

Laser induced fluorescence and laser absorption measurements for the diagnostics of hydride atomizers

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Abstract: Laser-induced fluorescence (LIF) was used for measurement of absolute concentration of various radical species and free atoms of metals in plasma and flame environments. The obtained concentration values were compared with absorption measurements and a good agreement was observed. Both techniques contributed to better understanding of the processes taking place in hydride atomizers, i.e. the devices used in analytical chemistry for the determination of elements at trace concentration levels.

Keywords: laser-based diagnostics, LIF, absorption, plasma, DBD, atomizers.

1. Introduction

Plasma, flames and other reactive environments are sources of reactive radical species, which are responsible for number of chemical reactions taking place both in the volume of plasma (or flame etc.) and at solid surfaces exposed to plasma. Radical species are key reactants in processes like combustion, thin film deposition, decomposition of volatile compounds etc. However, detection of radicals and, namely, space- and time-resolved measurement of their concentration are often challenging: In most of cases, radicals are electrically neutral, which excludes the possibility to detect them by standard electric methods. The vast majority of radicals is usually in the ground (or metastable) state, which makes their measurement by spontaneous emission spectrometry difficult. Finally, their life-time is usually short, which excludes their detection by most of ex situ methods.

However, spectroscopic detection of reactive radical species can be realized by means of absorption or photoluminescence methods. Simple absorption is a straightforward method for measurement of absolute concentration values, but it lacks of spatial resolution and high sensitivity. High sensitivity and spatial resolution can be simply achieved by fluorescence methods, namely by laser induced fluorescence (LIF), but the calculation of absolute concentration based on LIF measurements may be complicated, because the determination of the fluorescence quantum yield is in number of cases difficult [1,2]. Consequently, it is desirable to verify the results of fluorescence measurements by other methods, e.g. by absorption. This contribution presents LIF measurement of various radical species in two types of so-called (hydride) atomizers, which are based on plasma of a dielectric-barrier discharge (DBD) or on miniature flame in a heated silica tube.

Hydride atomizers are routinely used in analytical spectroscopy for ultratrace determination of elements such as As, Se, Pb, Sn, Bi, Sb or Te by atomic absorption or fluorescence spectrometry. Their role is to decompose (atomize) volatile analyte hydrides efficiently since exclusively their free atoms can be detected by absorption or fluorescence. Usually, the investigated analyte is transformed from a liquid sample solution into a volatile compound in a (hydride) generator placed outside the

atomizer. The trace amount of volatile hydride is then supplied to the atomizer together with working gas (Ar), hydrogen and, eventually, oxygen or air. In the atomizer, hydrides are decomposed and the resulting free analyte atoms are detected by absorption or fluorescence. This method enables to detect elements with concentrations at the ng/ml levels. The knowledge of the spatial distribution of free analyte atoms in the atomizer is important for understanding and further improvement of atomizers.

2. Experimental

Measurements were realized in a DBD atomizer [3-5] and in a heated quartz tube atomizer (QTA) [6]. The DBD atomizer is based on a volume DBD ignited inside a rectangular-shaped silica optical arm (with inner dimensions 7 mm X 3 mm X 75 mm) with two planar electrodes placed on outer surfaces of the largest sides of the atomizer, see Fig. 1. The electrodes were supplied with sinusoidal voltage with a frequency close to 28 kHz. A smaller silica tube with inner diameter 2 mm is welded to the centre of the optical arm and serves as an inlet of the gas mixtures from the hydride generator to the optical arm.

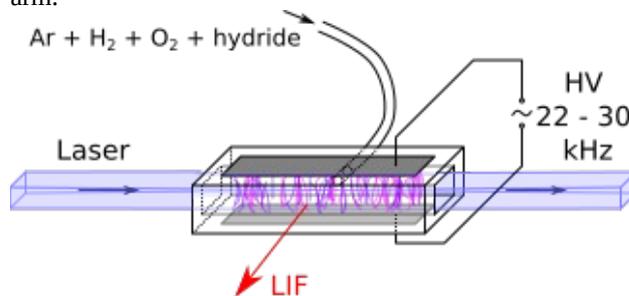


Fig. 1. Schema of the DBD atomizer.

QTA is also a T-shaped atomizer composed of an optical and an inlet arm. In this case, the optical arm is a heated cylindrical silica tube. No discharge is generated in the QTA. The decomposition of hydrides in QTA is provided by atomic hydrogen radicals [7] produced in the "microflames" arising from a reaction between molecular hydrogen and oxygen in the optical arm of QTA heated to 900 °C. The design of QTA used in this work made

possible to supply oxygen or air to its optical arm not only through the inlet arm, but also through several holes in the wall of the optical arm [8,9].

