

DECOMPOSITION OF HALOGENATED MOLECULES IN A MICRO-STRUCTURED ELECTRODE GLOW DISCHARGE AT ATMOSPHERIC PRESSURE

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Abstract. A Micro-Structured Electrode (MSE) discharge operating at 1 bar is applied as a detector of halogenated hydrocarbons. Due to its physical properties ($T \sim 2000$ K and high electron number densities of about $10^{15} - 10^{16} / \text{cm}^3$) this microplasma has comparable performances as classical plasmas used in analytical spectroscopy. The small size (μm range) and a low power consumption makes it suitable for integration in miniaturized devices for chemical analysis.

1. Introduction

In the last years, the trend in analytical spectrometry was directed to the miniaturization of analytical instruments and the creation of portable lab-on-a-chip devices with similar properties like large scale laboratory instruments. Besides the goal of reducing size and weight, miniaturization offers additional advantages such as the possibility to bring the laboratory to the sample which may increase the analytical performances, portability for personal use and personal dosimetry, lower the cost and reduces the needed quantities of analyte samples.

Plasma sources are efficient atomisation and excitation devices. In combination with different analysis techniques (emission spectroscopy, absorption spectroscopy or mass spectrometry) they can be employed for the analysis of solid, liquid and gaseous samples [1].

In the category of non-thermal plasmas, the interest in using MSE discharges recently increased due to their multiple application possibilities (surface treatment, reduction of pollutants and generation of UV and VUV radiation) using high pressure operation and low power consumption [2-5]. The micro-dimensions of the discharge combined with convenient plasma parameters make it very attractive also for analytical applications.

In this paper we demonstrate, by applying atomic emission spectroscopy technique, the efficiency of a MSE atmospheric pressure discharge for the measurement of halogenated hydrocarbons.

2. High pressure MSE discharge operation

The MSE is a multilayer system consisting of two metallic foils (Cu, Ni, Pt or W) separated by an insulator (Kapton, mica or ceramic). A hole with a diameter varying from tens to hundreds of μm is drilled through the structure. Applying direct current (DC) or alternative current (AC) a weakly ionized plasma is produced between the electrodes in pure noble gases, gas mixtures or air. The operation of the discharge depends mainly on the ratio between the hole diameter and the distance between the electrodes, the gas pressure and the current density. Due to the reduced dimensions of the holes, high pressure can be applied for the generation of a stable discharge according to the Paschen law. The discharge can be operated in the pressure range from a few tens of mbar up to 2 bar.

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Recently, spectroscopy has been applied to determine the discharge parameters [6]. Diode laser atomic absorption measurements performed on a MSE discharge operating in Ar revealed an increase in the gas temperature from room temperature at 50 mbar to 1200 K at 400 mbar. The electron density increased with the pressure up to $5 \times 10^{15}/\text{cm}^3$ at 400 mbar. Scaling these values to atmospheric pressure, we can expect that the gas temperature and the electron density should be close to 2000 K and $10^{16}/\text{cm}^3$, respectively. Knowing that the ionisation energy is different, the values for He as plasma gas should be within one order of magnitude smaller than those obtained in Ar. The discharge has a strong non-homogenous distribution of the electrons and the excited atoms following the change of the cathode fall length with the increase of the pressure. In Fig.1 the schematic view of the microstructure and a CCD recorded image of the plasma in Ar at 400 mbar are presented.

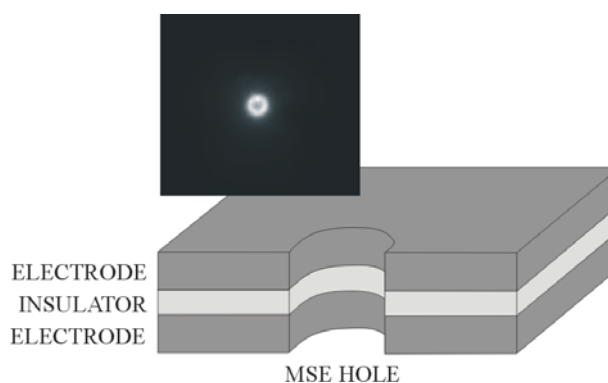


FIGURE 1 Schematic view of the structure and an end-on CCD recorded image of the plasma in Ar at 400 mbar

In the present experiment a structure with 30 μm Pt electrodes and Al_2O_3 as insulator was used. The diameter of the hole was 100 μm and the distance between electrodes 250 μm , respectively. Due to the reactivity of the halogens, noble metal electrodes with a low erosion rate were applied. Attempts to use a system with copper electrodes and Kapton as insulator failed due to the fast erosion of the cathode and the Kapton. The discharge was operated in He as well as Ar with reduced admixtures (less than 50 ppm) of halogenated hydrocarbons (CCl_2F_2 , CHClF_2) in the pressure range of 0.7 – 1.4 bar. The presence of the added analytes had almost no influence on the plasma operation conditions.

