



Development of a continuous flow hydride generation laser-induced breakdown spectroscopic system: Determination of tin in aqueous environments[☆]

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ABSTRACT

The design, construction and optimization studies of a continuous flow hydride generation laser-induced breakdown spectroscopic system, HG-LIBS, for the determination of tin in aqueous environments is presented. Optimization of the Laser Induced Breakdown Spectroscopy (LIBS) signal with respect to carrier gas flow rate, analyte, acid (HCl) and reductant (NaBH₄) concentrations and flow rates was performed by using spectral emission intensity from the neutral Sn(I) line at 284.0 nm under atmospheric pressures. With flow rates of 5.0 mL/min for NaBH₄ and 2.5 mL/min for HCl, optimum NaBH₄ and HCl concentrations were determined as 2.0% (w/v) and 1.0% (v/v), respectively. The hydride generation efficiency of the system was tested for tin hydride, stannane (SnH₄), by inductively coupled plasma mass spectrometer (ICP-MS). It was found that higher than 99% of the analyte was released into the gaseous phase. Upon optimization, the minimum detectable Sn concentration was found as 0.3 mg/L in water samples. That corresponds to more than two orders of increase in sensitivity compared to methods that employ common sample introduction techniques in liquids analysis by LIBS. Over 90% recoveries were obtained from spiking experiments with river, tap and drinking water samples. Results illustrate potential use of the continuous flow HG-LIBS system for monitoring of Sn concentrations in aqueous environments.

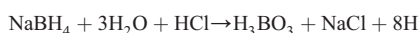
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1. Introduction

Arsenic, antimony, bismuth, germanium, lead, selenium, tellurium and tin are some elements that have environmental and technological importance. Quantification of these elements in environmental samples can be done by introducing aqueous solutions of these elements directly to atomic spectroscopic instruments, such as atomic absorption spectrometer, AAS, atomic emission spectrometer, AES, atomic fluorescence spectrometer, AFS, inductively coupled plasma mass spectrometer, ICP-MS and inductively coupled plasma optical emission spectrometer, ICP-OES. These elements can also be determined in the form of their volatile hydrides by using a type of sample introduction technique called *hydride generation* (HG) [1,2]. There is a great interest in the field of analytical chemistry in exploring the analytical capabilities of HG with respect to speciation analysis [3–5] and multi-element determinations [6,7] since its first use in 1968 by Holak [8].

Hydride generation is a chemical derivatization technique in which some elements of the periodic table mentioned above form

their volatile hydrides as indicated in the following reactions [1] when they react with strong reducing agents, such as sodium borohydride, NaBH₄ and hydrochloric acid, HCl.



Here, *E* is the desired metal, *m* is the oxidation state of the metal and does not necessarily equal to the *n*. EH_{*n*} is the volatile metal hydride. In this technique, elements are separated from other accompanying materials in the form of gaseous hydrides and are introduced to the sample cell for atomization leaving the sample matrix in the liquid waste. Thus, spectral and chemical interferences can be eliminated. Therefore, significant increase in sensitivity, by 10–100 folds, over commonly used liquid sample introduction techniques has been reported [9–11].

The generation of volatile hydrides followed by atomic spectroscopic detection (AAS, AES, ICP-OES or ICP-MS) is the most common method of choice for the determination of toxic metals at trace levels of concentration, (µg/L–ng/L). These techniques provide high sensitivity but require laborious and time consuming sample collection steps for analyses to be conducted in the laboratory. In addition, the chemical identity of the sample may change during its delivery from the field to the laboratory. For this reason, there is a growing demand for rapid, real time, in situ and sensitive analysis techniques for

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environmental research applications. Laser Induced Breakdown Spectroscopy (LIBS) [12–14], is a very suitable technique to develop portable sensors and the utilization of this technique for the determination of environmental pollutants is increasing. There are several portable-LIBS sensors developed for environmental and industrial applications [15–18].

Applications of LIBS in bulk liquids [19–21], are few due to the difficulties experienced during analysis. Those difficulties are splashing, bubble formation and shock wave formation after focussing the laser beam on liquids. Liquid analysis by LIBS also suffers from poor signal quality, reduced plasma emission and low limits of detection due to shot to shot signal fluctuations. In order to overcome some of these difficulties, various approaches including: formation of the plasma on liquid surfaces [22], on droplets [23,24] on flowing-jet liquids [25] and use of double pulses for plasma formation [26,27] have been employed by several groups in LIBS community.

Here, we present design, construction and optimization studies of a continuous flow hydride generation sample introduction technique hyphenated with laser-induced breakdown spectroscopic detection (HG-LIBS) for the determination of hydride forming elements in aqueous samples, under atmospheric pressures. Yet, our work specifically focuses on optimization of the hydride generation conditions for the detection of tin (Sn) in standard and real water samples, however, this technique is also applicable to all other hydride forming elements like As, Se, Sb, Pb, Bi, Ge and Te when suitable experimental conditions are satisfied.

