ns pulse in water and 1-mJ, 6-ns pulse in isooctane. The maximal bubble radii were 0.75 mm in water and 1 mm in isooctane. The solid lines present numerical solution.

Liquid	Water	Isooctane
Total energy	1 [mJ]	1 [mJ]
Maximal bubble radius	$0.75 \; [mm]$	1 [mm]
Bubble Energy	$0.157 \; [mJ]$	$0.396 \; [mJ]$
Rate of total energy	15.7 [%]	39.6 [%]
Rayleighs formula (Calculated value)	$10.8 \; [m/s]$	$12.67 \; [m/s]$
Rayleighs formula (Measured value)	10.48 [m/s]	$12.5 \; [m/s]$

Table 1. Summary

6.2. Shock waves

Shock wave velocity investigation with using the method of the measurement based on record under short constant exposition time was found to be available and reproducible method along from the plasma center (APPENDIX Fig.9.). This method is restricted from above by the first definable exposition and with camera resolution. Because the exposure time was 100 ns and after this time was the shock wave velocity almost equal to speed of sound, gives this method in this interval only an average value. The velocities calculated from the measured path of the first shock wave edge are in Fig. 6. The shape of shock wave depended at the beginning strong on the plasma shape. This shape deformation was feeble far from the plasma centum (APPENDIX Fig.7. and Fig.8.). The shock wave velocity far from the plasma centum converged to speed of sound in liquid. The measurement of speed of sound with using LDI showed a good agreement with result of camera recording. The measured velocities by LDI were 1030 m/s in isooctane and 1450 m/s in water. The shock waves velocities calculated from the measured path of speed ring (Fig.4.) were approximately 1050 m/s in isooctane and 1450 m/s in water.

ACKNOWLEDGMENTS

Cavitation bubbles and shock waves produced by cavitation bubble creation in liquids were studied. The strong differences in bubble behavior water and isooctane were evident. The technique of the measurements with using multi exposition record was successfully applied. The shock wave velocity measurement showed new possibility to investigation of these phenomena. LDI was successfully used for the verification of the speed of sound in liquid. The sequential work will be concentred on the improving of the LDI system for smaller beams distance, using holographic photography by the investigation of the bubble creation, schlieren photography application for the shock wave investigations and determination of the physical properties inside the bubble.



Figure 6. Experimentally determined shock waves velocity in water (square line) and isooctane (ring line) after 1-mJ 6-ns pulse in water and 1-mJ, 6-ns pulse in isooctane.

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APPENDIX A. FIGURES SECTION

Figure 7. The shock waves reflection in isooctane.



Figure 8. The shock waves propagation in water.



Figure 9. The shock wave in isooctane recorded by multi exposure.

5.2 Time-resolved measurements

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Time-resolved measurements of shock-induced cavitation bubbles in liquids

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Abstract A novel experimental method for the measurement of cavitation bubble dynamics is presented. The method makes use of a collimated cw HeNe laser beam that is focused onto a photodiode. A cavitation bubble centered in the laser beam leads to refraction and thus changes the diode signal. With sufficient temporal resolution of the measurement, the evolution of the bubble dynamics, and in particular, the collapse, could be well resolved (limitation is only due to diode response and oscilloscope bandwidth). In the present work this is demonstrated with cavitation bubbles generated with high-power nanosecond and femtosecond laser pulses, respectively. Bubble evolution is studied in two different liquids (water and glycerine) and at different temperatures and pressures.

1 Introduction

Cavitation is a major source of erosion, for instance, of ship propellers, pumps and water turbines. In such systems, low pressure regions (pockets) exist where the water pressure suddenly becomes very low, almost a vacuum range.

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R. Reuter · U. Teubner Institute of Physics, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany These growing pockets, i.e. the "cavitation bubbles" propagate to high pressure regions, where they collapse spontaneously [1].

To investigate the cavitation phenomena experimentally, different methods of bubble generation are possible. One of them uses a powerful short laser pulse that is focused into a liquid generating an optical breakdown. During the successive plasma recombination, a fast growing and nearly spherical bubble arises. When the radius has reached its maximum, the bubble contracts continuously to a minimum and finally collapses with one or more rebounds. The onset and collapse of the bubble are usually combined with shock wave emission (laser-generated bubble and shock waves, LGBS). The life time of a cavitation bubble depends on the initial laser energy into the liquid breakdown and bubble formation usually in the order of a few microseconds up to several milliseconds. In the case of LGBS, referring to the shock waves, the time is much shorter, i.e. of the order of 10 ns to a few microseconds, respectively. Consequently, a corresponding temporal resolution although it is not easy to obtain would be required in LGBS experiments.

For experimental investigations on cavitation bubble dynamics, in general, there are two different methods, i.e., high-speed shadow photography with 10^4-10^8 frames/s [2, 3] and probe beam deflection (PBD) [4, 5]. With increasing distances from the plasma, these authors were able to obtain information on bubble dimension and wall velocities. A further method limited to very small bubbles is based on Mie scattering [6].

The present work reports on measurements of an alternative, novel and inexpensive optical method to enable a timeresolved insight into the formation and collapse of cavitation bubbles. Different energies, temperatures, and pressures have been studied in liquids with different viscosity (glycerine (propane-1,2,3-triol) and distilled water).

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aperture r_a





driving pulse

The method provides also information on resulting shock waves from the initial state until the end of the rebound process. Under the assumption of a nearly spherical bubble, the method allows continuous measurements with temporal and spatial resolution of a complete cycle of bubble dynamics with a temporal resolution better than 20 ns depending on the sample rates of photodiode and oscilloscope. Contrary to Englert et al. [7], who studied luminescence of laser-induced bubbles by using a photomultiplier, a linear photodiode and a Gaussian diagnostic laser beam permit the calculation of the bubble radius in the present work.

2 Method of bubble diameter measurement

The principle of the method relies on laser beam deflection from a bubble that is centered on the axis of a HeNe laser beam of diameter r_0 ("diagnostic beam", see Fig. 1). At a distance L behind the bubble, an aperture of radius r_a discriminates most of the deflected light. The undeflected part of the beam is collected and focused onto a photodiode. With respect to the signal in absence of a bubble, the measured signal is reduced by a polarizer and allows the bubble diameter to be deduced with temporal resolution. The temporal resolution is only limited by the readout system consisting of a fast photodiode and a fast oscilloscope. Laser beam deflection at the bubble could be simply estimated from geometrical optics (for details see Appendix A). Briefly, the parallel diagnostic beam hits the bubble of radius r_b , which is generated within a liquid by a further laser system ("driving pulse") on the beam axis. The bubble is described as a homogeneous sphere of gas (or steam) with a refraction index (n_b) smaller than that of the ambient liquid (n_a) .

Parallel rays of the diagnostic beam which propagate at $y > y_3$ (Fig. 9) from the optical axis are refracted by the bubble with a total deflection angle, ϵ , that depends on *y* coordinate and r_b . When *y* exceeds a certain value $y > r_b \cdot n_a/n_b$, total reflection occurs. In both cases, this results in divergent rays behind the bubble, which are mostly blocked by the aperture located far behind the bubble. Rays propagating $y \ge r_b$ are not affected and may still pass through the aperture where they will be detected.

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To estimate the resulting "intensity" J of the diagnostic beam behind the aperture as a function of r_b , first an estimate of J in the absence of the bubble is made by integration of the diagnostic beam profile over the aperture area (Gaussian profile with $1/e^2$ diameter r_0 , and intensity on axis I_0 ; see Appendix A):

$$J_0 = \frac{\pi r_0^2 I_0}{2} \left[1 - e^{-2(\frac{r_a}{r_0})^2} \right]$$
(1)

If now, a bubble with a relative radius $\zeta = r_b/r_a$ is generated on axis of the diagnostic beam, ray deflection occurs. To deduce the bubble diameter, even for expanded bubbles, the following requirement must always be fulfilled: $r_0 > r_a > r_b$.

If one assumes that all deflected rays are blocked by the aperture (this is the case for $L \rightarrow \infty$), the detected intensity is reduced to

$$J(\zeta) = J_0 \left[1 - \frac{q - e^{-2(\frac{r_a}{r_0}\zeta)^2}}{1 - e^{-2(\frac{r_a}{r_0})^2}} \right]$$
(2)

(*q* is a correction which here is identical to 1). Due to the temporal evolution of the bubble size, ζ and hence $J(\zeta)$ depend on time *t*. When *J* is focused onto a diode with a linear response, from Eqs. (1) and (2) the bubble diameter could be deduced as a function of *t* (still $q \equiv 1$):

$$r_b(u(t)) = r_0 \sqrt{-\frac{1}{2} \ln\left[q - \left(1 - u(t)\right)\left[1 - e^{-2\left(\frac{r_a}{r_0}\right)^2}\right]\right]}$$
(3)

where $u(t) = J(\zeta(t))/J_0$, i.e. the ratio of the photodiode signal with bubble at time *t* to the signal in absence of the bubble.