The discharge works in a stable mode for currents ranging from 4 mA to 8 mA. The input power density is about $1 \text{ MW}/\text{cm}^3$ at a current density of $60 \text{ A}/\text{cm}^2$. The voltage-current characteristics of the discharge measured in He and Ar are presented in Fig. 2. The gas voltage is constant and does not exceed 250 V for any of the pressure values, corresponding to a normal glow discharge operation.

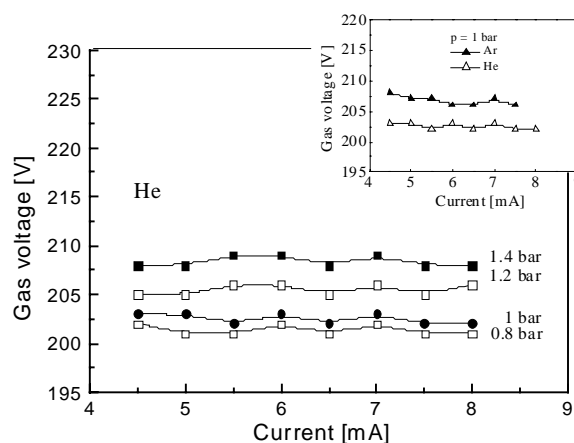


FIGURE 2 U I characteristics of the discharge operating in He and Ar

3. Detection of halogenated hydrocarbons by emission spectroscopy

Atomic emission spectroscopy was applied for the detection of chlorine and fluorine resulting from the decomposition of the molecules. The experimental arrangement consists of a very small echelle spectrometer working in the 640-970 nm range (diffraction orders 120-80) and a CCD camera with a resolution of 1024×1024 pixels [7]. The plasma emitted light is imaged 1:1 on the $20 \mu\text{m} \times 200 \mu\text{m}$ spectrometer entrance slit through an optical fibre. The entire spectral range is recorded simultaneously with an exposure time of 50 ms. In Table 1 the measured emission lines belonging to the investigated halogens and to the buffer gas are presented.

The measurements were performed mainly in He because both Cl and F atomic lines can be recorded while in Ar fluorine could not be measured. This is due to the fact that the excited fluorine levels are higher than those of Ar.

TABLE 1 emission lines

Element	λ [nm]
Cl	912.114
Cl	894.802
Cl	837.594
Cl	754.707
F	739.868
F	733.195
F	755.223
F	742.564
He	728.134
He	667.815
H	656.358
N	868.028
O	844.675
O	794.754
O	777.194
Ar	811.531
Ar	750.386
C	965.843
C	909.483

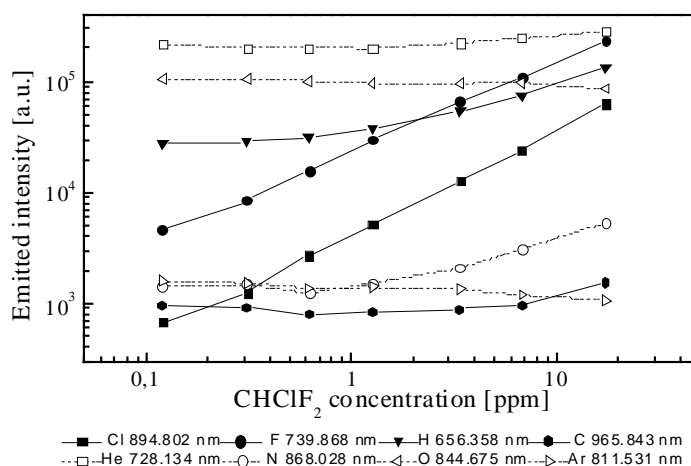
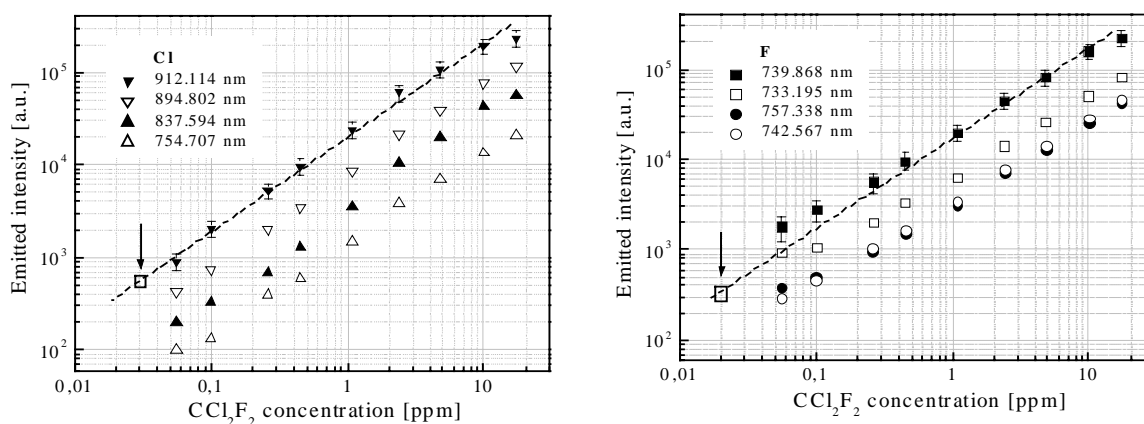
**FIGURE 3** Evolution of the emitted lines with the halogenated molecule concentration in He, $p=1$ mbar, $I = 4$ mA

