Analysis by diode laser absorption spectroscopy in a linear dielectric barrier discharge

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Abstract: The diagnostic as well as the application of a miniaturized dielectric barrier discharge as detector for analytical spectrometry were investigated using diode laser absorption spectrometry of the excited species produced in the plasma.

OCIS codes: (300.1030) Spectroscopy, absorption; (300.6260) Spectroscopy, diode lasers

1. Introduction

Recently we reported on the detection of halogenated hydrocarbons by diode laser atomic absorption spectrometry (DLAAS) in a linear dielectric barrier discharge (DBD) at reduced pressure [1]. It was shown that introduced halogenated molecules were completely dissociated and the detection limits of the excited chlorine and fluorine atoms were similar to those obtained in a microwave discharge [2] even if the average power of the DBD is much smaller (< 1 W). In order to improve the upper results the plasma parameters of the miniaturized discharge were studied by a diagnostic method based on spatial and temporal resolved diode laser absorption measurements of excited atoms in the discharge. The determination of the gas temperature and electron density might help to understand the mechanisms which leads to a complete dissociation of the introduced molecules and to improve the detection of analytes.

2. Experimental arrangement

The linear dielectric barrier discharge consists of two parallel aluminum electrodes (50 mm length, 0.7 mm width) covered by a glass type dielectric (ε_r= 6) layer of 20 µm with an interelectrodic space of 1 mm. The discharge is operating at reduced pressure (10 - 100 mbar) in argon as well as helium with a gas flow of 10 - 1000 ml/min. The applied voltage has a rectangular shape with a frequency of 5 - 20 kHz and an amplitude of 750 Vpp. The discharge shows a transient behavior. The halfwidth of the current peak is about 10 µs and the discharge is ignited over the whole length of the electrodes.

In order to explain the analytical results obtained for the detection of halogens, we proposed a method of investigation that can give detailed information about the production of excited atoms between the electrodes. The experimental arrangement for diode laser absorption measurement with a high spatial and temporal resolution is shown in Fig.1.

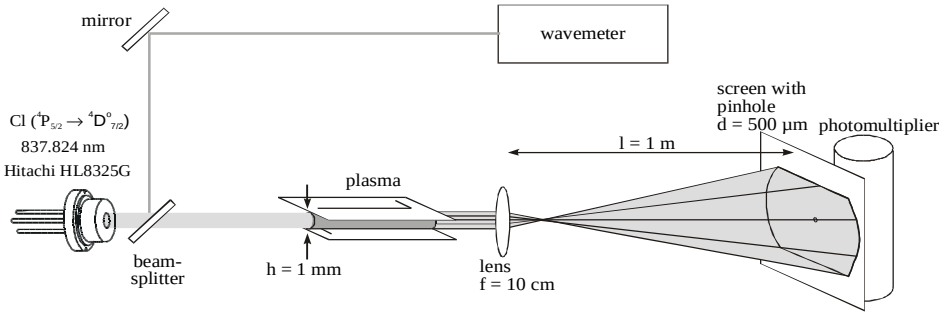

Fig. 1. Schematic view of the experimental arrangement with high spatial resolution

The collimated beam of a laser diode is passing the discharge channel and is imaged by a lens (f = 16 cm) on a screen at a distance of 1 m. A pinhole of 200 µm selects a small part of the transmitted laser beam representing a limited area in the plasma. A fast Hamamatsu photomultiplier placed very close to the pinhole is used as a detector. Moving the pinhole from the cathode to the anode side the distribution of excited species was investigated with a spatial resolution of about 50 µm. The absorption signals were measured on the whole period of the applied voltage in order to study also the temporal behavior of the excited species.

