CORRIGENDUM

Corrigendum: Characterization of the effluent of a He/O2 micro-scaled atmospheric pressure plasma jet by quantitative molecular beam mass spectrometry (2010 New J. Phys. 12 013021)

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In this corrigendum, we report and correct an error in the calibration procedure of the molecular beam mass spectrometry (MBMS) diagnostics used for measurement of atomic oxygen densities in the effluent of a micro-scaled atmospheric pressure plasma jet (μ-APPJ) in He/O2 gas mixture (Ellerweg et al 2010 New J. Phys. 12 013021). The difference in the tuning of the used electron impact ionization mass spectrometer at low electron energy used for O atom detection ($E_{el}\rightarrow 18\,\text{eV}$) and for the measurement of the calibration gases CH4 and Ne ($E_{el}\rightarrow 70\,\text{eV}$) has resulted in the underestimation of the O atom densities by a factor of 2.9. The O signal detected with a calibration gas corrected according to new MBMS measurements with updated mass spectrometry setup, as well as a detailed description of the calibration procedure, are provided here. The corrected O densities provide much better agreement with the results of the two-photon absorption laser induced fluorescence (TALIF) diagnostic and the corrected MBMS data, the TALIF data, or an average of both should be used in the future for the μ-APPJ source.

Introduction

Absolute densities of reactive species are very important information for understanding plasma-chemical processes in low- and atmospheric plasmas and the radical interaction with surfaces or liquids, allowing for example the quantitative estimation of reaction yields. Additionally, absolute densities are essential for validation of plasma simulation models. One of the available diagnostics is the molecular beam mass spectrometry (MBMS), which can provide absolute densities of ground state species at a plasma-facing surface based only on their mass and ionization threshold, without a necessity of existence of accessible optical transitions for absorption measurements or problems with non-radiative quenching in fluorescence measurements. Still, a careful comparison of the signal measured for the species of interest with a signal measured for a calibration species with known density has to be performed to obtain absolute density information. In this corrigendum, we discuss first the calibration procedure, pointing out the source of error we had in our previous work [1]. After that, we present the updated figures with corrected O atom densities, which were scaled up from the original values to the new density values as obtained in the new MBMS measurement campaign.

Calibration procedure

The gas mixture at one atmosphere is sampled through a sampling orifice (diameter typically at or below 100 μm) into a differentially pumped system with several pumping stages, where a molecular beam (MB) is formed. Even reactive species are preserved in the MB, because they are transported downwards without any collisions with walls and a collision-less flow regime is established a few diameters behind the sampling orifice. The species in the MB are ionized in electron impact collisions in the ionizer of the mass spectrometer and the formed ions are extracted, filtered according to their mass and energy, and detected with secondary electron...
multiplier detectors. The measured signal of the species $i$ at the detector $S_{\text{detector}}$ (in counts/second) is proportional to the unknown density in the gas mixture $n_i^{\text{mixture}}$ according to the formula [2, 3]:

$$S_{\text{detector}} = n_i^{\text{mixture}} F_{\text{sampling}}^{\text{mixture}} \sigma_i(E_{\text{cal}}) I_{\text{emission}} L_{\text{ionizer}} \beta_{\text{extraction}} T(m_i),$$

(1)

where $n_i^{\text{mixture}} F_{\text{sampling}}^{\text{mixture}} = n_i^{\text{ionizer}} F_{\text{sampling}}^{\text{ionizer}}$ is the factor taking into account the reduction of the species $i$ density in the expansion and transport in the MB into the ionizer after its sampling through the sampling orifice, $\sigma_i(E_{\text{cal}})$ is the ionization cross section at the used electron energy, $I_{\text{emission}}$ is the electron emission current through the ionizer, $L_{\text{ionizer}}$ is the effective ionizer length, $\beta_{\text{extraction}}$ is the ion extraction efficiency from the ionizer, and $T(m_i)$ is the mass-dependent transmission function of the quadrupole and energy filter. The transport of neutral species from the sampling orifice to the detector is illustrated in figure 1.

Most of the mentioned factors cannot be measured directly and the calibration of the measured signal is performed with the measurement of selected stable calibration species with known density $n_i^{\text{cal}}$. By dividing formula (1) for species $i$ with the same formula for calibration species, we obtain:

$$n_i^{\text{mixture}} = F_{\text{sampling}}^{\text{mixture}} \sigma_i(E_{\text{cal}}) n_i^{\text{cal}} T(m_i)^{-1} S_{\text{detector}}^{\text{mixture}} S_{\text{detector}}^{\text{cal}} = n_i^{\text{ionizer}} F_{\text{sampling}}^{\text{ionizer}} \sigma_i(E_{\text{cal}}) n_i^{\text{cal}} T(m_i)^{-1} S_{\text{detector}}^{\text{ionizer}} S_{\text{detector}}^{\text{cal}},$$

(2)

where the same $I_{\text{emission}}$ has been used for both measurements and where we have assumed that $\beta_{\text{extraction}}$ and $L_{\text{ionizer}}$ are the same for both $i$ and calibration species. Expression (2) simplifies further for non-collisional sampling (species mean free path $> \text{diameter of the sampling orifice}$, e.g. in case of low-pressure plasma analysis), because the reduction of the species density on the way into the ionizer is only a function of system geometry:

$$F_{\text{sampling}}^{\text{ionizer}} \beta_{\text{extraction}}^{-1} = \frac{1}{4} \left( \frac{r}{\chi} \right)^2,$$