If the deflected rays are not totally blocked, the correction q in Eqs. (2) and (3) is no more identical to one, but becomes a function of $\zeta(u(t)) = r_b(u(t))/r_a$:

$$q(\zeta) = e^{-2[\frac{r_a}{2L(\frac{n_a}{n_b}-1)}\zeta]^2}$$
(4)

Hence, Eq. (3) becomes more complicate and has to be solved by iteration (the initial value of ζ and r_b , respectively, could be estimated from Eq. (3) (with q = 1); furthermore, for $r_a \ll L$ Eq. (4) may be linearized). However, as

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may be seen from following sections, a correction is not always necessary. As an example, within the present the work, $r_a = 2 \text{ mm}$, $L \ge 500 \text{ mm}$, $n_a = 1,33$, $n_b \approx 1$ (water and steam, respectively) and thus, for $\zeta \le 1$ the deviation of qfrom 1 is smaller than 7×10^{-5} !

3 Experimental setup

Cavitation bubbles have been induced by two different laser systems into distilled water and glycerine, respectively (driving pulse in Fig. 1). The liquid has been kept in a quartz glass cuvette (volume = $3 \times 3 \times 3$ cm³) at a temperature T = 25 °C and a pressure p = 1 bar. Alternatively a stainless steel container (80 mm inner diameter and 200 mm height) is used to allow the temperature to be controlled in the range of 20 °C < T < 100 °C and the pressure to be kept between 0.2 bar < p < 1 bar (absolute values).

Two different laser systems have been used for inducing cavitation bubbles. A femtosecond laser was used for the experiment with different laser energies in water (laser fluence of max. 80 J/cm², pulse duration (FWHM) $\Delta \tau = 150$ fs,



Fig. 2 Schematic sketch of the experimental setup

wavelength $\lambda = 775$ nm, CPA 2110 Ti:Sapphire, Clark-MXR, Inc.). A Q-switched Nd:YAG laser (laser fluence of 0.2 MJ/cm², $\Delta \tau = 6$ ns, $\lambda = 532$ nm, Solo III PIV 15, New Wave Research) was used for measuring glycerine and water, respectively, at different temperatures and pressures. The experimental setup using the container is shown in Fig. 2. Measurements with the femtosecond laser have been carried out by using the quartz glass cuvette.

An expanded, collimated diagnostic beam of a HeNe laser ($\lambda = 633$ nm, D-7517, Polytec) in TEM00 mode crosses the bubble driving beam perpendicularly and is then detected by means of a PIN photodiode (BPW 34, Osram). The cavitation bubble generation is centered exactly in the middle of the diagnostic beam proved by a beam profiler (LBP-1, Newport). Figure 3 demonstrates the dip located in the maximum of the Gaussian beam.

The diagnostic beam (HeNe laser) is focused to the PIN diode, covered with a 633 nm interference filter (Schott, 10 nm band width) to discriminate environmental light. An oscilloscope (TDS7154B, Tektronix) is used to read out the voltage U(t). A polarizer allows the intensity of the diagnostic beam to be adjusted. Part of the beam is blocked by the cavitation bubble. Thus, the temporal evolution of the diode voltage U(t) depends on the temporal evolution of the bubble volume V(t). Then, under the assumption of a spherical bubble geometry, the radius $r_h(t)$ of the bubble can be calculated as described earlier (Sect. 2). The assumption of the spherical bubble geometry is verified by a separate series of CCD images (SensiCam, PCO, fitted on a microscope) during the measurements (see Fig. 4, Table 1). This is only valid within the first bubble before the collapse. During the first rebound, the spherical condition for the shape of the shadow area (two-dimensional) is not fulfilled as shown in Fig. 4 ($\Delta t = 190 \ \mu s$). However, the measurement from the image of the non-spherical area leads to an "equivalentspherical" area of nearly the same bubble dimension estimated by the novel measurement method presented in this paper (Table 1).



Fig. 3 Image in false color of the HeNe laser beam profile to verify the alignment of the cavitation bubble in the middle of the Gaussian beam

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4 Results and discussion

The aperture of the experimental setup (Fig. 1) acts like a 'schlieren device', if strong gradients occur. It is a very sensitive possibility to detect initial and collapse shock waves as well as the time-depending bubble formation which can be seen in Fig. 5.

Figure 5a shows the bubble radius $r_b(t)$ for different laser energies induced by a femtosecond laser. The advantage of this method can be clearly seen in Fig. 5b. Beside the radius distribution $r_b(t)$, also the onset and collapse of the bubble are detectable (insert A and B). A temporal resolution of



Fig. 4 Comparison of bubble radii measured in water by the introduced method (r_b , open triangles, black line as an example of bubble evolution) and CCD images (r_{pho} , solid squares) at various time delays Δt after plasma ignition; Nd:YAG laser

Table 1 Radii of bubble size deduced from CCD images (r_{pho}) and comparison to r_b deduced from present method at time delays Δt after plasma ignition

$\Delta t \ (\mu s)$	r _{pho} (mm)	$r_b (\mathrm{mm})$
65	0.92	0.94
115	0.70	0.81
145	0.39	0.38
190	0.55	0.57

and r_0 lead to an error of r_b of ± 5 %. Comparison of r_{pho} determined from shadow images of the bubble and measured

radius r_b can be realized with an error of $\pm 10\%$ (see Fig. 3). In Fig. 5a it can be seen that the collapse radius r_c decreases with increasing laser energy E, indicated by a dashed line. However, the bubble structure at the initiation and immediately before the collapse is not exactly spherical but more or less parabolic. As a consequence, the used measuring method delivers the correct bubble start and collapse times, respectively, but the 'bubble radius r_b ' is an 'equivalent radius' to the real shadow area in the measuring plane of the bubble.

20 ns and a spatial resolution of 3 μ m have been obtained, which depend only on the sample rate of the oscilloscope

and read out of the diode. Measurement accuracies of $U(\zeta)$

In Fig. 6, the bubble radius r_b has been measured in glycerine as a function of time with a constant temperature $T_0 = 30$ °C and different initial liquid pressures $p_0 = 1$ bar (black) and $p_0 = 0.43$ bar (red). With decreasing initial liquid pressure p_0 , the bubble dimension increases as well as the collapse time t_c (time difference between maximum bubble radius and collapse). The measurements in glycerine depected in Fig. 6, do not show collapse shocks either for $p_0 = 1$ bar or for $p_0 = 0.43$ bar.

The temperature dependence of the bubble radius is shown in Fig. 7. The initial pressure remains $p_0 = 1$ bar = const. with $T_0 = 30$ °C (black curve) and $T_0 = 66$ °C (red curve). Similar to Fig. 7, also both the bubble dimension r_b and the collapse time t_c increase with increasing temperature T_0 of the liquid. In contrast to Fig. 6b, now a collapse shock wave is visible due to a reduced viscosity at higher temperature (Fig. 7b, red curve).

Figure 8 shows the bubble wall velocities v_b as a function of the bubble radius r_b during the shrinking-process from the maximum bubble radius r_{max} to the minimum bubble radius r_c (collapse radius, Fig. 8a). Low Nd:YAG laser energy (7 mJ) has been used to achieve a nearly spherical bubble geometry. The results are compared to those obtained by



Fig. 5 Bubble time-distribution in water induced by a femtosecond laser: (**a**) for different laser energies; (**b**) *inset* for indicating the bubble initiation (A) and the first collapse (B)

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Fig. 6 (a) Bubble radius in glycerine as a function of time at constant temperature $T_0 = 30$ °C and various initial liquid pressures p_0 ($E_{(Nd:YAG)} \approx 10$ mJ, $r_0 = 1.836$ mm); (b) time-enlarged scale of the first bubble







Rayleigh's equation [8]:

$$v_b = \frac{2p_{\infty}}{3\rho_1} \left[\left(\frac{r_{\max}}{r_b} \right)^3 - 1 \right]^{\alpha}; \quad \alpha = 0.5$$
(5)

where p_{∞} is the pressure in infinite liquid, ρ_1 is the liquid density, and r_{max} is the maximum bubble radius. The first phase of the bubble shrink process shows excellent agreement, but the last phase (before collapse) is different. Experimental results for the complete bubble shrinking process could be found in the investigation of Peel et al. [5], where an exponent of $\alpha = 0.17$ was found (Fig. 8b). The discrepancy of α is due to the fact that Peel et al. [5] applied the higher laser energy in their investigation (i.e. 140 mJ) as compared to the present work (7 mJ).

A detailed investigation is beyond the scope of the present work and will be presented elsewhere [9].

5 Conclusion

A novel and powerful optical method to diagnose cavitation bubbles in liquid is presented. It allows the experimental analysis of the dynamics of laser-driven cavitation bubbles. The main advantages of bubble measurements is the high temporal and spatial resolution from the onset to the collapse of a single cavitation bubble as well as the detection of the combined shock waves generated by a single shot of a high power laser. Values of 20 ns and 3 μ m, respectively, are limited by the read out system consisting of a fast photodiode and a fast oscilloscope. The error of r_b is ± 5 %. Fig. 9 Geometry of four different rays at four different distances from the optical axis: (0) on axis, (1) below angle of total reflection, (2) at total reflection, (3) ray without deflection



Although limited to spherical bubbles, CCD images during the measurements do confirm that the present method is well applicable. Especially during onset and collapse, deviation from spherical geometry was observed. However, even in that case, the bubble radius determined with the present method could be considered to be an equivalent radius.

The advantage of the novel method is its easiness to assemble, whereas the acquisition of CCD images and also the setup of the illumination are much more complicated. Furthermore, the presence of shock waves and temporal evolution of the cavitation bubble is indicated immediately.