Tin is a naturally occurring element and may be present in the environment in both organic and inorganic forms. Organic tin compounds are extremely toxic to marine organisms while inorganic tin compounds are regarded as non-toxic. Although, it is unknown at what level tin contributes to toxicity, the Agency for Toxic Substances and Disease Registry (ATSDR) of the United States [28] derived the oral minimum risk levels (MRL) of 0.0003 mg/kg/day and 0.3 mg/kg/day for tributyltin (TBT) and tin (II) chloride, respectively. The release of tin to the environment from anthropogenic sources exceeds tin release from geological sources 110 times. Inorganic tin is applied as coating a protective layer on other metals to prevent corrosion and also used in glass industry in the production of frost-free windshield. Organotin compounds are applied as fungicides, insecticides and as polymer additives in antifouling paint as a ship hull preservative. When control measures are inadequate excessive concentrations of tin and tin compounds may enter the environment by leaching from the consumer products and from the disposal of products in landfills. There is no value established by the WHO in drinking water guideline regarding tin and tin compounds due to low level of toxicity, however, according to Florida and Minnesota State regulations in the USA the MRL for tin in drinking water is given as 4.2 mg/L and 4.0 mg/L, respectively [28].

Due to its environmental, technological and biological importance there are several studies in literature on the determination of tin by HG coupled to atomic spectroscopic detectors [9,29–31], however, studies on the measurement of tin in liquids by LIBS are few. In one of the studies on direct analysis of liquids by LIBS performed by Fichet et al. [32], LIBS was used to quantify trace amounts of 12 elements including tin, in water and oil samples of a nuclear plant. They have tried to eliminate a common problem of splashing, in liquids analysis by LIBS, by focussing the laser beam on the sample surface with a tilted angle of 15°. They reported a detection limit of 100 mg/L and 80 mg/L for tin in water and in oil samples, respectively.

The analytical capability of the liquid analysis by LIBS, in terms of detection limits, may be improved by converting relevant metal species to their metal hydrides. To our knowledge, one of the only two studies in the literature on the chemical generation of volatile hydrides followed by LIBS detection was carried out by Singh et al. [33]. They have used a batch type hydride generation method in which reductant and acidic analyte were mixed in a closed system. Measurements were performed in an evacuated cell, by mixing the

hydrides with a carrier gas (He, N₂) with predetermined concentrations and pressures. They have investigated the effect of the type of the carrier gas and ambient pressure on temporal emission behaviour of LIBS signal on tin (Sn) and arsenic (As) hydrides. They have observed that the neutral atomic emission of Sn at 284.0 nm decreases exponentially with time in N₂ atmosphere while the signal increases logarithmically under identical experimental conditions in He atmosphere. Authors report no quantitative data for the detection limit of the studied elements.

The other study on HG-LIBS is a MSc thesis by Kunati [34] at Youngstown State University. In this study, HG-LIBS results for As, Sn and Te are compared with the results from HG-LIF (Laser Induced Fluorescence) and HG-ICP-AES. They report the same detection limit of 1.0 mg/L for three elements studied (As, Sn and Te) by HG-LIBS system equipped with Czerny-Turner monochromator and PMT detection.

Cheng et al. [35] has studied the measurement of metal hydrides; phosphine (PH₃), arsine (AsH₃) and diborane (B₂H₆) concentrations, (1–400 mg/L), in helium gas standard at low pressures. The detection limits for phosphine, arsine and diborane were determined to be 1.0, 3.0, and 1.0 mg/L by volume, respectively.

This paper focuses on the systematic investigation of the chemical and instrumental parameters of the HG-LIBS system for quantitative analysis of environmentally important elements that can form volatile hydrides. Results specifically obtained for tin hydrides, stannanes, SnH₄, are presented in detail.

2. Experimental

The experimental set-up for continuous flow HG-LIBS system comprised of a hydride generation unit, a plasma cell and LIBS detection unit is schematically shown in Fig. 1. Here, volatile hydrides generated in a continuous flow reaction system are carried through a Teflon tubing into a five armed Teflon plasma cell in which laser pulses of 150 mJ energy are used to create plasma. Spectral lines emitted from the plasma are collected at 90° angle with respect to incoming laser beam and imaged by a pair of plano-convex lenses onto a 600 µm diameter fiber optic cable and transferred into an echelle spectrograph equipped with an ICCD detector.

2.1. Hydride generation unit

A continuous flow hydride generation (HG) unit, given in Fig. 2, utilizes a four-channel peristaltic pump (*Longer Precision*) with adjustable speed to deliver acidified analyte and NaBH₄ solution to a 3-way PTFE connector

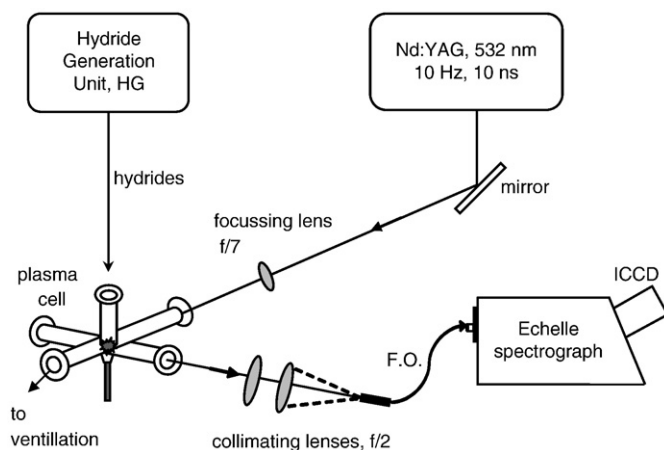


Fig. 1. Schematic diagram of the HG-LIBS set-up. Volatile hydrides from the hydride generation system are carried through the five armed Teflon plasma cell. 150 mJ laser pulses are used to create plasma. Spectral emission from the plasma is collected by a pair of plano-convex lenses (10 cm F.L.), imaged onto the fiber optic cable and transferred into the spectrograph to be detected.