The laser setup is shown in the Fig. 2. A three-component laser system consisting of a Q-switched pumping laser (Quanta-Ray PRO-270-30), a dye laser (Sirah) and a frequency doubling / mixing / tripling unit was used to produce approx. 8 ns long laser pulses with a wavelength between 204 and 290 nm. The laser beam was sent through the atomizers along the axis of the optical arm. The fluorescence signal was detected by an ICCD camera. Scattered laser and spontaneous discharge/own radiation were blocked by an interference filter placed in front of the camera.

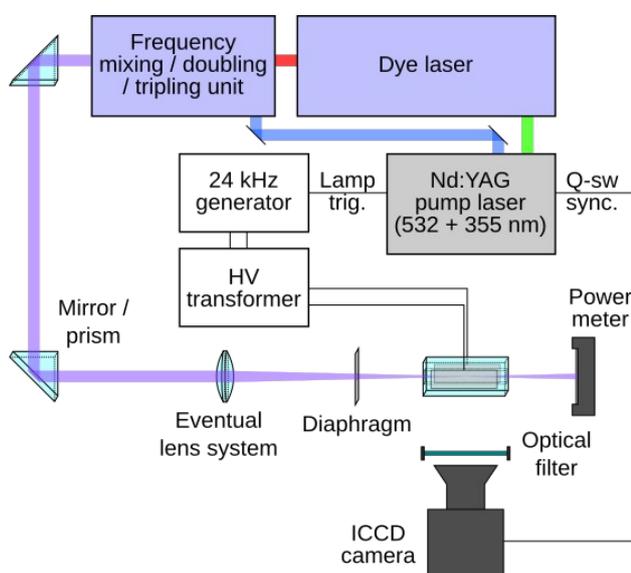


Fig. 2. The diagnostics setup.

3. Results

3.1 LIF method, absolute concentration values and their comparison with absorption

For LIF measurement and evaluation, the methods already described in [10-13] were used. Partially saturated regime was used, which enables to increase the signal-to-noise ratio with respect to the widely used linear regime, that is characteristic for low laser pulse energies. Calibration of LIF was based on Rayleigh scattering of laser on air [14].

Several species (e.g. Te, Bi, Pb, Sn, H, O, OH) were detected in various atomizers by LIF. As an example, Figure 3 shows obtained values of bismuth concentration in the QTA as a function of Ar (working gas) flow-rate and position in the atomizer. The concentration was in the order 10^{17} m^{-3} , which indicates that bismuth hydride is fully decomposed (atomized) in the QTA.

The next figure 4 shows the dependence of Bi concentration on the amount of air that was added to the gas mixture. This figure demonstrates that change of the reducing hydrogen-rich environment to oxidizing environment leads to a decrease of Bi free atom concentration. This result is in agreement with findings discussed in the next section 3.2.

Finally, the concentration profiles obtained by LIF were used for prediction of the absorption of laser pulses in both the atomizers (DBD, QTA). For used experimental conditions the predicted values of absorption varied between 10 % and 50 %, depending on atomizer type, used analyte (Bi, Te), analyte concentration in the standard solution fed to the hydride generator and atomization conditions. These values were compared with real measured absorption values and the differences varied between only 8 % and 15 %, which demonstrates a high reliability of LIF measurements, when a careful measurement and data evaluation is realized.

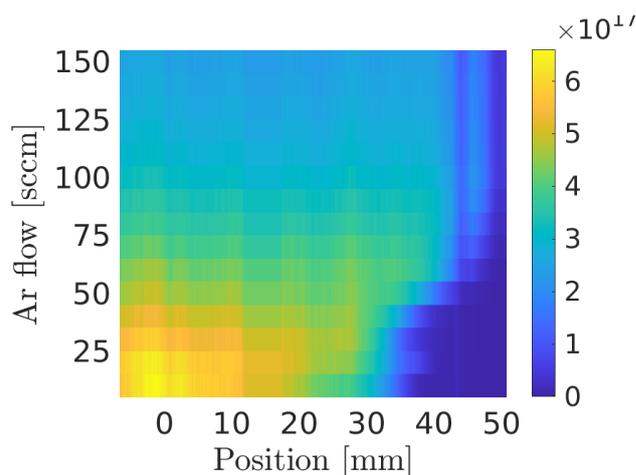


Fig. 3. Concentration of Bi [10^{17} m^{-3}] in the atomizer (QTA). Zero position is the position of the inlet of gases, that was localized in the center of the optical arm.