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Appendix A: Ray optics of beam deflection and estimate of diode signal

A.1 Refraction geometry

Figure 9 shows the geometry of rays of the diagnostic beam when a bubble is present. If y is not too large, e.g., $y = y_1$, the ray is refracted at both interfaces between liquid and bubble as shown in Fig. 9. The total angular change could be calculated from the following geometrical relations and from Snell's law, respectively:

$$\alpha_1 + \beta + \gamma = \pi$$
$$\gamma = \epsilon + \alpha_1$$
$$\epsilon = 2(\beta_1 - \alpha_1)$$
$$\sin \alpha_1 = \frac{y_1}{r_b}$$
$$\frac{\sin \alpha_1}{\sin \beta_1} = \frac{n_b}{n_a}$$

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As long as

$$\frac{n_a}{n_b}\frac{y_1}{r_b} \le 1$$

refraction occurs. By means of the above six equations the angle of deflection ϵ can be calculated as

$$\epsilon(y_1, r_b) = 2 \cdot \left(\arcsin\left(\frac{n_a y_1}{n_b r_b}\right) - \arcsin\left(\frac{n_a y_1}{n_b r_b}\right) \right) \tag{6}$$

In the opposite case (ray at $y = y_2$ or at $y = y_3$), the ray is totally reflected or unaffected (see Sect. 2).

A.2 Diode signal without bubble

For an intensity profile of the diagnostic beam with a Gaussian intensity profile (see Sect. 2),

$$I(r) = I_0 \cdot e^{-2(\frac{r}{r_0})^2}$$

the power measured behind an aperture of diameter 2R is obtained by integrating over the aperture area, i.e.

$$P(R) = 2\pi I_0 \int_0^R e^{-2(\frac{r}{r_0})^2} r \, dr \tag{7}$$

For an aperture like that in the setup shown in Fig. 1, $R = r_a$ has to be inserted. This yields $P(R = r_a) = J_0$ and thus leads to Eq. (1) in Sect. 2.

A.3 Diode signal with a bubble present and the aperture positioned in infinity (i.e. $L \rightarrow \infty$)

In this case, the bubble acts like a disk. Due to deflection it blocks part of the diagnostic beam. This part could be calculated with Eq. (7) by setting $R = r_b$. In the present setup (see Fig. 1), behind the aperture, J_0 , is thus reduced to $J(\zeta) = J_0 - P(R = r_b)$ which yields Eq. (2) in Sect. 2 (with $q \equiv 1$). Now, it is assumed that the diode signal, i.e. the voltage $U(\zeta)$, is proportional to $J(\zeta)$ and U_0 is the signal obtained for J_0 . Defining $u(\zeta) = U(\zeta)/U_0$, this is equal to $J(\zeta)/J_0$ and can thus be solved for r_b with Eq. (2). The result is Eq. (3) (with $q \equiv 1$).

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Fig. 10 Geometry of "leakage rays"

A.4 Diode signal with a bubble present and the aperture positioned at finite distance

If *L* is finite, rays that are only very slightly deflected may pass the aperture and thus lead to a "leakage signal" on the photodiode (see Fig. 10). As may be seen from the image observed behind the aperture (Fig. 3), in particular, this is the case for the ray on the axis and for those rays that are very close to the optical axis: The maximum value of ϵ that leaks through the aperture is obtained from $\epsilon_{max} \approx (r_a - y_{max})/L$ which usually is very small (because $r_a \ll L$). By inserting ϵ max into Eq. (6) (with small angle approximation of the argument) Eq. (6) may be solved for y_{max} .

Although the bubble still blocks part of the diagnostic beam, the blocked signal consequently has to be calculated again by an integration similar to Eq. (7), but now with integration from y_{max} to r_b (instead of integration from zero to

 r_b). This leads to modifications of Eqs. (2) and Eq. (3) with a correction q that depends on ζ or r_b , respectively. The resulting q is given by Eq. (4) (one may note that q = 1 for L as expected for the case that the aperture is very far away).

Finally, it should be mentioned that rays at large values of y (y close to r_b) get totally reflected also at small angles ϵ and thus may leak through the aperture, too. However, as in the case above, it was verified that again, this leakage is neglible.

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6 Laser-induced breakdown spectroscopy applied to historical iron samples

The application of LIBS has been evaluated from qualitative to quantitative analysis in various fields of multi elemental analysis. Especially metals and alloys processing, scrap material processing and sorting are large fields of industrial application. The carbon content is important for mechanic properties. Alloys including chromium, nickel, wolfram, vanadium, manganese, etc. can easily be distinguished by LIBS. Historical iron samples contain, contrary to modern steel samples, mainly iron. Carbon was added by the production. Only a few additional elements like sodium, calcium, magnesium, manganese, sulfur were found. Some of them are related to the traditional way of the iron production and some are related to corrosion (Ca, Mg). Iron has a dense term scheme, therefore overlapping with other compounds. Further insight into the samples is provided by the investigation of slag inclusions with a size of approx. 200 μ m. They contain various oxides and have potential for tracing the original ore. Slag inclusions can be investigated with micro LIBS. The method refers to a focused laser spot of sizes $< 40 \ \mu m$. Sample preparation as in metallographical investigations, e.g. SEM-EDX, Vickers hardness, and determination of crystal structure are necessary. Therefore, a statistical approach of spectra taken on the surface of (unprepared) iron samples is desirable and promising.

The investigation of organic compounds is challenging due to the similar principal constituents carbon, oxygen, hydrogen, and nitrogen. Data evaluation by statistical methods allows to differentiate among organic material such as bacteria or fungi.

Homeland security is a further research field with the same problematic differentiation of elements. In both fields, chemometrics have been applied and show potential for an improved data evaluation of spectroscopic results. For the same reason, principal components analysis is applied to spectra of historical iron. LIBS in combination with PCA is a feasible and fast approach to group elements according to their chemical composition. A larger dataset containing samples with known origin combined with an analysis of standard samples would give a further insight to historical iron alloys.

The results are presented in the following paper, which has been submitted to the Journal of Cultural Heritage.

Laser-induced breakdown spectroscopy applied to historical iron samples

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Abstract

Laser-induced breakdown spectroscopy (LIBS) has been applied to a vast amount of cultural heritage samples to reveal their elemental composition. This is often one of the major key information to identify as well the origin as the technological skills of the historic craftsmen and artisans. The Emden Armory (Rüstkammer), Ostfriesisches Landesmuseum, holds an unique collection of weapon and armor objects. Historic iron alloy samples of the 16th to 19th century are primarily under investigation. LIBS spectra have been recorded by inducing laser spots of a typical size of approx. 100 μ m on the sample. Optical emission signals of swords, rapiers, spontons, rifles and armor samples

are dominated by a vast amount of iron lines accompanied by lines of different minor elements (e.g. Mn, Ca, Mg, Cu). Principal components analysis (PCA) is applied in order to discriminate the spectra with variations mainly in the amplitude. Additionally, micro LIBS using a microscope objective to focus a Q-switched Nd:YAG laser beam @ 1064nm (fluence = 28 J/cm^2) down to spot sizes of approx. 10 µm is adopted to investigate slag inclusions of the historic iron alloys. Plasma emission is guided via a quartz fiber to a Czerny-Turner spectrograph and recorded with an ICCD camera. Delay times of about 300 ns are applied to allow for plasma cooling and line emission built-up. These spatially high resolved spectroscopic data are implemented into the PCA evaluation. No additives like nickel or chromium are observed. Sodium and calcium are present both in slag and iron in almost all of the historic samples most probably related to corrosion. Components of PCA scatter plots reveals for example iron, magnesium, sodium, calcium, and titanium.

6.1 Introduction

Laser-induced breakdown spectroscopy (LIBS) has been applied to a diversity of cultural heritage samples to reveal their elemental composition [GDP+10]. This is often one of the major key information for material scientists and archaeologists to identify the origin of the artifact. It also helps to understand the manufacturing process and thereby the technological skills of the historic craftsmen and artisans. The Emden Armoury (Rüstkammer), Ostfriesisches Landesmuseum, holds an unique collection of weapon and armor objects (16th-19th century). Iron samples before Bessemer, Thomas, or Siemens-Martin methods are primarily under investigation.

Short pulsed laser radiation (ns) enables to ablate any material sample. None or minimal sample preparation is needed. Since material abrasion is negligible (approx. 10-20 µg/pulse) also precious archaeological objects can be investigated. Insight to the ore composition can be obtained by investigation of slag inclusions. Slag inclusions are mainly dominated by different oxides like e.g. FeO, MnO, SiO₂, Al₂O₃, CaO, TiO₂, K₂O, MgO, SO₃, Fe₂O₃, P₂O₅. The composition is related to their origin [Buch08]. Micro LIBS (with spot size $\leq 40 \ \mu m \ [FLM+06]$) allows to analyze slag with typical dimensions of 10 µm to 200 µm.