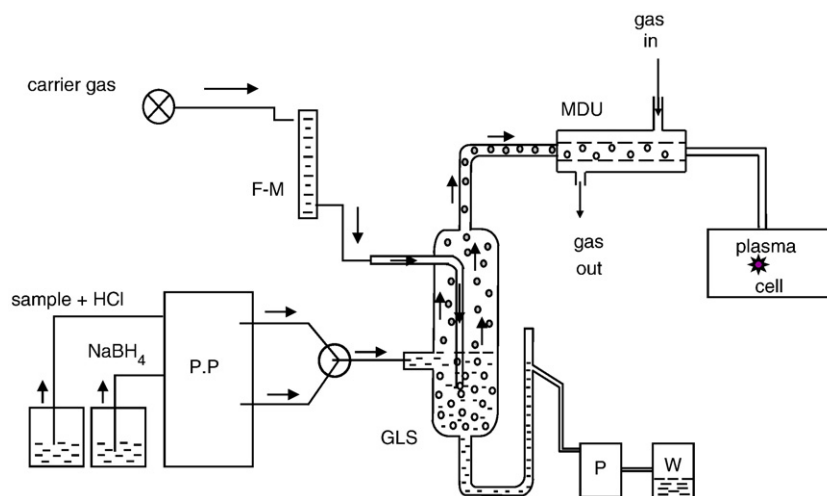


Fig. 2. Schematic diagram of continuous flow hydride generation, HG, unit. P.P: peristaltic pump, GLS: gas–liquid separator, HCl: hydrochloric acid, NaBH₄: sodium borohydride, F–M: flow meter, MDU: membrane drying unit, P: pump, W: waste.

(Supelco) where hydride generation reaction starts. Gaseous hydrides produced from this reaction were first carried into a U-type gas–liquid separator, GLS, separated from the liquid waste by a continuous flow of carrier gas (N₂), and then carried into a nafion membrane dryer (Perma Pure). Inert purge gas, N₂ or Ar, flowing over the exterior surface of the membrane tubing in counter-current direction with respect to sample flow was employed to remove water vapor from the hydrides. After passing the drying unit, hydrides were introduced into the sample/plasma cell from the top for plasma formation. One side arm of the cell was used for incoming laser beam another one situated at 90° was used for the collection of plasma emission. It is a closed system and these two arms were equipped with quartz windows. The remaining two arms were closed by connecting one to a ventilation system through a vacuum pump and another one to a pressure gauge, respectively. The system was under atmospheric pressures due to continuous flow of reagents during the experiments. Waste solution was pumped out from the GLS by using another peristaltic pump (ISMATEC, Germany) at a controlled flow rate. The carrying and drying purge gas flow rates were controlled by using two separate flow controllers (Cole Palmer). Five armed plasma cell machined from Teflon material provides chemical inertness for this corrosive environment.

2.2. LIBS set-up

A Q-switched Nd:YAG laser (Spectra Physics, LAB170-10) at 532 nm, with a pulse width of 10 ns and a repetition rate of 10 Hz was used to form plasma from tin hydrides (SnH₄). Laser pulse energy measurements were performed by a power/energy meter (Ophir, Nova II). The laser beam was focused inside the 5 armed Teflon cell, by using 175 mm focal length (*f*/7) plano-convex lens and the plasma emission was collected at an angle of 90° with respect to incoming laser beam by means of two 100 mm focal length (*f*/2) plano convex lenses. The collected light was launched onto an optical fiber (Ocean Optic, 600 µm diameter) coupled to an echelle type spectrograph (ME5000, Andor Inc. *f* = 195 mm), equipped with a gated, image intensified charge coupled detector, ICCD (iStar DH734, Andor Inc.). The spectrograph and detection system's spectral range is between 200 and 850 nm with 0.08 nm resolution at 400 nm. Wavelength calibration of the spectrograph was done by using Hg–Ar spectral calibration lamp. The detector gain was kept at 100 with 10 µs delay and 3 ms gating time, for almost all experiments.

2.3. Standards and reagents

Tin standard solutions were prepared daily from stock Sn solution (1000 mg/L in 20% HCl, High-Purity Standards) through appropriate

dilutions with ultra pure water. Standard and real samples were acidified with concentrated HCl to reach a desired acid concentration. All reagents were of analytical grade or higher purity. Sodium borohydride solutions were prepared by dissolving appropriate amount of NaBH₄ powder (Sigma-Aldrich) in 1.0% (w/v) NaOH (Riedel-de Haën) for stabilization and used without filtration.

River Water Reference Material for trace metals, SLRS-4, was obtained from NRC, Canada, Ottawa and used without dilution. No detectable tin concentration was listed among 22 metals for which certified values are in the range of low ppb levels. Tap water was from İzmir-Urla municipal water supply and drinking water was a bottled spring water (Pınar) from Aydın, Turkey.

