The microhollow cathode discharge as analytical plasma: diagnostics, applications and limitations

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In the last years, the interest in developing miniaturized discharges increased considerably due to advantages such as: low power consumption, high power densities, relatively high electron densities and temperatures. There are already more than 50 papers published in the last years. The microplasmas are applied in surface modification, as excimer radiation generators, for sterilization in medicine, as ionization source for ion mobility spectrometry or as excitation and ionization source in emission and mass spectrometry. In analytical spectrometry the interest in microplasmas is due to the so-called ‚lab on a chip‘ concept [1], where they are integrated as spectroscopic detection units.

If large sized plasmas are scaled to small dimensions the similarity laws are working bu due to the limited size of the discharges, the loss mechanisms are much different compared to macroplasmas. The diffusion to the wall outranges all losses. This leads on one hand to relative high electron temperature in this kind of discharges and on the other hand to a pronounced heating of the wall. This energy has to be removed either by high gas flows or by additional cooling systems.

This work is an overview about what can be done with miniaturized plasmas, from the fundamental investigations to applications. The microhollow cathode discharge will be presented in detail bu correlations with other miniaturized discharges will be also performed. Two aspects will be emphasized: first, the diagnostics of the microhollow cathode discharge at high pressure and then the application of this plasma in analytical spectrometry for the analysis of gaseous and volatile organic halogens.

The microhollow cathode discharge (MHCD) is the miniaturized version of the classical hollow cathode discharge [2]. It consists of two metallic layers with an insulator in between. Through this sandwich a hole is drilled with dimensions in the 100-300 µm allowing operation at atmospheric pressure in noble gases or gas mixtures. In comparison with some other d.c. plasmas, it has the advantage of enhanced electron density and ionization capability due to the pendulum of electrons in the hole of the structure.

As diagnostic tool for the determination of the plasma parameters, optical measurements in particular emission and absorption spectroscopy were performed. These methods are non-invasive and easier to apply than others such as laser induced fluorescence or Thomson scattering. Absorption measurements with diode lasers allow the determination of plasma parameters, such as spatial distribution of excited species, gas temperature and electron density Emission spectroscopy offers the possibility to detect several transitions simultaneously, while high resolution emission spectrometry allows line profile analysis. The intrinsic parameters, electron density and gas temperature, were determined by the examination of the absorpti line profiles, investigating the corresponding linewidths and lineshifts. The MHCD was operated in Ar as well as in He in the pressure range from 200 mbar to 1000 mbar. A few transitions from metastable and resonance levels (801.699 nm, 800.838 nm, 811.755 nm) were used in Ar while in He only the 667.997 nm transition can be studied with fundamental wavelength of laser diodes. It has to be mentioned that line profile analysis by diode lasers at

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high pressure is a challenging task due to the very broad absorption. In addition to the Doppler broadening, Stark broadening contributes to the line profile. Therefore, a new technique will be presented based on line width and shift measurements. The procedure for the determination of electron density and gas temperature in Ar delivers good results. The same model applied to the He plasma reveals data with large uncertainty since the shifts and widths due to Stark broadening are small and could hardly be resolved. The experiments were performed besides absorption spectroscopy also with high resolution emission spectroscopy. In the case of the He plasma, the collisiona radiative model (CRM) developed in [3] was applied for the determination of electron density and electron temperature in the plasma. The high resolution emission line profiles were used for the evaluation of the gas temperature. We obtained electron densities at atmospheric pressure of ^{14}/cm^3 and 5x10^{15}/cm^3 for He and Ar while the gas temperature was close to room temperature in He and 1500 K in Ar. The results for Ar and He are in very good agreement with [4] and [5].

The analytical performances of the MHCD will be presented as well. The system, employed as excitation and ionization source for emission or mass spectrometry delivered very good analytical results for the detection of halogens. Three different sample introducti systems were tested, introducing the sample (i) either continuously with gas mixtures, (ii) after separation with a gas chromatograph or (iii) by the use of permeation sources. MHCD operated in static mode was combined with emission spectrometry and operated in jet mode with mass spectrometry. Both systems show excellent analytical capabilities. The limits of detection for chlorine in halogenated molecules are in the order of few pg/s (low ppb$_{v/v}$ range). The analytical figures of merit are comparable or even better than those of conventional large-scale plasmas and of commercial devices based on plasma spectrometry. The lifetime of these microplasmas is a few months for operation in He. They are characterized by robustness and reproducibility.

The limitations of the microplasmas will be also pointed out. It was already demonstrated that these microplasmas are suitable as gas detectors but they fail in measuring liquid samples as it is possible in laser induced plasmas. Only a few publications report measurements of liquid samples but the detection limits are poor.

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