Sample No.	Object	Age
1	Spring of a halberd (polearm)	middle to end 16^{th} century
2	Spring of a halberd (polearm)	middle to end 16^{th} century
3	Cleaning shell/sleeve, attachment ramrod	$19^{\rm th}$ century
4	Gun barrel	$19^{\rm th}$ century
5	Gun (lock)	unknown
6	Bottom buttplate	$18^{\rm th}$ or $19^{\rm th}$ century
7	Morion	middle to end 16^{th} century
8	Musket-rest	first half $17^{\rm th}$ century
9	Bottom buttplate of a musket	$17^{\rm th}$ century
10	Leg protection of a pikeman	beginning $17^{\rm th}$ century
11	Musket lock (origin: Suhl)	first half 17^{th} century,
12	Rapier	$16^{\rm th}$ to $17^{\rm th}$ century
19	Unidentified sword (possibly Ottoman)	unknown
20	"Handja", Ottoman	$18^{\rm th}$ century
21	"Sponton" (iron with gold inlay)	$17^{\rm th}$ century
22	Spanish rapier	$17^{\rm th}$ to late $17^{\rm th}$ century
23	Turkish rifle (Wallbüchse)	18 th century
00	Construction steel (EN 10025-2:2004-10)	

Table 6.1: Historical iron samples

6.2 Methods and Samples

Archaeological Context

In this study, we have characterized iron weapon and armor objects which belong to the collection, partly on permanent exhibition (sample No. 20-23) of the Emden Armory (Rüstkammer), Ostfriesisches Landesmuseum, Germany. No. 13-18 are different gold, silver, and bronze coins, whose results are to be published separately. Most of the samples from the storage have been found in Northern Germany [Poti02]. Some of them are not well preserved. Especially the rapier dating from late 16th to early 17th century (sample 12), buried in soil, is heavily corroded. Table 6.1 comprises all information available on the historic iron objects and samples.

Sample Preparation

In general, investigations using LIBS can be carried out on the surface of any objects with nearly no or only little sample preparation. The analysis of slag impurities with micro LIBS has been applied to samples which have been prepared for SEM-EDX, metallographical investigation like Vickers hardness, and the determination of crystal structure. Part of the objects, held by a fixing clamp of chrome nickel steel, have been embedded in phenolic resin (No. 4) or phenolic resin with carbon (No. 1, 2, 3, 8, and 11) or epoxy with copper (No. 6). All samples have been polished with Al_2O_3 grinding compound. Diluted nitric acid (97 % ethanol) has been used for etching except sample 2.

Slag inclusions and pure metal of each sample have been analyzed at several sites. Sample designations in the plots refer to sample names and the measurement position separated by an underline.

6.3 Experimental Setup

LIBS

A Q-switched Nd:YAG laser beam @ 1064 nm, pulse duration 5 ns, is focused with a set of lenses and an off-axis mirror onto the sample (fluence $\approx 0.3 \text{ MJ/cm}^2$). Hence, the laser-induced plasma emission is guided via a quartz fiber (core diameter: 600 µm) to the Echelle spectrometer (Aryelle 200, LTB) and recorded with an ICCD camera. Delay times of 250ns are employed to allow for plasma cooling and line emission built-up [GMA07].

Micro LIBS

A sample is attached onto a three axis mount underneath a Zeiss Epiplan-Neofluar 20X/0.50 HD microscope objective (Fig. 6.1). The surface illumination is provided via a 90° beam splitter by a collimated halogen lamp through the objective. With the help of an achromatic lens (f = 100 mm), the image of the sample is projected by the objective onto a CCD camera (the imaging source, DFK 41BU02.H, 1280×960 pixel). A Q-switched Nd:YAG laser beam @ 1064 nm, $\tau_p = 5$ ns, E = 22 µJ (Tempest 10, New Wave Research, USA), is directed by a 90° dichroic mirror to the objective and focused onto the sample. The spot size at the ablation zone is about 10 µm in diameter for in single pulse irradiation. Plasma emission is collected by a 600 µm core diameter multimode quartz fiber and guided to an Acton Research (USA) SpectraPro spectrograph equipped with an intensified CCD detector (i-star DH734, Andor, UK, 1024×1024 pixels, 13×13 µm² pixel area, Gen II intensifier). The Czerny-Turner spectrograph has a focal length of 275 mm and a grating of 300 lines/mm blazed at 300 nm. Triggering is

done by the internal trigger of the spectrograph and a delay gate generator (DG 535, Stanford Research Systems, USA). 300 ns delayed, the camera gate window width of the spectrograph is set for about 10 μ s. Trigger rate is chosen to be 2 Hz.



Figure 6.1: Experimental setup for slag analysis with 10 μ m laser spot

6.3.1 Scanning electron microscopy and energy-dispersive X-ray spectroscopy

The springs of a halberd (sample No. 1 and 2), the cleaning shell (No. 3), and the bottom buttplate (No. 6) have been investigated by SEM-EDX to compare for the LIBS results. A scanning electron microscope (SEM, JEOL, T300) is connected to an energy-dispersive X-ray spectrometer with a X-ray detector (Tracor Northern, 20 kV). Elements with Z-number higher than 11 can be measured.

6.4 Results and discussion

Historic iron alloy samples of the 16th to 19th century as well as modern construction steel (EN 10025-2:2004-10) have been under investigation. Modern steel samples can easily be distinguished from historic ones by their specific doping metals. Recorded spectra of swords, rapiers, spontons, rifles and armor samples are dominated by lines of iron accompanied by different minor elements (e.g. Mn, Ca, Mg, Cu). No traces like nickel or chromium have been observed. Sodium and calcium have been found in most of the historic samples most probably due to corrosion [SPC91]. A sword called "Handja" with a folded blade is an exception and is similar to modern steel.

Further examination of spectroscopic data is performed using Principal Components Analysis (PCA). PCA is a widely used statistical technique [Smit03], [GUV+04] in chemometrics which facilitates projection of the input data set onto an N-dimensional space of independent vectors, called principal components. Each principal component is a linear combination of all samples of a spectrum such that the variance of the data in the new dataspace is maximized [CCG+05]. The PCA method is chosen because LIBS spectra of iron samples are dominated by multiple iron lines. The intensities of whose depend strongly on plasma parameters and other factors [DCP08]. A scatter plot of the principal components can reveal grouping of samples indicating the presence of a common element or elements within a group.

A Graphical User Interface (GUI) program, implemented in Matlab[™]is allowing to select easily a dataset for analysis. In order to gain a qualitative insight on the association of each principal component with a single or a group of chemical elements the option to reconstruct the original spectra using only a subset of the principal components was included in the software. All scatter plots refer to standardized values.

Screening of the data set by applying PCA referring to the samples in Tab. 6.1 is shown in Fig. 6.2a. The data set is taken by an Echelle spectrometer in the range of 210 nm to 870 nm. Several groups appear and the heavily corroded rapier (sample 12) has discordant values as well as the better preserved weapons (No. 19 to No. 23). However, these groups do not refer to utilization or age of the material. The grouping is closer related to the corrosion condition. If one reduces the spectral range down to 390 nm to 600 nm (Fig. 6.2b) construction steel points out clearly.



Figure 6.2: Scatter plots of all samples from Tab. 6.1 in the range of (a) 210 nm to 870 nm and (b) 390 nm to 600 nm

Due to the fact that focal spot sizes of ca. 100 μ m do have only minor contributions of probably specific slag inclusions, spectra are dominated by intense and densely packed iron emission lines. Therefore micro LIBS has been applied specifically to slag inclusions as an approach to overcome these drawbacks. Slag inclusions may contain specific elements, which can be related to the mining area of the ores. Inclusions of several samples are investigated by SEM-EDX, which is a standard method for historic iron samples [Buch08].

All slag and iron spectra taken with micro LIBS rely on polished and etched sections. Fig. 6.3a shows a slag inclusion observed via the ablation microscope objective. Fig. 6.3b shows a SEM image of two distinct laser spots on iron resulting from 10 pulses each. The inset refers to the optical microscopy of the very same spots. The spot size of 10 μ m for a single pulse or of 20 μ m for 10 pulses fits pretty nicely to typical inclusion dimensions under investigation by micro LIBS. In order to cover each sample characteristics statistically representative all spectra recorded by the Czerny-Turner spectrograph have been taken at several sites of each sample. To demonstrate iron and slag spectra three different historic objects including the spring of a halberd (No. 2), a cleaning shell (No. 3), and the bottom buttplate (No. 6) are compared in Fig. 6.4. Iron spectra show a high similarity as has been expected. Slag spectra reveal a higher heterogeneity in the elemental composition and concentration on each sample (refer to Fig. 6.5 and 6.6). Slag spectra of sample 2 (spring of a halberd, Fig. 6.4a) recorded at ablation site No. 2, contains at least Mg, Si, Al, Ca, and Fe. Three EDX measurements on different slag inclusions of sample 2 clearly indicate Fe, Si, Ca, K, Al, Mn, P, and



Figure 6.3: a) Image of a slag inclusion of a cleaning shell (sample 3) and b) two laser spots of 10 accumulated pulses each (SEM image and CCD image (inset))

Mg. Each single element, phosphorus and magnesium, could not be detected only in two different sites separately. The deviation among a single sample is depicted in the scatter plots. Buchwald and Wivel [BuWi98] have demonstrated that the analysis of slag inclusions leads to the differentiation of even homogeneous metals. Inclusions are, however, in local equilibria with the adjacent metal. Differences like in the cleaning shell or attachment for a ramrod (sample No. 3), can be analyzed by a PCA plot 6.5b. Micro LIBS spectra of several slags of this artefact are dominated by the elements Fe, Ca, Si, and Cu at certain locations. The latter is related to component 3. Site 10 yields similar results like a slag of sample 2, spring of a helbard. The elemental contribution of copper can be explained by the fact that a thread inside the cleaning shell is connected to the outer tube using copper brazing. Iron grains in this sample contain no copper as verified by EDX (Fe, Si, Cl, K, Ca, La, S). Fig. 6.5b clearly shows the presence of copper in the slag of the bottom buttplate (No. 6), site 3. Traces of copper can't be validated in the same object on site 1. No spectral lines connected to copper have been found in the LIBS spectra, but Mg, Si, Al, Ca, and Fe is clearly visible. EDX of sample 6 on a further slag site indicates Fe, Si, Ca, K, Cu, Mn, Ti, P, Al, and Mg. This findings underline the necessity to perform slag analysis preferably with both methods on the very same site. Aluminum oxide powder is the most common grinding material and might lead to cross contaminations. This is taken care of by either carefully pre-cleaning the surface by initial laser shots of each sample or using an alternative grinding compound.



