LIF study of hydride dissociation in electric discharges

P. Dvořák(*)[1], M. Mrkvičková[1], W. Khan[1], N. Bolouki[1], T. Medek[1], A. Obrusník[1], J. Kratzer[2], M. Svoboda[2], J. Dědina[2]

[1] *Dep. of Plasma Physics and Technology, Faculty of Science, Masaryk University, Brno, Czech Republic*

[2] *The Czech Academy of Sciences, Institute of Analytical Chemistry, Brno, Czech Republic*

(*) pdvorak@physics.muni.cz

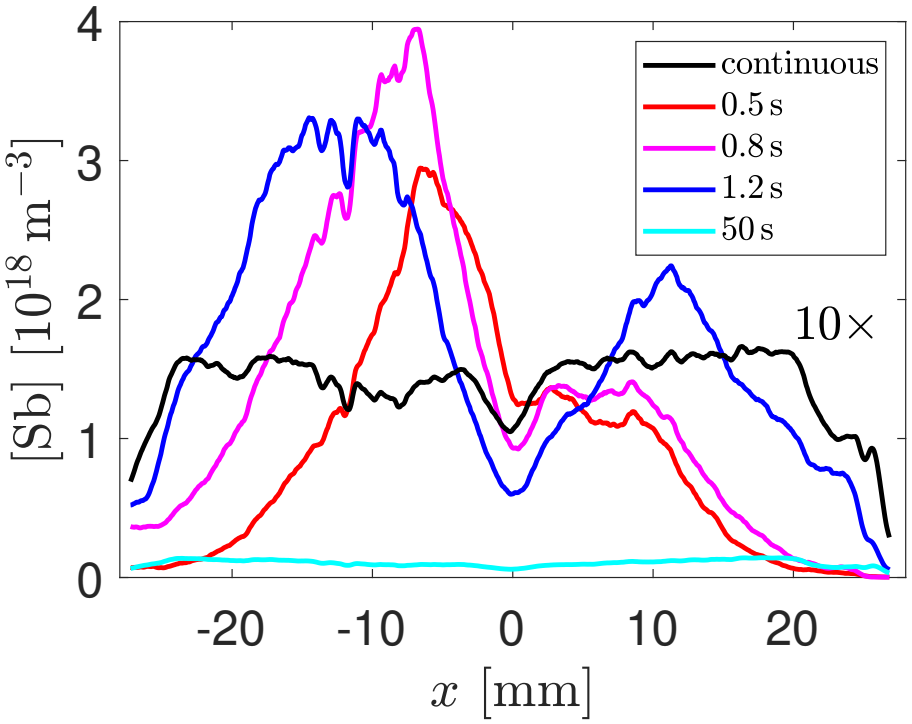
The fact that plasma is able to dissociate number of molecules is the basis for number of plasma applications including applications in analytical chemistry, where plasma is used for the dissociation of volatile compounds, frequently hydrides, which are used as carrier molecules for number of toxic, hazardous or biogenic elements [1]. Recently, dielectric barrier discharges (DBDs) have been systematically studied as atomizers, i.e. as a tool for the decomposition of hydrides or other volatile molecules [2]. The situation in DBDs is relatively complicated, because the volume dissociation of hydrides combines with surface reactions on walls, which can lead to unwanted losses of analyte atoms or be used for in-situ preconcentration of analytes and to improve the detection limit of the analytical methods.

Our work is a systematic (TA)LIF study of reactive species in various atomizers, including both the dominant radicals originating from the main plasma gases (i.e. atomic hydrogen [3, 4], atomic oxygen [5], OH radicals) and various free analyte atoms (Pb, Te, Bi, Se, Sn, Ge, Sb) [6, 7]. In order to increase the LIF signal-to-noise ratio, we developed a LIF method based on partially saturated fluorescence [8] and verified it by comparison with absorption measurements. The laser-based diagnostics on discharge-based atomizers were supplemented by E-FISH measurements of the electric field in the discharge. Experimental results were complemented by a numerical model of the plasma chemistry and gas flow in the atomizers.

Regarding the atomization mechanisms, we confirmed the theory that the decomposition of hydrides in both plasma and flame atomizers is based on reactions with atomic hydrogen, we revealed differences in spatial distribution of various analytes demonstrating the important role of the surface reactions, explained the difference of the performance of various atomizers, observed the preconcentration of analyte atoms on the wall and explained why a small (i.e. significantly substoichiometric) amount of oxygen manages to initiate the preconcentration on walls.

As an example of LIF measurements, the fig. 1 shows the distribution of free Sb atoms in a DBD atomizer, when stibine (SbH_3) from a 1 ng/l-solution was supplied to the plasma together with Ar and H_2. The results obtained with a continuous supply of SbH_3 (black curve) reveal a nearly homogeneous distribution of free Sb atoms through the whole active discharge (-25 to +25 mm). The homogeneous distribution of Sb atoms through the whole reactor and the relatively high Sb concentration demonstrate a good performance of the DBD for atomization of SbH_3.

The colour curves show the increase of Sb concentration (by more than an order of magnitude) which was reached by the Sb preconcentration on walls and which had a character of a wave travelling from the discharge center towards its edges. The strong increase of Sb concentration demonstrate the possibility to control the surface reactions and use them for analyte preconcentration and improvement of the detection limit of studied species in DBD-based atomizers.



Spatial profile of the concentration of free Sb atoms in a DBD atomizer. The black curve (10-times increased) shows the situation when SbH_3 is continuously fed to the DBD. The colour curves show Sb distribution in various moments of the release process after the pre-concentration of Sb on the reactor walls.

[1] J. Dědina, D.L. Tsalev 1995 *Wiley and Sons Inc.* Hydride generation atomic absorption spectrometry
[2] S. Brandt et al. *Spectrochim Acta B* **126** (2016) 6.
[3] P. Dvořák et al. *Chemical Science* **10** (2019) 3643.
[4] P. Dvořák et al. *Plasma Sources Sci. Technol.* **26** (2017) 085002.
[5] P. Dvořák et al. *Plasma Sources Sci. Technol.* **26** (2017) 065020.
[6] K. Bufková et al. *Spectrochim Acta B* **171** (2020) 105947.
[7] M. Albrecht et al. *Spectrochim Acta B* **166** (2020) 105819.
[8] M. Mrkvičková et al. *Combustion and Flame* **241** (2022) 112100.

Acknowledgement: This research has been supported by the Czech Science Foundation under Contract 23-05974K, by the Project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic and by the Czech Academy of Sciences (Institutional research plan RVO: 68081715).