3. Results and discussion

3. 1. Absorption measurements in the buffer gas

Plasma diagnostic measurements for the determination of the excited atom density, gas temperature and electron density were performed studying the argon atoms excited on the metastable ($1s_5 \rightarrow 2p_8$, 801.699 nm) and resonance ($1s_4 \rightarrow 2p_6$, 800.836 nm) states. The highest concentration of excited argon atoms was always near the temporary cathode around 12 µs after the start of the current pulse. The absolute density of both resonance and metastable states were 2 x 10^{12} atoms/cm³ and 10^{13} atoms/cm³, respectively.

The gas temperature and the electron density were calculated from the absorption line profiles of the resonance transition taking into account all significant broadening mechanisms (Doppler-, pressure- [3] and Stark-broadening [4]). At the temporal maximum of the current peak the gas temperature reaches a maximum value of around 1000 K and the electron density is higher than 10^{15} /cm³ at the spatial maximum of the excited atom density, in the vicinity of the temporal cathode. During the remaining time of the discharge cycle and in other positions the gas temperature is close to room temperature and the electron density is much lower and cannot be calculated with the proposed method. There is complete dissociation in this very thin layer of high electron density.

3. 2. Measurements on halogenated hydrocarbons

Taking into account the spatial distribution of excited argon atoms it is expected to improve the detection of Cl atoms if the measurements are restricted to the volume of high atom density. The distribution of excited Cl atoms on the metastable ($^4P_{5/2}$) level was measured in Ar and He with an admixture of 150 ppm CCl_2F_2 by measurments of the 837.824 nm line.

Fig. 2 presents the spatial and temporal distribution of excited Cl atoms for one period of the applied voltage in argon and helium. The flow rate was 200 ml/min and the pressure 20 and 30 mbar, respectively.

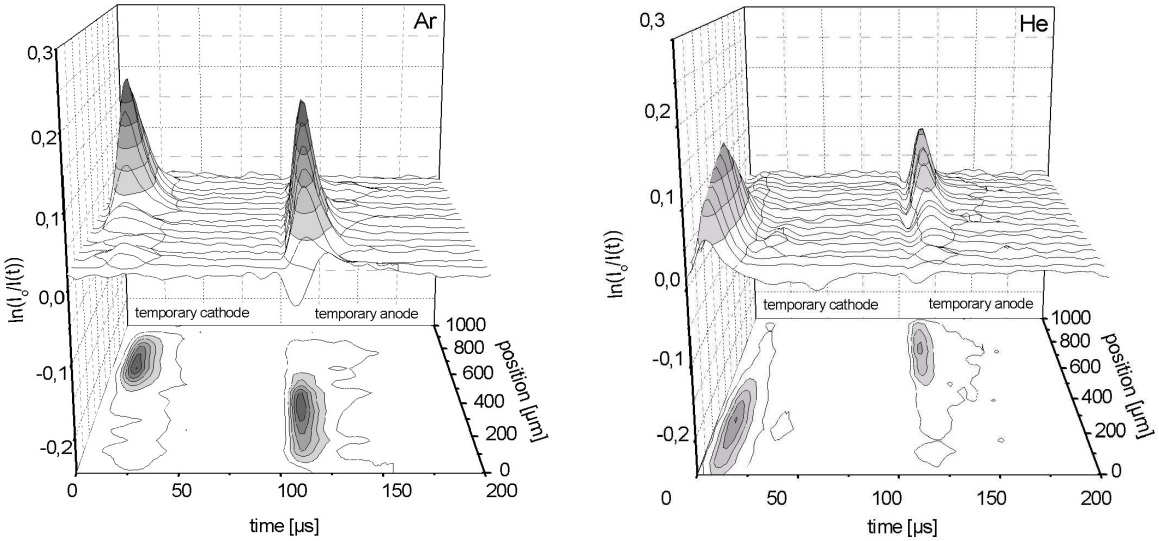

Fig. 2. Spatial distribution of excited Cl atoms in argon (left) and helium (right)