Figure 6.4: Spectra of slag inclusions (a) and iron (b) of three different samples: Spring of a halberd (No. 2), cleaning shell (No. 3), and bottom buttplate (No. 6)

Copper is been used as an additive to the epoxy resin to provide electric conductivity in the case of SEM measurements. Applying the latter method sample 06 05a slag of a bottom buttplate reveals most probably a contamination with aluminum from the grinding compound. LIBS spectra only show significant aluminum lines at first laser shot in contrast to other slag signals. Actually this signal vanishes rapidly after the first laser pulse. The discrepancy on copper traces might also be due to fact, that REM measurements didn't use a pre-cleaning process. Considering recombination plots iron is prevalent also in slags. The scatter plots depend on the wavelength range selected, which might be limited by the grating used in the experimental setup or related to the spectral preselection for the PCA. In the wavelength range between 420 nm and 730 nm component 2 is mainly related to titanium and component 3 to copper. Component 5 reveals mainly sodium although these lines are recognizable also in other components. The lower wavelength range from 240 nm to 570 nm is related to copper and iron in the second component, magnesium to the third, copper to the fourth, calcium to the fifth, and titanium to the sixth component. Sodium is not present in components of the lower wavelength range due to it's solely characteristic dublet at 589.0 nm and 589.6 nm. The ratios SiO_2/Al_2O_3 , Al_2O_3/CaO , and others have indeed been helpful in identifying the production site or provenance of a historic iron object [BuWi98]. Other groups like Coustures et al. [CBT+03] and Desaulty et al. [DDH+09] established a link between an initial ore and the semi-finished products. The number of samples used in this investigation and the knowledge of the ores concerning origin and elemental



Figure 6.5: Scatter plot of slag spectra in the range of 420 nm to 730 nm, (a) component 1 and 2, (b) component 3 and 4



Figure 6.6: Scatter plot of slag spectra in the range of 240 nm to 570 nm, (a) component 1 and 2, (b) component 3 and 4

composition [DCP09] needs to be strongly and systematically enlarged to verify these theses. It has been evaluated that PCA leads to clearer results when the database includes mainly the first laser pulse to examine slag inclusions and iron of polished and etched sections. The slag is not necessarily deep enough to allow for several laser pulses. The employed setup is unsuitable to observe the unwanted event of drilling through the slag. The spectra will be influenced by this effect. Iron alloys beneath the slag causes homogenized spectra and samples, respectively. Unspecific measurements on the surface of iron alloys lead to material related PCA values if the first measurement has been discarded. Calcium and sodium enrichment in the upper layer depend on the level of corrosion. The relevance of the sodium and calcium containing components is rising and therefore not related to the ingredients.

6.5 Conclusions and outlook

The present study of historic iron alloys has shown that LIBS in combination with PCA is a feasible and fast approach to group elements according to their chemical composition. However, laser spot sizes of ca. 100 μ m in typical LIBS experiments tend to result in difficult to analyze spectra due to a high spectral density of iron emission lines therefore hiding minor elements. This has been taken care of by a micro LIBS setup using a high spatial resolution of 10 μ m sample area. Slag inclusions are exactly on this dimension range therefore allow to distinguish historic metal artifacts on this base. Micro LIBS demands for a sample preparation (laser cleaning or electrochemical etching) in order to clearly show crystal grain structure and slag inclusions. A larger dataset containing samples with known origin combined with an analysis of standard samples would give a further insight to the historic iron alloys. The comparison of the data set with ores of the sample origin would also be revealing. This might lead to a rapid analysis by LIBS without destructive cleaning method of the surface.

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7 Discussion

7.1 Laser-induced breakdown spectroscopy on heavy metals in aqueous solutions

Contaminants in liquids have been investigated by a number of groups using several methods, e.g. focusing the laser onto the surface of the liquid [CRL84], rigid glass body of a vial [ZYS99], liquid jets at laminar flow [NHC97], and into bulk liquids directly [NIS+96]. LIBS after liquid-to-solid matrix conversion is tested on ice cubes [CTT+01] and solid pellets of calcium hydroxide [DAB+06]. Large impact to the limits of detection occurs with single or double-pulse excitation. Geometrical assembly of laser beams (inline or perpendicular), time delay between the pulses, and gate delay influence the signal as well. Application of double-pulses was first tested in liquids by Cremers [CRL84].

The quantitative analysis with LIBS is based on several assumptions. The hypotheses include stoichiometric ablation, local thermodynamic equilibrium, and a plasma which is optical thin. Therefore, line intensities are increasing with the number density of atoms or ions in the plasma. A quantitative information can be obtained from calibration curves. Standard samples with varying concentrations as well as the unknown samples need to be analyzed at identical conditions.

The feasibility of the use of LIBS for the detection of metals and trace metals in aqueous solutions was demonstrated exemplarily with chromium, manganese, palladium, and indium.

Chromium is toxic depending on the oxidation state even though indistinguishable from one another by LIBS. Cr (III) is an essential nutrient that becomes toxic only in high doses while Cr (VI) has been classified by the WHO as an human carcinogen. In this work the LOD of Cr is 200 mg/L and down to 40 mg/L with a signal-to-noise ratio of 2:1 at a wavelength of 357.9 nm. This result has been achieved by a single pulse experiment with a simple and non failure-prone setup. Results in literature for detectable concentrations vary from 0.1 - 200 ppm [CrRa06]. Diaz Pace *et al.* [DAB+06] analyzed a conversion of liquid solution into solid pellets of calcium hydroxide with a subsequent measurement in air leading to a LOD of 1.2 ppm Cr at 357.9 nm. Nevertheless, matrix conversion is not realizable in case of online or remote analysis. In contrast double-pulse measurements carried out directly in liquid samples lead to an improved LOD of 0.92 ppm Cr measured at 238.6 nm by Lazic *et al.* [LJF+07].

Single pulse experiments in liquid samples tend to have higher quenching effects compared to measurements under atmospheric conditions, hence depressing spectral line intensities. Creation of a gaseous atmosphere inside the liquid in terms of a cavitation bubble overcomes this restriction. Cavitation bubbles are easy to obtain in doublepulse experiments evolving from the first laser-induced plasma. In advance, reduced spectral line width is estimated at low pressure inside the cavitation bubble compared to measurements on air at atmospheric pressure [Nyga93]. Therefore time delay Δt to induce second plasma for LIBS is a crucial parameter to be set at maximum bubble radius depending on cavitation bubble evolution.

In this work dissolved manganese is investigated in distilled water by two methods of double-pulse LIBS. One method involves fiber guided lasers and therefore needs a target to achieve sufficient power density for the breakdown. The second method employs two laser beams focused directly into the medium. Manganese itself is not harmful even though it belongs to the group of heavy metals. The element is a geochemical marker for tidal and seasonal fluctuations in the wadden sea, whose concentration is influenced by changes due to bioactivity. A LOD of 80 μ g/L is determined experimentally from the excitation of the liquid sample using a double-pulse laser system at a wavelength of 532 nm. Measurements at lower concentrations down to 20 μ g/L are feasible but lead to an unsatisfying relative standard deviation.

The quantitative analysis of manganese in pure water is carried out using the spectral line triplet at 403.08 nm, 403.32 nm, and 403.45 nm of Mn I. The calibration plot is based on the ratio of the intensities of the manganese triplet and the intensity of the ionic line of strontium at 407.77 nm, which has been added as internal standard. Strontium is chosen because emission lines of analyte and internal standard are observable in the same wavelength range of the spectrometer. Preferable analyte and internal standard should have similar vapor pressures. Results based on silicon as internal standard and target at the same time lead to poor correlation of line intensities. Ko *et al.* [KSN89] pointed out that the atomization process of elements having different vapor pressures is not correlated within short delay times. The vapor pressure of manganese (121 Pa at 1517 K) is 25 times higher than that of silicon (4.8 Pa at 1683 K) and only in the factor of two different to vapor pressure of strontium (246 Pa at 1042 K). Moreover, because of the different state of aggregation between the trace and the target elements, different times of ablation, excitation, and emission are expected, therefore resulting in a poor correlation.

