

Atomizers of tin hydride studied by laser-induced fluorescence

M. Mrkvičková^{1(*)}, P. Dvořák¹, B. Štádlerová², J. Kratzer²

¹ *Department of Plasma Physics and Technology, Faculty of Science, Masaryk University, Brno, Czechia*

² *Institute of Analytical Chemistry of the Czech Academy of Sciences, Brno, Czechia*

(*) mrkm@mail.muni.cz

Hydride atomizers play a crucial role in analytical chemistry by allowing for ultra-trace level determinations of elements in solutions. In particular, they are essential components in the hydride generation atomic absorption or fluorescence spectrometry (HG-AAS or HG-AFS) method [1]. This method boasts impressive detection capabilities for elements like As, Se, Pb, Sn, Bi, Sb, or Te, reaching sensitivities of 100 ng l^{-1} for AAS and even 10 ng l^{-1} for AFS, respectively. The process involves the reduction of the analyte through a reaction with NaBH_4 , producing the corresponding hydride. Under optimized conditions, the generation efficiency approaches nearly 100% for common hydride-forming elements. Subsequently, the hydride is atomized to liberate free analyte atoms. This is accomplished by the device known as the "atomizer". Finally, the free atoms are detected using atomic or fluorescence spectroscopy.

Various atomizer types have been developed, such as those based on flames (diffusion flame atomizer), high-temperature tubes (quartz-tube-atomizer) or electrical discharges (DBD atomizer). Each of these atomizers is suited for different analyte atoms. While the quartz-tube-atomizer and the DBD atomizer yielded comparable detections for tellurium atoms, the DBD setup performed significantly poorer in the case of tin hydride (stannane) decomposition [2] without a clear explanation for this discrepancy.

Our study aims to investigate the efficacy of stannane molecule decomposition into free atoms using two specific atomizer types: diffusion flame atomizer and DBD atomizer. The diffusion flame is ignited at the end of silica tube (inner diameter 6 mm) in the mixture of argon, hydrogen, and stannane flowing into the surrounding air. The DBD atomizer is based on a volume dielectric barrier discharge ignited inside a silica optical arm (inner dimensions $8 \text{ mm} \times 3 \text{ mm} \times 75 \text{ mm}$) with two planar electrodes on its outer surfaces. Two power-supply regimes are tested: sinusoidal voltage of frequency 33 kHz and peak-to-peak amplitude of 10 kV, and rectangular voltage with a frequency of 29 kHz and peak-to-peak amplitude of 7 kV (thus, the effective voltage was similar in both cases).

The laser-induced fluorescence method (LIF) was employed to analyze the spatial distribution of tin atom concentrations inside atomizers under varying conditions. Tin atoms were excited by laser pulses with a wavelength 224.6 nm, the consequent fluorescence radiation of wavelength 365.6 nm was observed by ICCD camera. In the case of the diffusion flame atomizer, the laser beam was extended by couple of lenses to a thin sheet, facilitating comprehensive observation of the entire flame height under all operational conditions. To enhance the signal-to-noise ratio, a partially saturated LIF technique [3] was implemented. Additionally, calibration of concentration values was achieved through the absorption of laser beam energy.

An illustrative example of the fluorescence signal obtained from the diffusion flame atomizer is provided in Figure 1. Two feeding conditions are compared: a) 180 sccm Ar + 120 sccm H_2 + tin hydride, and b) 700 sccm Ar + 300 sccm H_2 + tin hydride, mimicking thus typical atomization conditions employed in AAS and AFS, respectively. Lower flow rates resulted in a 5 mm high active flame with tin atom concentration centered in the flame core, while higher flow rates extended the active flame to 20 mm, redistributing tin atoms towards the flame tip and edges.

The spatial maps of atomic tin concentrations in both atomizer types under various conditions will be presented. As the atomisation is supposed to be controlled by reactions of stannane with atomic hydrogen [4], the LIF results will be accompanied by information on the spatial distribution of hydrogen atoms measured by the TALIF method. In the case of the DBD atomizer, the electric field evolution in the two power supply regimes will be determined by the electric field induced second harmonic generation (EFISH) method. Based on all the results, we will further discuss potential strategies for improving various atomizer efficiencies.

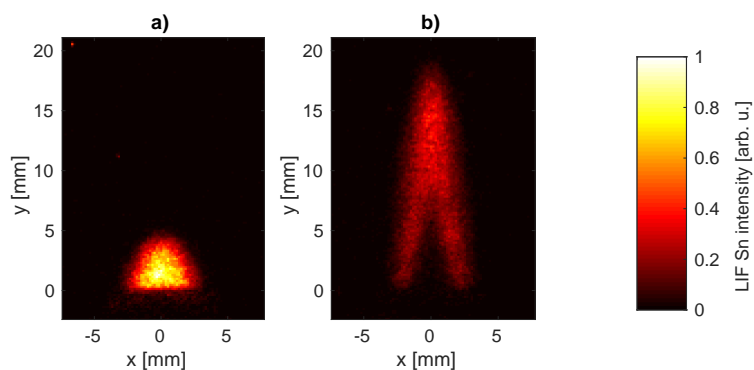


Fig. 1: Examples of LIF Sn signal captured in the diffusion flame atomizer fed by a) 180 sccm Ar + 120 sccm H₂ + tin hydride, and b) 700 sccm Ar + 300 sccm H₂ + tin hydride. In both cases, the tin hydride was generated from a sample containing 100 ng ml⁻¹ Sn.

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References

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