At low pressure the maximum density of excited Cl atoms in an argon discharge is close to the temporary cathode and spatially narrow, similar to the results obtained by the measurements of excited Ar atoms. In helium the distribution is broader and the highest excitation processes are taking place in between the middle of the discharge and the temporary anode. With the increase of the pressure, the maximum starts to move in the direction of the cathode. Also the relative density of excited Cl atoms is smaller in helium than in argon. This different spatial distributions of excited atoms can mainly be explained by the presence of electrons. The electron density in a He plasma is smaller than in an Ar plasma at the same operating conditions and as a consequence the probability of electron collisions in He is less. The position of the maximum density of the excited Cl atoms in these two buffer gases is determined by the mean free path of the electrons which is in argon three times smaller than in helium [5]. Electrons produced close to the cathode are moving further in helium than in an argon discharge.

Taking into account the obtained results, the absorption signal of Cl excited atoms was measured only in the plasma volume at 100 µm from the cathode in dependence on CCl_2F_2 concentration. In Fig. 3 the calibration curve of CCl_2F_2 in argon in comparison with the former calibration curve obtained measuring in the whole plasma volume is shown. The absorption was measured by a phase sensitive detection using the plasma modulation of the DBD. The signal dependence on concentration is also linear and the restriction of the absorption to the volume with the highest atom density increases the value of absorption by one order of magnitude. The detection limit calculated with the 3σ - criterion without any spatial resolution was about 5 ppb and in the new conditions this can be one order of magnitude better using a low noise detector.

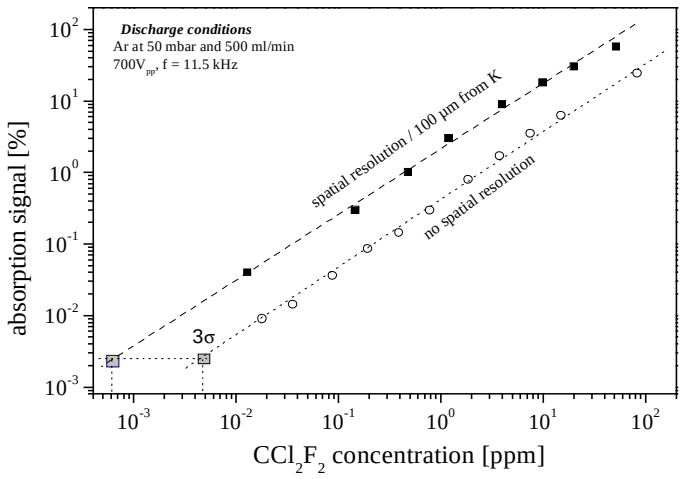

Fig. 3. Detection of CCl_2F_2 by the absorption of Cl atoms with and without spatial resolution

4. Concluding remarks

The experimental method described to study the distribution of excited atoms by diode laser spectroscopy with a high spatial resolution enable us to study the plasma parameters and to improve the detection limit of analyte by measuring only in the plasma volume containing the maximum density of excited species. The results explain the reasons for the good applicability - complete dissociation and low detection limits - of the DBD in analytical systems. Experiments applying this discharge as a selective detector for gas chromatography are under way in our laboratory.

5. References

[1] M. Miclea, K. Kunze, G. Musa, J. Franzke and K. Niemax, "The dielectric barrier discharge - a powerful microchip plasma for diode laser spectrometry", Spectrochim. Acta Part B **56,** 37-43 (2001).

[2] A. Zybin, C. Schnürer-Patschan and K. Niemax, "Wavelength modulation diode laser atomic absorption spectrometry in modulated low pressure helium plasmas for element-selective detection in gas-chromatography", J. Anal. At. Spectrometry **10,** 563-567 (1995).

[3] D.P. Aeschliman, R.A. Hill and D.L. Evans, " Collisional broadening and shift of neutral argon spectral lines", Phys. Rev. A **14,** 1421-27 (1976).

[4] H. Griem, *Plasma Spectroscopy* (McGraw-Hill, New York, 1964)

[5] A. von Engel, *Ionized gases* (Oxford University Press, 1975)