3. Results and discussion

Instrumental and chemical parameters of HG-LIBS system were systematically studied in order to provide high efficiency of hydride generation and LIBS detection for tin in aqueous environments. Optimization procedures for each parameter are given in detail below and optimized conditions used throughout the experiments are tabulated in Table 1.

3.1. Optimization of instrumental parameters for HG-LIBS

In order to maximize LIBS signal, some of the key parameters, like laser energy, detector delay time, gate time and gain were studied first. The percentage of the pulse energy deposited into the Sn hydride, stannane, plasma was quantified from pulse energy measurements between 80 and 175 mJ/pulse laser energy range. This energy range corresponds to average power density of 1.9–4.2 TW/cm² for a diffraction limited beam size of 23 µm. As it is shown in Fig. 3(a), the plasma absorbs 65% of the input pulse energy when 80 mJ/pulse laser energy is applied. Increasing input laser energy to 175 mJ/pulse, percent absorption increases only up to 76%. This so called 'saturation effect' has been observed previously by some other researchers [36,37]. They explained that, after sufficient energy is deposited for ionization, excess energy is used to enlarge the size of the plasma rather than increasing the plasma temperature or electron density. Within the content of this study, temperature and electron density calculations have not been performed, however, the change in the physical size of the plasma was evident as the laser energy increases during the experiments.

Spectral line intensity measurements for 284.0 nm neutral tin, Sn (I), emission as a function of laser pulse energy were performed and presented in Fig. 3(b). From 80 mJ to 100 mJ pulse energy, LIBS signal

Table 1

Optimum chemical conditions^a for the generation and detection of tin hydrides, SnH₄, with HG-LIBS system.

NaBH ₄ conc.	2.0% (w/v) in 1.0% NaOH (w/v)
NaBH ₄ flow rate	5.0 mL/min
HCl conc.	1.0% (v/v)
Acidified sample flow rate	2.5 mL/min
Carrier gas (N ₂) flow rate	137 mL/min

^a 150 mJ/pulse energy, Td: 10 µs, Tg: 3 ms and 5.0 mg/L Sn solution were used.

intensity was increased more than two times. However, after 100 mJ/pulse energy, no significant change in LIBS signal intensity was observed. Also, at high laser energies, RSD of the signal calculated for seven sequential measurements was quite high, ranging from 20% to 25%, due to increased shot to shot variation. However, experiments were performed at 150 mJ/pulse laser energies, to ensure complete breakdown for all laser shots.

In order to determine optimum time interval for detecting tin lines from the luminous plasma, detector gating parameters and gain were optimized from time resolution experiments. Typically, long integration time (Tg) is preferred with plasmas that have a long lifetime to maximize signal. In this work, 10 µs delay time, Td, 3 ms gate time, Tg, and a gain setting of 100 were found as optimum conditions for spectral emission measurements of tin by LIBS. A representative 10 shot accumulation spectra acquired from the tin hydrides, stannanes, by HG-LIBS system was given in Fig. 4. The peaks labeled between 260 and 330 nm (270.65 nm, 284.0 nm, 286.3 nm, 300.9 nm, 303.4 nm,

317.50 nm and 326.2 nm) correspond to neutral emission lines of Sn (I) for the experimental conditions selected and well consistent with NIST atomic spectral database.

For quantitative analysis of Sn in aqueous solutions, the resonance line at 284.0 nm was chosen. The spectral range between 330 and 580 nm was not represented in the figure, due to the presence of no valuable information regarding tin analysis. The second part of the spectrum between 580 and 665 nm, contains well resolved sodium doublet at 589.0 nm and 589.6 nm and hydrogen alpha line at 656.3 nm with relatively high signal strength. Excess amount of hydrogen is produced from the hydride generation reaction as well as from the decomposition of tin hydride in the plasma and also from the moisture content of the hydrides. Strong sodium lines indicate Na transport from the GLS to the plasma cell along with the hydrides.

3.2. Optimization of chemical parameters for HG-LIBS

Hydride generation conditions; like concentration, flow rate of reagents and carrier gas were optimized individually in trials in order to maximize signal to noise ratio for the determination of Sn in aqueous environments. During optimization of chemical parameters, instrumental parameters like laser energy, detector delay and gate times were kept fixed at optimum conditions as 150 mJ, 10 µs and 3 ms, respectively. Analytical signals were obtained from the average of minimum 5 replicate measurements, each constitute an accumulation of 10 laser shots of 150 mJ/pulse energy. In most of the optimization experiments, tin solutions with 5.0 mg/L concentration were used.

3.2.1. Effect of NaBH₄ and HCl concentration on HG-LIBS signal

In order to investigate the effect of reductant concentration on the efficiency of tin hydride generation for LIBS detection, NaBH₄ solutions between 0.1% and 10.0% (w/v) concentrations were prepared and made alkaline with 1.0% (w/v) NaOH for stability. As can be seen in Fig. 5(a) there is a marked increase in tin hydride production with increasing NaBH₄ concentration up to 2.0% and maximum LIBS signal was obtained at 5.0% NaBH₄ concentration. In cases where better detection limits are not required, 2.0% (w/v) NaBH₄ concentration with slightly lower sensitivity was employed in our experiments in order to reduce NaBH₄ consumption. The analyte and reductant flow rates of 2.5 and 5.0 mL/min were used, respectively. HCl concentration was kept at 1.0% and N₂, as a carrier gas, with a flow rate of 137 mL/min was used throughout the experiments.