Both laser pulses are guided into the liquid by an optical quartz fiber. As a result of numerical aperture, the fiber tip needs to be positioned in front of a target to absorb energy until an optical breakdown occurs. The target material is chosen due to its absorption properties. Cross contamination of emission lines from target and analyte needs to be excluded. Silicon is a first choice target for investigating manganese. Furthermore, the target leads to plasma ignition on a spatially confined area. This configuration yields a stable cavitation bubble, and following the second laser pulse, a reliable plasma ignition at the bubbles maximum expansion ($\Delta t \approx 80 \ \mu s$).

The concentration of manganese in the wadden sea is measurable by LIBS during summer because these values are in a range of max. 90 μ g/L and decrease to only ca. 0.5 μ g/L in winter time. The method is suitable for the monitoring of drinking water. The German Drinking Water Ordinance and the WHO set the limit of manganese in drinking water at 50 μ g/L and 100 μ g/L, respectively. Higher values causes a negative taste and color in combination with a high amount of iron.

In general, the sensitive LIBS analysis can be applied to other elements. The choice of a silicon target is not necessarily transferable to other elements in aqueous solutions. Palladium, a platinum group element (PGE), is in exhaust passing catalytic converters and found in urban air. It accumulates on road surfaces and in roadside soil. Transport of PGE via surface drainage following strong rainfall results in a contamination of aquatic environments. There is now increasing evidence that a fraction of PGE in the environment is bioavailable, and eventual uptake into the biosphere is raising concerns about potential risks for humans and the environment. Palladium concentrations ranging from 5 mg/L to 80 mg/L are measured with a linear correlation coefficient of R = 0.9978. Chromium is added as an internal standard. Related to electroless metal deposition an enrichment uniquely of palladium is observed on the silicon target. Several targets like metals, ceramics, and polymers (polycarbonat, polyethylene terephthalate, polyamide, polyoxymethylene) are tested. They are not suitable due to interfering lines, melting, or because they do not support reliable breakdown. Accumulation on a target might be potential for enrichment if dependency, e.g., of concentration and surface interaction are known, but are not tested in this work. Zhao et al. [ZCZ+10] have shown, that an electrolysis on pure aluminum as a cathode is an enrichment method that allows good

LODs, e.g. $0.176 \ \mu g/L$ for manganese. After electrical-deposition for a given time, the aluminum rod was taken out of the liquid to perform immediately elemental analysis by LIBS in air. The accumulated material amount of manganese did not depend linearly on deposition time.

A setup without a target eliminates interaction with the target surface. Fibers guided lasers beams by can not be focused and need to be replaced by lenses. Inducing a plasma without an absorber requires higher power density or improved focusing. A LOD of 0.3 mg/L Mn was determined in a targetless double-pulse experiment ($\Delta t = 70 \text{ }\mu\text{s}$). Due to much higher power density without the absorbing target intense plasma emission is observed. Interference of resulting hydrogen γ, β , and ϵ line emission is a drawback. The challenge is to induce a reliable optical breakdown without an excess of energy delivered, hence avoiding strong interferences.

Lazic *et al.* [LJF+07] were using a double-pulse system with a similar delay time of $\Delta t = 75 \ \mu s$. They reported that the reduction of energy has led to a reduction of the LOD by one order of magnitude. Energy is reduced from 92 mJ to 72 mJ for Laser 1 @ 1064 nm and from 214 mJ to 144 mJ for Laser 2 @ 1064 nm. The LOD of manganese is 2450 ppb for the high pulse energy scenario and 390 ppb for the low pulse energy scenario. 1000 spectra were accumulated. In any case, the energy delivered by Laser 1 was at least four times higher than in this work while Laser 2 was operated at approximately the same energy setting in this investigation without a target [KRN+10]. Accumulating 150 spectra equates to a LOD of 300 ppb.

Fig. 7.1 depicts fast imaging of the plasma onset occurring at the interface of the cavitation bubble. The images show only a weak contrast at the boundary of vapor filled bubble to surrounding liquid. They are recorded using a bandpass filter (BG3, Schott) to reduce the high emission intensity of the plasma. Thus the onset of the plasma ignition becomes visible. The picture clearly show that the plasma starts it's evolution from the bubble's liquid-gas interface. The laser beam passes the whole bubble before the higher absorption of the liquid leads to a breakdown in the bubble. The increase of absorption indicated with a density change from gas to liquids is a crucial parameter for the onset of the plasma.

Fig. 7.2 shows images of a cavitation bubble and the plasma spot. The focus was kept at a constant position, while the bubble itself was shifted from left to right relative to this position. The plasma onset occurs always at the bubble interface, despite of the fact that the laser beam is stationary focused onto the same horizontal position at



Figure 7.1: Plasma (induced by Laser 2 from below) in a cavitation bubble (induced by Laser 1 from right side) with the onset at the interface of the bubble; 100 ns exposure time

the center of the cavitation bubble. The higher absorption shows a higher relevance compared to the adjustment of the laser focus.



Figure 7.2: A plasma on the border of a cavitation bubble, which has been shifted from left to right

The utilization of a target shows advantages in the LOD and an easy adjustment of bubble laser and plasma laser. Both are simply guided by the very same fiber onto the target. A disadvantage might be the interaction of target material and analyte. The ablation of the target material urges for a stirring of the liquid to avoid deposition of target debris. The fiber needs to be placed at a distance of few 100 μ m apart from the target. Both are mechanically affected by shock waves and the fiber tip might be damaged. Therefore a method without a target has been applied in order to overcome above mentioned restrictions.

A comprehensive compilation of published LIBS LOD values is given by Cremers and Radziemski in Table C1 [CrRa06].

7.1.1 Resonance fluorescence spectroscopy

The double-pulse experiment with a target is extended to resonant excitation of selected species. Thus signal intensities are resonantly and selectively enhanced measurements of particular emission lines in complex matrices (such as saltwater), or elements with interference lines (such as iron) are feasible. Quantitative analysis has been carried out on the test element indium in pure water by detecting and measuring of spectral line intensity at 410.2 nm $(6s^2S_{1/2} \text{ to } 5p^2p_{1/2})$ enhanced by resonant excitation of the 451.1 nm line $(5p^2P_{3/2} \text{ to } 6s^2S_{1/2})$. Indium is not of particular interest in the field of environmental analysis, but the excitation scheme allows to suppress completely the tunable laser excitation line by spectral separation. The linear correlation coefficient R = 0.9976 between intensity and indium concentration is excellent. The limit of detection in the case of 10 mg/L of indium needs to be improved, but the correlation observed without adding an internal standard is promising. The signal intensity of OES is increased 360 times by RFS.

Resonance fluorescence spectroscopy is also denoted resonance-enhanced LIBS. Cheung's [Cheu06] results show improved LODs in aqueous samples by 20 - 1000 times.

7.1.2 Plasma temperature and electron density

Temperatures and electron densities of a plasma induced into a cavitation bubble are evaluated between 0.7 μ s and 2.8 μ s after plasma ignition. Results are shown in Figure 7.3. Setup [KRN+10] describes the experiment.

Temperature determination is carried out by using H_{α} line at 656.3 nm and H_{β} line at 486.2 nm of the Balmer series [Grie64]. Only two lines of the same element are used for temperature calculation by Eq. 2.11 due to experimental drawbacks like the spectral bandwidth of the spectrometer. The temperature is calculated to be approx. 6740 K ± 300 K at a delay time t_d of 1 µs. The electron density, determined from the line width of H_{β} is approx. $0.2 \cdot 10^{18}$ cm⁻³ at $t_d = 1$ µs. Error is mainly dominated by the parameter $C(n_e, T)$ which is 5 % for H_{β} . A peak power density of $3.1 \cdot 10^{19}$ W/cm² and a laser pulse energy of 77 mJ, respectively, are used.

Cremers *et al.* [CRL84] presented measurements in bulk liquid. They calculated a temperature of 7950 K and an electron density of $0.9 \cdot 10^{18}$ cm⁻³ at a delay time $t_d = 1 \ \mu$ s and the gate pulse width $t_b = 0.25 \ \mu$ s. The electron density was evaluated from lines of lithium I (670.8 nm) and of calcium (Ca) I (422.7 nm). The intensity ratio of Ca II at 393.4 nm to Ca I at 422.7 nm was used to measure the temperature of a spark in water. The experimental setup refers to a single pulse experiment using a Nd:YAG laser @ a wavelength of 1064 nm, 15 ns pulse width, and an energy of about 45 mJ/pulse. The laser beam was focused by a pair of 50 mm lenses into the liquid.

Samek *et al.* [SBK+00] determined temperatures of 7000 K extracted from H_{β}/H_{γ} at 1 µs. The electron density was calculated for H_{β} line at 14.4 · 10¹⁶ cm⁻³. The experiment



Figure 7.3: Plasma temperature and electron density in a cavitation bubble in water

was carried out on a laminar water jet. A Nd:YAG @ $\lambda = 1064$ nm, $\Delta \tau_p = 4.5$ ns, and laser pulse energy of 60 mJ was focused to a diameter of about 250 µm onto the water surface.

The determined temperature of the plasma in a cavitation bubble is slightly lower than temperatures described in liquids by Cremers *et al.* [CRL84] and Samek *et al.* [SBK+00]. The mentioned results of three different experiments are comparable in terms of the use of Nd:YAG lasers at their fundamental wavelength for plasma excitation. The values calculated by Cremers result in a higher temperature by less energy. Unfortunately the focal diameter is not given to compare irradiances. The electron density shows comparable values. The temperature calculated from Samek is around 300 K higher than the temperature evaluated in this investigation. This value is within the error bar. Altogether, the irradiance used in this work is much higher due to a smaller spot size. Nevertheless, the results refer to the analysis of different elements and different setups as well and are therefore of the same order of magnitude.