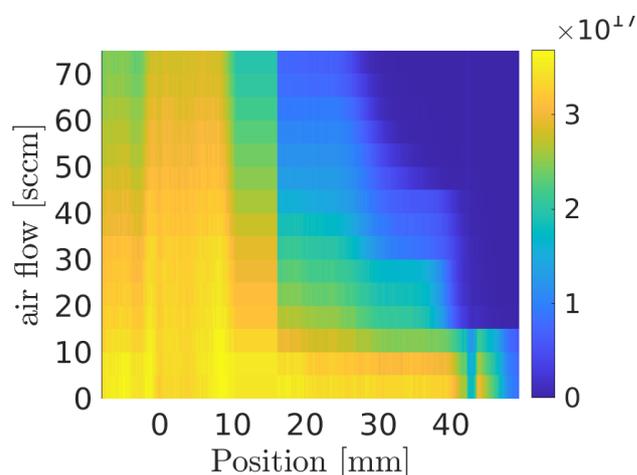


Fig. 4. Concentration of Bi [10^{17} m^{-3}] in the atomizer (QTA) as a function of the flow rate of air.

3.2 Analyte deposition on atomizer wall

The possibility to detect free analyte atoms was used also for study of the deposition of analyte free atoms on the walls of the atomizers. We can demonstrate the trapping of analyte on the example of LIF of Bi measured in the QTA. We observed that sufficient addition of oxygen causes practically instantaneous vanishing of the LIF signal in the regions exposed to oxygen. This is shown in the Fig. 5, where fluorescence signal of Bi was

lost in regions on the right side from the first oxygen supply localized at the position 14 mm. (Oxygen was supplied at the beginning of measurements till 3 s and then in periods 14 s – 33 s and 48 s - 65 s.) However, when the flow of oxygen was stopped, the signal appeared again and its intensity was significantly increased for several seconds (Fig. 5). This observation confirms that:

- Bi atoms were not lost from the atomizer, but they were deposited on atomizer walls.
- Bi atoms can be desorbed from atomizer walls in the reducing environment rich on hydrogen and poor in oxygen.

Due to these two facts, analyte can be practically preconcentrated: By means of oxygen, analyte can be trapped on atomizer walls. After sufficient feeding period the analyte can be evaporized almost all at once, which increases both analyte concentration in the gas phase and intensity of measured signal. As a result, higher sensitivity of the analytical method and lower limit of detection can be reached.

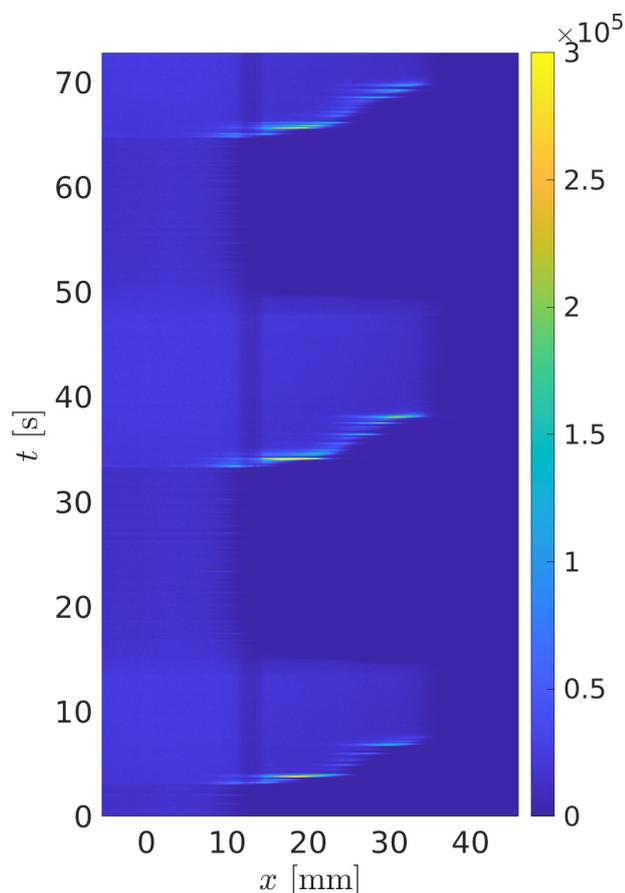


Fig. 5. LIF signal of Bi during a period, when the additional flow of oxygen was alternately switched off and on. Oxygen was supplied in positions 14 mm, 30 and 44 mm.

4. Acknowledgement

This research has been supported by the Czech Science Foundation under Contract 23-05974K and by the Project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

5. References

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