The type and concentration of an acid has a considerable effect on the efficiency of hydride generation. Several reports [9] exist on the use of acetic, sulfuric, tartaric, hydrofluoric and nitric acid for a vigorous reaction with NaBH₄, but hydrochloric acid, HCl, is the most widely used one. Optimization of acid concentration was performed in the range of 0.1%–2.5% HCl (v/v) concentrations, while keeping NaBH₄ solution at 2.0% (w/v) concentration. As shown in Fig. 5(b), relative intensity of the LIBS signal has increased upto 1.0% HCl concentration and showed a little variation between 1.0% and 2.5% concentration. The maximum LIBS signal from 5.0 mg/L Sn solution at 284.0 nm was obtained from 2.0% HCl (v/v) concentration, however, 1.0% HCl concentration with a slightly lower sensitivity was selected as optimum acid concentration for hydride generation to avoid excessive acid consumption.

3.2.2. Effect of sample and carrier gas flow rates on HG-LIBS signal

Sample and reagents were introduced into the GLS continually by using a peristaltic pump. The flow rates of acidified sample and reductant were adjusted by selecting pump tubings of proper sizes, at a fixed pump rate. The effect of sample flow rate on Sn signal intensity was shown in Fig. 6(a). Typically, increasing sample flow rate increases tin signal intensity due to increased amount of analyte loading into the GLS. As optimized, reductant and acid concentrations

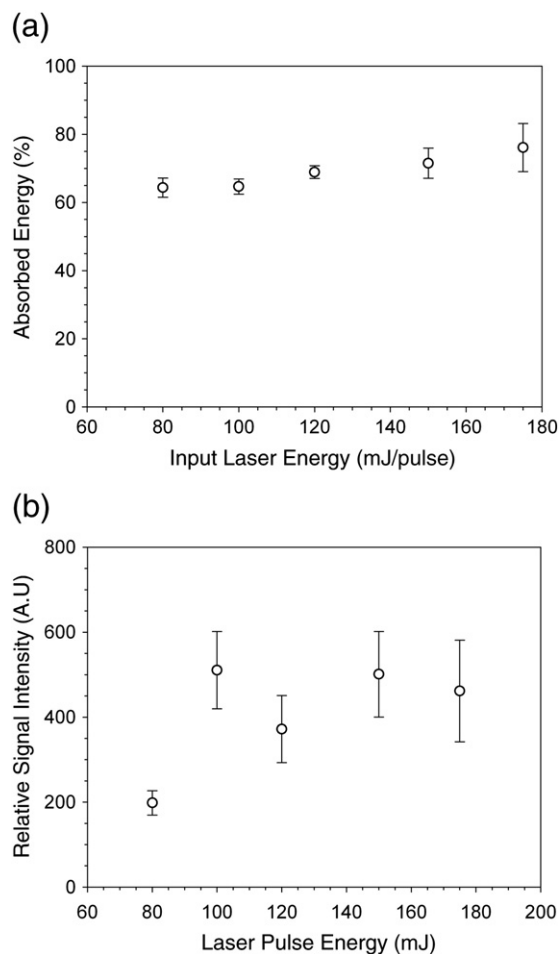


Fig. 3. (a) Absorbed energy by the Sn plasma with respect to input pulse energy. (b) Variation of Sn(I) line intensity at 284.0 nm as a function of laser pulse energy. Td: 10 µs, Tg: 3 ms, solution with 10.0 mg/L Sn concentration was used. Error bars represent variation in signal intensity for seven replicate measurements.