Fig. 3 shows the intensity of the emission lines of different elements in dependence on the CHClF_2 concentration in He at 1 bar and 4 mA. The intensities of the emitted lines of the buffer gas are independent of the molecule concentration. The intensities of the Cl and F lines are linearly dependent on the CHClF_2 concentration. Assuming the complete dissociation and atomisation of the introduced molecules, it is expected that the H and C signals are also linearly dependent on the CHClF_2 concentration. However this is not the case. The reason may be due to H_2O contamination of the plasma gas and the formation of parasitic species, such as CO or CO_2 in the discharge.

Fig. 4 presents calibration curves for Cl and F from CCl_2F_2 in He. For this purpose we pre-mixed the halogenated hydrocarbons with He before the gas was introduced into the plasma. The measurements started always from an initial mixture of He with 17 ppm halogenated molecules and this mixture was diluted down to a concentration when the signal was 3 times the noise. The calibration curves are linear over 3 orders of magnitude, but at small concentrations it can be noticed that the calibration curves of the F lines are not linear due to a contamination of the discharge walls by fluorine.

Nevertheless, CCl_2F_2 detection limits of 20 ppb in He were found using the Cl 912.114 nm as well as the F 739.868 nm lines. This was also obtained with other halogenated hydrocarbons, not shown in Fig. 4. The detection limits with Ar as a buffer gas are of the same order of magnitude.

**FIGURE 4** Calibration curves of Cl (left) and F (right) in He with CCl_2F_2 . The detection limit is shown by a square in every figure

In order to study the capability of complete dissociation we measured the Cl and F line intensities with CCl_2F_2 and CHClF_2 in the He MSE discharge, varying the species concentrations. The results are shown in Fig. 5. It can be seen that the F line intensities are independent of the species within the experimental errors. On the other hand the Cl line intensities obtained with CCl_2F_2 is a factor of two higher than with CHClF_2 as it is expected from the stoichiometry.

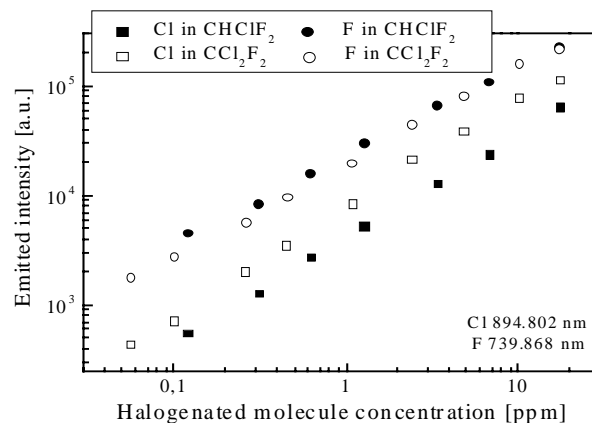


Fig. 5 Cl and F emitted signals from different halogenated molecules in He, $p = 1$ bar, $I = 4$ mA

4. Conclusions

It has been shown, that the MSE discharge can be successfully applied in analytical spectrometry. The detection limits for halogenated hydrocarbons are in the low ppb range. The efficiency of the discharge for the dissociation of halogenated hydrocarbons was demonstrated. Therefore it can be expected that the MSE discharge can be a powerful small detector applied in gas chromatography.

5. References

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