7.2 Cavitation bubbles and dynamics

The understanding of the temporal and spatial evolution of the cavitation bubble is necessary for the analytic approach by LIBS within the gaseous environment of a cavitation bubble. A high spatial reproducibility is important to ensure plasma ignition inside the cavitation bubble. The knowledge of the temporal evolution is significant for the timing of a double-pulse measurement. Line intensities show the best signal-to-noise ratio when the plasma is induced at the bubble's maximum expansion. This results from a low pressure inside the cavitation bubble. After expending the driving laser energy the bubble starts to shrink because the pressure of the surrounding liquid is much higher than the vapor pressure inside the bubble.

The spatial "jitter" of a series of bubbles is easy to observe by subsequent CCD camera images. A measurement of the complete temporal and spatial evolution is more challenging due to a large dynamic range of shock waves (≈ 100 ns) and bubble life time (> 100 µs). Fast imaging and multi exposure recording with 100 ns shutter resolution is appropriate for the examination of selected parts of the bubble evolution and shock wave emission. The bubble dynamics in distilled water and isooctane, as an example for retrograde fluids, has been investigated. Bubble size, collapse time, and oscillation behavior are largely different in water and isooctane. The maximum expansion of the rebound bubble after the collapse in isooctane is more than two times larger than in water. After the first collapse, the bubble shape is slightly deformed and resembles the initial plasma shape.

A novel optical method allows to measure simultaneously at high temporal ($\Delta t = 20$ ns) and spatial ($\Delta r_b = 3 \ \mu m$) resolution from the onset to the collapse of a single cavitation bubble. This includes also the detection of the combined shock waves generated by a single pulse of a high power laser. Although limited to spherical bubbles, CCD images, recorded during the measurements do confirm that this method is well applicable.

Contrary to other groups ([LJF+07], [EMW11]), who studied luminescence of laserinduced bubbles by using a photomultiplier, a photodiode and a Gaussian diagnostic laser beam permit the calculation of the bubble radius in the present work. The differences in bubble dynamics are demonstrated in distilled water and glycerine for its high viscosity and density. Especially during onset and collapse, deviations from spherical shape are observed. However, even in that case, the bubble radius determined with the developed method can be considered as an equivalent radius. This setup allows an easy check for timing.

7.3 Statistical data evaluation

The data evaluation of LIBS spectra with complex and similar chemically composition is challenging and could be improved by statistical data evaluation. Especially the investigation of organic samples show a lack of selectivity, because the majority of material is represented by carbon, oxygen, hydrogen, and nitrogen. At the same time, there is a high demand for remote probes in the field of microbiology or homeland security for the determination of bacteria and explosives, respectively. The potential of pattern recognition and clustering of spectrum signals are studied for classification or prediction of concentrations of unknown elements by artificial neural network, fuzzy logic, and, chemometrics. Artificial neural network supports, e.g., material identification [KSM+10]. Hatch *et al.* [HTJ+12] differentiated between various copper-containing and stainless steel alloys as well as unknowns by fuzzy logic. Chemometrics in terms of PCA, PCR, MLLSR, or PLS has been used successfully, e.g. by [YDS12], [DCP09], and [HLB03]. Hybl *et al.* [HLB03] demonstrated that PCA allows to distinguish e.g. pollen and fungal spores in biological aerosols.

The PCA method is applicable for complex samples. Historical iron alloy samples of the 16th to 19th century were investigated. Museums show special interest in the composition and origin of ancient material. The samples were analyzed with laser spot sizes of ca. 100 μ m, typical in LIBS experiments. Iron was found to be the main component. Steel refining elements which enable modern alloys to be distinguished by LIBS, like chromium, nickel, tungsten, vanadium, etc., have not been in use at those times. Furthermore, the high spectral density of iron emission lines hides minor elements. LIBS in combination with PCA is a feasible and fast approach to group elements according to their chemical composition. A larger data set containing samples with known origin combined with an analysis of standard samples would provide a further insight into the historical iron alloys. Comparing the database with ores of the sample origin would also be revealing. Yaroshchyk *et al.* [YDS12] validated samples with 12.6 – 67.9 % iron with goodness-of-fit R^2 of 0.97.

For getting a closer insight to PCA results, slag inclusions were analyzed by micro LIBS using a high spatial resolution of 10 μ m. This allows for the determination of oxides origin from ores. Buchwald and Wievel [BuWi98] demonstrated that the analysis of slag inclusions leads to the differentiation of even homogenous metals.

8 Conclusions and outlook

The trace analysis of heavy metals in liquid samples and their quantification by spectroscopy is particularly relevant in fields of industrial processing and environmental monitoring. It has been shown here that laser-induced breakdown spectroscopy is a reliable technique for qualitative and quantitative analysis. Features like *in situ* measurement capability, simultaneous multi-elemental detection, and real-time measurement in the laboratory and the field make LIBS a powerful and attractive analytical tool. A further advantage is the ability to use samples with hardly any preparation. The necessary sample volume is negligible and therefore the analysis is almost non-destructive. The challenges of the method originate from the side effects of the intrinsic advantages. The small size of the focused laser beam excites only a small amount of the sample. This includes that the inhomogeneity of the sample is very critical for the accuracy. The small amount of excited sample material and short pules excitation yields a lower emission signal compared to continuous excitation sources, e.g. ICP. Care has to be taken, that surface contaminants do not influence strongly the analysis. In case of liquid samples homogeneity can be assumed.

The aggregation state of the sample plays a major rule in terms of detection sensitivity. Surfaces of solid matter e.g. iron are easy to excite and limits of detection are reasonable high because quenching processes can be neglected for measurements in air under atmospheric standard conditions. The analysis of liquid samples is challenging in terms of limits of detections. Quenching processes in liquids strongly reduce the optical emission signal. Transferring the measurement in liquids to a gaseous environment of a cavitation bubble overcomes this restriction. Gas samples do not suffer from quenching but low material density makes high irradiances necessary.

LIBS on heavy metals in aqueous solutions:

This work demonstrates the quantitative trace analysis capability of double-pulse LIBS in aqueous solutions. The spectral analysis in single and double-pulse setup and the implementation of internal standards were successfully applied to several elements with environmental concern. The double-pulse cavitation bubble method is based on two subsequent laser pulses at a delay time Δt of approx. 80 µs. The plasma ignition of the first laser pulse generates a cavitation bubble. Subsequently LIBS is carried out in the cavitation bubble with the second laser pulse.

Chromium compound toxicity depends on the oxidation state of the metal. The World Health Organization (WHO) has classified chromium (VI) to be a human carcinogen. Chromium has been analyzed with a limit of detection of 200 mg/L. The first test leads to a simple and non failure-prone setup. Even if promising, the proposed method using single pulse excitation of a Nd:YAG laser at a wavelength of 1064 nm does not yet yield the linear accuracy required for a quantitative analysis of chromium concentration in drinking water. Despite this fact oxidation stages of environmental relevance are not distinguishable. Double-pulse measurements need to be applied to increase the sensitivity.

Manganese is a geochemical marker for tidal and seasonal fluctuations in the wadden sea. Like sodium chloride it is influenced by high and low tide but additionally shows influence by seasonal changes due to other mobilizations, e.g., the reduction of organic material. Dissolved manganese in distilled water has been determined with an experimentally obtained LOD of 80 μ g/L. Measurements down to 20 μ g/L are possible but include a higher RSD. Values in the lower ppb range are typically not achieved by LIBS. Therefore the results approach standard laboratory analytics. An optical emission signal is obtained from the excitation of the liquid sample on a target using a double-pulse laser system at a wavelength of 532 nm. Strontium is chosen as an internal standard. The achieved limit of detection allows manganese in seawater to be measured during summer time. Manganese in seawater appears in the range of max. 90 μ g/L in summer time down to min. 0.5 μ g/L in winter time. The method is applicable to drinking water monitoring.

In general, this method can be applied to another chemical element, i.e. palladium, by exchanging the sample after checking cross contamination with the target. Palladium belongs to the platinum group elements (PGE). PGE from catalytic converters in exhaust fumes can be found in urban air and accumulate on road surfaces and in roadside soil. Palladium is measured at concentrations ranging from 5 mg/L to 80 mg/L with a linear correlation coefficient of R = 0.9978. Electroless metal deposition of palladium on the silicon target is observed, while chromium and manganese are not affected by silicon.

A potential accumulation on the target, depending on the combination of analyte and target, has to be taken into consideration. This side effect might be powerful enrichment if parameters are known or nonlinear dependency. To avoid these effects the setup has been modified towards a method without a target. An excellent linear correlation of manganese concentrations is evaluated with strontium as internal standard. The method eliminates target influence but leads to reduced sensitivity, e.g. an LOD of 0.3 mg/L for manganese. In order to meet trace analysis requirements, the method needs additional improvement to be comparable with standard methods like ICP-MS.