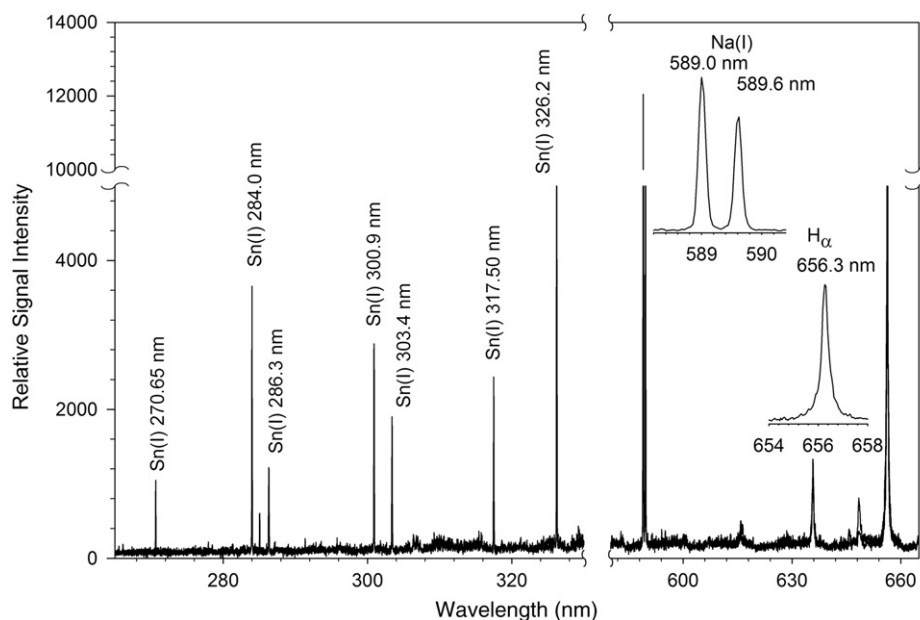


Fig. 4. Representative neutral atomic emission lines of Sn, Na and H_{α} obtained from HG-LIBS system by using 150 mJ laser pulses. Data correspond to the optimal time delay and gate width. Td: 10 μ s, Tg: 3 ms, was used. 10.0 mg/L Sn in 1.0% HCl, 2.0% (w/v) $NaBH_4$ in 1.0% (w/v) NaOH and 137 mL/min carrier gas (N_2) flow rate were utilized.

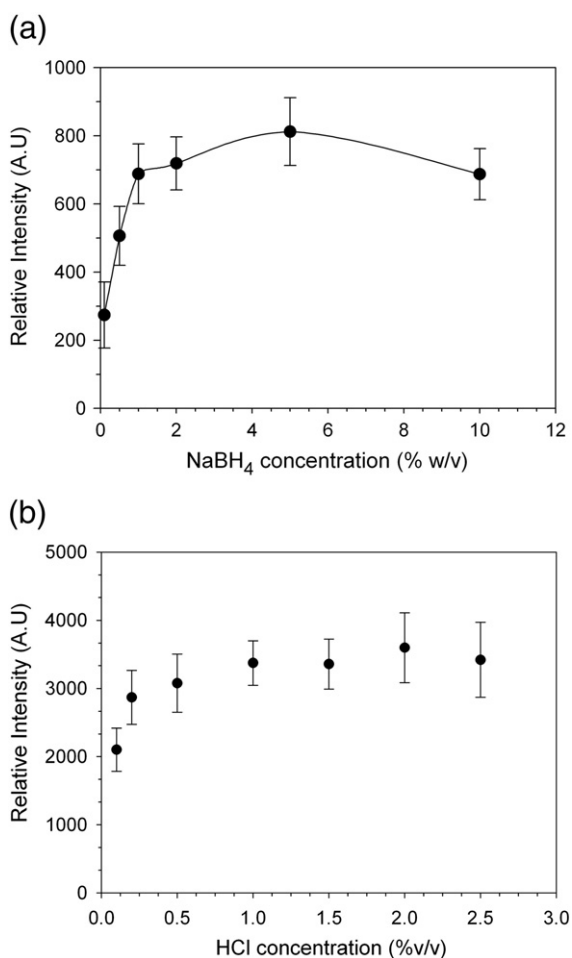


Fig. 5. Effect of concentration of $NaBH_4$ (a) and HCl (b) solution on Sn signal intensity. During the optimization of $NaBH_4$, 1.0% (v/v) HCl and during the optimization of HCl, 2.0% (w/v) $NaBH_4$ were used. LIBS signal was obtained from 5.0 mg/L Sn solution at 284.0 nm. 10 shot accumulation with Td: 10 μ s, Tg: 3 ms and laser energy of 150 mJ/pulse is used. N_2 was used as a carrier gas with a flow rate of 137 mL/min.

of 5.0% $NaBH_4$ and 1.0% HCl were used for the observation of the effect of sample and carrier gas flow rate on LIBS signal strength. There is a sharp increase in signal intensity when sample flow rate increases from 1.0 mL/min to 2.5 mL/min. Beyond this value, the variation in tin signal is not significant therefore 2.5 mL/min sample flow rate was selected as optimum.

In HG systems, the carrier gas, N_2 or Ar, is used to transport volatile hydrides from the GLS to the atomization cell. Therefore, the carrier gas flow rate is very critical in terms of efficient transportation and atomization conditions. The variation in signal intensity with respect to carrier gas flow rate for our experimental set-up is given in Fig. 6 (b). The optimum carrier gas flow rate was obtained at 137 mL/min N_2 . At flow rates less than this value the signal is low, which may be originating from the loss of the hydrides due to the condensation on inside walls of both the GLS and Teflon tubing that connects GLS to plasma cell.

At flow rates higher than 137 mL/min N_2 , signal intensity starts to decrease. This can be attributed to fast flushing of the tin hydrides by the N_2 gas from the sample cell so that the residence time of tin atoms decreases. Also, at high flow rates of the carrier gas, the ratio of the number of analyte atoms to the number of carrier gas atoms in the focal volume would have been decreased (dilution effect), which may result with reduced line intensities.

Plasma diagnostics in the presence of different background gases is an active area of research in LIBS. The type and amount of the background gas can have different effects on temperature, electron number density and excitation conditions of the plasma [33,38]. Singh et al. [33] have observed different temporal emission behaviours for As and Sn hydrides in the presence of N_2 and He environment. Laser-induced breakdown spectroscopic detection of chemical hydrides in the presence of different background gases needs to be studied in detail for quantitative analysis.

3.2.3. Efficiency of hydride generation

The hydride generation efficiency of HG-LIBS system under optimum chemical conditions was determined from the measurement of analyte concentration in the waste liquid by ICP-MS. It was found that higher than 99% of the analyte was recovered into the gaseous phase while lower than 1% of the analyte remained in the waste liquid.

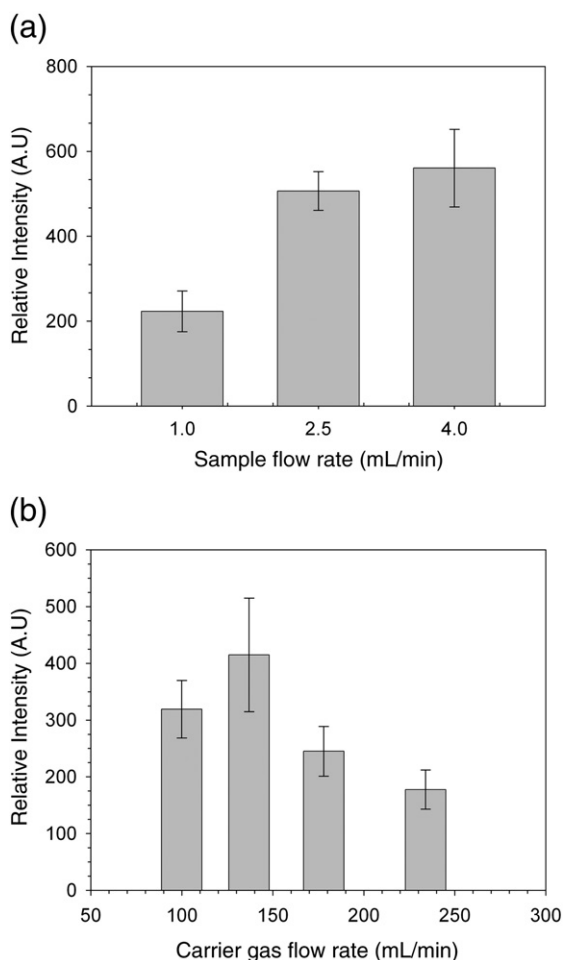


Fig. 6. Effect of sample flow rate (a) and carrier gas flow rate (b) on determination of tin by HG-LIBS. Accumulation of 10 laser shots, 150 mJ/pulse energy, Td: 10 μ s, Tg: 3 ms and 5.0 mg/L Sn solution in 1.0% (v/v) HCl were used. 5.0% (w/v) NaBH₄ in 1.0% (w/v) NaOH and carrier gas (N₂) flow rate of 137 mL/min were used.

3.3. Effect of using membrane drying unit, MDU, on Sn signal intensity

Removal of water content from the volatile hydrides is a common approach employed in HG sample introduction technique as it improves the sensitivity of the technique. Among several desolvation techniques [1], use of naphion membrane desolvating unit, MDU, for the removal of humidity is recently becoming more popular. In principle, a dry purge gas, N₂ or Ar flows over the exterior surface of the membrane tubing, while wet gas (hydrides in this case) flows in a

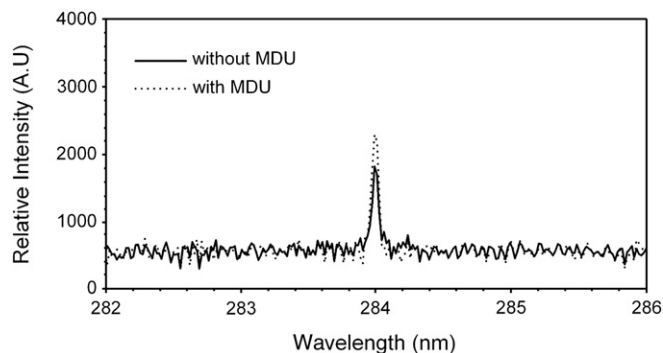


Fig. 7. The effect of membrane drying unit on Sn(I) signal intensity at 284.0 nm, under optimum hydride generation conditions. 30% enhancement in S/N was obtained when drying unit was used.

Table 2

Effect of using membrane desolvating unit, MDU, on LIBS signal.

	S/N*	% RSD	
		BG	Signal
Without dryer	24.37	22.98	43.29
With dryer	31.61	24.38	19.24
Enhancement	30%		

Data is from eight single laser shots of 150 mJ/pulse energy. Signal is defined as the peak area under 284.0 nm Sn(I) line minus the background intensity, BG. Noise was defined as three times the standard deviation of the background intensity.

counter-current direction inside the tubing (see Fig. 2). The water from the gaseous hydrides is extracted by the humidity gradient between the inside and outside of the tubing. We have used N₂ as a purge gas with flow rates less than the carrier gas flow rate. The effect of membrane drying unit on tin signal intensity was shown in Fig. 7 and also % RSD values of the analyte and the background signal with and without MDU were given in Table 2.

More than 50% decrease in RSD value of the signal was obtained with the use of a membrane desolvating unit while RSD of the background, BG, does not change much. This enhancement in RSD of the signal corresponds to 30% enhancement in signal to noise ratio. Data were obtained from eight single laser shots of 150 mJ/pulse energy. Signal is defined as the peak area under 284.0 nm Sn(I) line minus the background intensity. Noise was defined as three times the standard deviation of the background intensity.