Resonance fluorescence spectroscopy:

The influence of complex matrices or interfering elemental spectra can be strongly reduced by RFS, which has proven to enhance signal intensities. Indium was chosen as a test element due to its excitation scheme. It enables emission lines to be acquired separately from spectral lines resonantly excited by a narrow band tunable dye laser. The developed methodology is intended for the investigation of difficult matrices (such as salt water), or elements with interfering lines (such as iron).

Cavitation bubbles and dynamics:

Laser-induced breakdown spectroscopy in cavitation bubbles has been verified to be a practical method for the elemental analysis of dissolved metals. Special emphasis on the understanding of the temporal and spatial evolution of the cavitation bubble is therefore necessary. The evolution and the bubble shape are strongly depending on the laser energy, fluence, power density, focusing of the laser beam, and liquid medium.

A novel and powerful optical method to record cavitation bubbles in liquids has been developed to analyze the dynamics of laser-driven cavitation bubbles. The main advantages are the high temporal and spatial resolution from the onset to the collapse of a single cavitation bubble. This includes also the detection of the combined shock waves generated by a single pulse of a high power laser. Values of $\Delta t = 20$ ns and $\Delta r_b = 3$ µm, respectively, are limited by the read out system consisting of a fast photo diode and a fast oscilloscope. Distilled water and glycerine for its high viscosity and density have been under investigation to identify the differences in bubble are displayed immediately.

Principal components analysis:

Statistical data evaluation methods to analyze samples with similar principal constituents is challenging for LIBS. Chemometrics is an upcoming technique providing a typification into various sample groups. The statistical data evaluation like principal components analysis (PCA) is a methodical add-on to interpret the outcome of complex spectroscopic results. It allows one to differentiate within similar sample groups, e.g. microorganisms, pollen, or historical iron alloy samples like in this work. For a better understanding of PCA grouping the samples were investigated by micro LIBS using a high spatial resolution of 10 μ m sample area. Slag inclusions in the historical iron samples are exactly within this dimension range that enables historical metal artifacts to be distinguished on this base. Micro LIBS demands a sample preparation (laser cleaning or electrochemical etching) in order to clearly show crystal grain structure and slag inclusions.

Outlook:

The results clearly show that laser-induced breakdown spectroscopy is a suitable method to analyze trace elements in liquid samples. The technique has the capability of tracing heavy metals with environmental concern at detection limits, e.g. $80 \ \mu g$ Mn, comparable to lab diagnostic. Further developments on the setup with a dichroic mirror for a better adjustment and laser beam overlap inside the cavitation bubble might improve the LOD. The use of higher data accumulation and averaging is also possible. The achieved limits of detection meet the requirements for online monitoring in industrial processes. Applicability in field measurements could be promoted by miniaturization of the experimental setup. A new generation of field spectrometers and especially the improvement of laser devices, e.g. the availability of high-power laser diodes, are suitable for miniaturization at low energy consumption. The implementation of standardized sample filtration in the case of seawater is necessary to compare the LIBS results obtained in water samples with standard laboratory analytics. In general, reliable LIBS applications require automated data evaluation including calibration standards.

The electroless deposition lead to the targetless LIBS analysis. It has not been under investigation systematically in the frame of this work. But it might turn out to have the potential for an enrichment of sample material without excessive effort and sample preparation. The internal standard calibration only works in the case of similar enrichment behavior of both analyte and standard. Therefore data evaluation by calibration-free LIBS should be taken into account, when usual calibration procedures with internal standards are not feasible. Saturation effects need to be taken into consideration.

Although cavitation bubbles are only provided a helpful tool to enable LIBS in liquids another research field on bubble dynamics opened up. At present, the novel method for measuring shock waves and the temporal and spatial evolution of the cavitation bubble is supported by fast imaging techniques. This allows also the observation of shock waves in the collapse which disappear at higher temperatures of the liquid and seem to be dependent on viscosity and vapor pressure. This investigation is ongoing research.

The resolution of 10 μ m achieved in micro LIBS is promising for spatially resolved analysis to obtain selective elemental composition. Further work is planned on slag inclusions on the surfaces of historical iron alloys without destructive sample preparation. This might lead to a rapid analysis by LIBS on valuable samples. Investigations concerning heavy metal concentrations in seashells as a function of growth are planned. The results should be compared with the edible mussel meet.
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Abbreviations and symbols

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
AES	Atomic emission spectrometry
Ar	Argon
CCD	Charged-coupled device
Cr	Chromium
EPA	Environmental Protection Agency
FWHM	Full width at half maximum
$\mathcal{H}_{\alpha,\beta,\gamma,\delta}$	Hydrogen (Balmer series)
HeNe laser	Helium-neon laser
Hg	Mercury
ICP	Inductively coupled plasma
IB	Inverse bremsstrahlung
In	Indium
Laser	Light amplification by stimulated emission of radiation
LDI	Laser doppler interferomter
LGBS	Laser generated bubble and shock waves
LIBS	Laser-induced breakdown spectroscopy
LOD	Limit of detection
LTE	Local thermodynamic equilibrium
MLLSR	Multiple linear least squares regression
MLR	Multiple linear regression
Mn	Manganese
Nd:YAG	Neodymium-doped yttrium aluminum garnet
OES	Optical emission spectroscopy
PBD	Probe beam deflection
PCA	Principal components analysis
PCR	Principal components regression
Pd	Palladium

PGE	Platinum group element
PIN	Positive intrinsic negative
$\mathrm{ppm/ppb}$	Parts per million/Parts per billion
PLS	Partial least squares regression
RSD	Relative standard deviation
S/N	Signal/Noise
Sr	Strontium
TEM	Transverse mode
WHO	World Health Organization
XRF	X-ray fluorescence

LIST OF SYMBOLS

ROMAN LETTERS

a_0	[m]	Bohr radius
A	$[s^{-1}]$	Einstein's coefficient of spontaneous emission
\vec{B}	[T]	Magnetic flux density
C	$[m \cdot s^{-1}]$	Speed of sound
$C(n_e, T)$	$[^{-3/2} \text{ cm}^{-3}]$	Coefficient for electron-density determination
$d_{1,2}$	[m]	Diameter (focus, laser beam)
D	[m]	Plasma depth
E	[eV]	Energy
\vec{E}	$[V \cdot m^{-1}]$	Electric field intensity
f	[m]	Focal length
f_O		Oscillator strength
g		Statistical weight
\hbar	$[eV \cdot s]$	Reduced Planck constant
Н	[J]	Enthalpy
Ι	[counts]	Intensity
I_{rad}	$[W \cdot cm^{-2}]$	Irradiance
J		Total angular momentum quantum number
L	[m]	Distance bubble to aperture
m	[kg]	Particle mass
M	$[\text{kg} \cdot \text{mol}^{-1}]$	Molar mass
\dot{m}	$[\mathrm{kg}\cdot\mathrm{s}^{-1}]$	Mass flowrate
n_e	$[cm^{-3}]$	Electron density
n		Refractive index

n	[mol]	Amount of substance
n^s	$[{\rm cm}^{-3}]$	Number density of species involved
p	[bar, Pa]	Pressure
P		Probability
r	[m]	Radius
\dot{R}	$[m \cdot s^{-1}]$	Bubble radius velocity
s		Species
S	[counts]	Elemental emission signal
Δt_b	$[\mathbf{s}]$	Gate pulse width
t_d	$[\mathbf{s}]$	Delay time
t_c	$[\mathbf{s}]$	Collapse time
T	[K]	Temperature
U	[V]	Voltage
$U^s(T)$		Partition function of the atomic/ionic level system
V	$[m^3]$	Volume
x, y, z	[m]	Cartesian coordinates
Z		Charge of particles

GREEK LETTERS

α	$[m^{-1}]$	Absorption coefficient
γ	$[s^{-1}]$	Radiation damping constant
κ		Adiabatic index (ratio of specific heat)
λ	[m]	Wavelength
$ln\Lambda$		Coulomb logarithm
ν	$[s^{-1}]$	Frequency
$\bar{\nu}$	$[\mathrm{m} \cdot \mathrm{s}^{-1}]$	Mean thermal speed
μ	[Pa·s]	Dynamic viscosity
ω	$[rad \cdot s^{-1}]$	Angular frequency
ρ	$[\text{kg} \cdot \text{m}^{-3}]$	Density
σ	$[N \cdot m]$	Surface tension
au	$[\mathbf{s}]$	Relaxation time
$ au_o$		Optical thickness
$ au_p$	$[\mathbf{s}]$	Pulse width
ζ	[m]	Relative radius

SUBSCRIPTS

b	Bubble
e	Electron
l	Liquid phases
u, l	Upper, lower excitation level
v	Vapor phases

Constants

С	Speed of light in vacuum	$299792458 \ {\rm m}{\cdot}{\rm s}^{-1}$
h	Planck constant	$4.135667516\cdot 10^{-15}~{\rm eV}{\cdot}{\rm s}$
k	Boltzmann constant	$8.6173324\cdot 10^{-5}~{\rm eV}{\cdot}{\rm K}^{-1}$
m_e	Electron mass	$9.10938291 \cdot 10^{-31} \text{ kg}$
N_A	Avogadro constant	$6.02214129 \cdot 10^{23} \text{ mol}^{-1}$
R	Ideal gas constant	$8.3144621~{\rm J}~{\rm mol}^{-1}~{\rm K}^{-1}$

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Publications

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Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit den angegebenen Hilfsmitteln selbstständig angefertigt habe.

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