3.4. Calibration graph for Sn

Under optimum conditions given in Table 1, a calibration graph was constructed for 284.0 nm neutral emission line of Sn(I) at various concentrations and presented in Fig. 8. Each point in the graph represents average peak area of seven sequential samplings for the concentration range of 1.0–75.0 mg/L tin. System has been washed between samplings of different concentrations with continuously flowing NaBH₄ and acid solutions until no tin signal was observed, in order to avoid contamination. As can be seen from the figure that, there is a linear increase in LIBS signal upto 20.0 mg/L tin concentration and a linear fit to the data passes from the origin with a regression constant of $R^2 = 0.9989$. After 20.0 mg/L, deviation from the linearity is observed. The regression constant decreases to $R^2 = 0.9843$ when data at 50.0 mg/L is included in regression analysis. This loss in sensitivity with increased concentration might be due to self absorption of the Sn(I) resonance line at 284.0 nm. However, after 50.0 mg/L concentration signal intensity drastically decreases. In LIBS measurements, the loss of sensitivity due to self absorbed lines

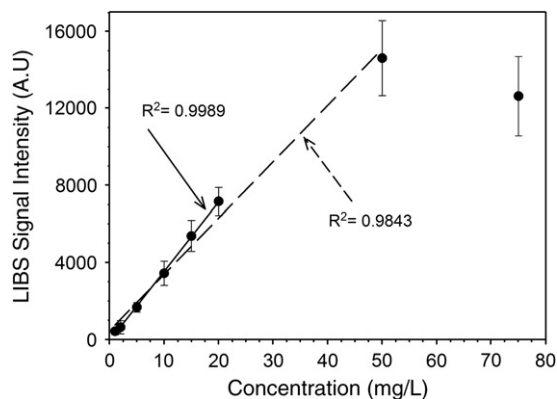


Fig. 8. Calibration graph for Sn(I) at 284.0 nm from chemically generated hydrides. Data represents average of seven replicate measurements each from the accumulation of 10 single laser shots. Td: 10 μ s, Tg: 3 ms, laser energy 150 mJ/pulse, 1.0% (v/v) HCl: 2.5 mL/min, and 5.0% (w/v) NaBH₄ in 1.0% NaOH: 5.0 mL/min were used.

Table 3

Recovery results from real water samples spiked with 10.0 mg/L Sn standard solution. Results are from the average of seven replicate measurements.

	% Recovery \pm SD
River water (SLRS-4)	91.4 \pm 10.0
Tap water (Urla municipal water)	94.1 \pm 16.3
Drinking water (spring water, Aydın)	96.4 \pm 12.1

generally exhibits a levelling off in signal strength rather than a drop down. Therefore, this drastic decrease in signal strength at relatively large concentrations may be attributed to the inefficiencies in hydride generation conditions. It appears that, chemical conditions of hydride generation, e.g. NaBH₄ and HCl concentrations, need to be reoptimized for samples with tin concentrations higher than 50.0 mg/L.

Based on 3 σ criterion, the detection limit (LOD) was determined as 0.3 mg/L. That corresponds to about 300 times enhancement in sensitivity compared to the literature data [31] that employs a common sample introduction method for LIBS analysis of Sn in aqueous samples.

3.5. Application to the real water samples

In order to test the applicability of HG-LIBS method to the quantitative determination of Sn in aqueous environments, real water samples ingested with standard Sn solution were analyzed. For this purpose, 10.0 mg/L Sn standard solutions were spiked into bottled water, tap water and river water (SLRS-4) and analyzed under optimized instrumental and chemical conditions. Results, listed in the Table 3, clearly indicate over 90% recoveries for all types of real water samples being 91.4%, 94.1% and 96.4% for river, tap and drinking water samples, respectively. Water samples were tested for Sn content by HG-LIBS system before spiking but no detectable Sn concentration was observed.

4. Conclusions

A continuous flow HG-LIBS system for the analysis of volatile hydride forming elements in aqueous environments has been designed, constructed and optimized. Compared to batch type systems this continuous flow system provides constant sample and reagent flow through the atomization cell, which in turn results with fairly constant LIBS signal, within shot to shot fluctuation range of the laser used. Although, the detection power and sensitivity of LIBS measurements are still at low levels compared to other atomic spectrometric methods that use hydride generation as a sample introduction technique, however, the analytical results obtained from HG-LIBS experiments so far are found to be suitable for the analysis of Sn in aqueous environments in the form of tin (IV) hydride, stannane, SnH₄. In order to obtain optimum hydride yield and reproducible LIBS signal, reaction conditions for Sn hydride were optimized. Optimum NaBH₄ and HCl concentrations were determined as 2.0% (w/v) and 1.0% (v/v) at a flow rate of 5.0 mL/min and 2.5 mL/min, respectively. A detection limit of 0.3 mg/L, based on three times the standard deviation of the background, has been measured from standard Sn samples, by utilizing neutral tin, Sn(I), emission line at 284.0 nm. Moreover, HG-LIBS sensitivity can be enhanced more by using element specific single channel detectors, like PMT.

Use of the membrane dryer between the GLS and the sample cell has provided 30% enhancement in S/N. Recoveries in the range of 91–96% were obtained from spiking experiments to real water samples.

Our future work will be on the application of the technique for the determination of other volatile hydride forming elements that pose a great danger to aquatic systems such as As, Cd and Pb at μ g/L levels of concentration.

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