(3)

with $r$ is the sampling orifice radius and $\chi$ the effective distance between the sampling orifice and the ionizer. The situation is more complex during the collisional sampling, which is the case during atmospheric plasma analysis. A supersonic free jet is formed behind the sampling orifice. The pressure drop in front of and at the sampling orifice, large density gradients behind it, and the presence of the second orifice/skimmer, all lead to a variety of
composition distortions [4]. Typically, light and small species radially diffuse much faster from the axis of the MB and the composition of the MB shifts towards heavier/larger species. These sampling effects are taken into account by using the same gas mixture during the calibration measurements as in the plasma analysis (the same collisional partners in the supersonic expansion with calibration species) and similar i and calibration species (similar mass and degree of freedom). The $F_{\text{cal}}$ and $F_{\text{sampling}}$ factors can be considered the same under these conditions.

The neutral species in the ionizer are ionized in an electron impact ionization process. The ion yield depends on the electron energy dependent ionization cross section, the electron density in the ionizer (proportional to the electron emission current), the spatial overlap of the electron cloud with the MB represented by $\beta_{\text{ionizer}}$, and ion extraction efficiency $\beta_{\text{extraction}}$. $\beta_{\text{extraction}}$ takes into account the probability that an ion leaves the ionizer in the direction of the ionizer exit hole into the following part of the mass spectrometer. As already mentioned before, both $\beta_{\text{ionizer}}$ and $\beta_{\text{extraction}}$ can be assumed constant under ideal conditions and they cancel in the calibration procedure. We explain below that this assumption is not valid for the case where the electron energy changes from a low energy region around 18–25 eV to a high energy region around 70 eV.

The final transport of the ions through the mass spectrometer to the detector is described by mass-dependent transmission efficiency $T(m_i)$, which mainly takes into account the discrimination of the heavier ions due to the longer transit time through the quadrupole mass filter (higher loss probability) at the same transport energy. This transmission function can be obtained by measuring under identical conditions calibration species with a variety of masses with known ionizer densities. The typical scaling of the $T(m_i)$ is with $(m_i)^{-\frac{1}{2}}$, where $z \ll 1$ [5].

**Source of error in our previous calibration**

Measurements with an updated setup (‘new MBMS’ here) on the COST reference microplasma jet [6] (a jet with the same geometry, electrode material (stainless steel) and operation parameters as the original μ-APPJ) have revealed a discrepancy between new and previously determined O atom densities, whereas the same ozone densities have been obtained. The only difference in the O atom calibration procedure performed in the original work and in the new measurements has been identified as a source of this discrepancy. This difference is the use of 70 eV electron energy during the measurement of calibration signal for CH$_4$ and Ne calibration species in the work and in the new measurements has been identified as a source of this discrepancy. This difference is the use of 70 eV electron energy during the measurement of calibration signal for CH$_4$ and Ne calibration species in the original work, whereas the O atoms have been detected at 18 eV electron energy to avoid dissociative ionization of O$_2$ or O$_3$ molecules (threshold ionization mass spectrometry). The new measurements were using Ne as calibration gas with the same mass spectrometer settings (tuning) during O atoms (at 18 eV) and Ne calibration gas (25 eV) measurements.

The effect of higher electron energy should not have, in the ideal case, any effect, because the ionization cross section at 70 eV electron energy has been used, providing the same $\beta_{\text{cal}}(E_{\text{cal}})/\beta_{\text{cal}}\beta_{\text{detector}}$ ratio in the formula (1), independent of electron energy. However, higher electron energy influences the whole distribution of electrons in the ionizer, influencing the effective ionizer length. The ions are also generated in the ionizer at slightly different locations and their extraction efficiency changes as well. These electron energy dependent changes in the ionizer demonstrated themselves in the slightly different tuning of the device which we used at 18–25 eV and 70 eV to obtain maximal ion signal (tuning procedure performed both at low and high electron energy). The Ne signal measured under experimental conditions and with electron energy of 25 eV has not been, unfortunately, recorded during the original measurements and the measured data cannot be, therefore, directly checked and recalibrated. We performed a test comparing the $\beta_{\text{cal}}(E_{\text{cal}})/\beta_{\text{detector}}$ ratio for Ne under low and high electron energies (25 and 70 eV) and otherwise the same conditions and mass spectrometer settings. The obtained difference was a factor 1.6, corroborating our conclusions about the source of the error. This factor is not 2.9 because the measurements have been performed in different MBMS setup (updated geometry with different position of the MB in the ionizer) and different mass spectrometry tuning.

**Updated figures from the original work**

Figure 2. shows the original data as a function of the O$_2$ admixture with rescaled O density with the factor 2.9 to the values measured in the new campaign, which are shown as well. The new measurements have been performed at constant absorbed power (653 ± 5 mW), which can be measured on the COST-jet with integrated calibrated current and voltage probes. On the contrary, the original MBMS data have been measured at the constant root-mean-square (rms) voltage of 230 V, which is also the applied rms voltage in the new campaign with O$_2$ admixture between 0 and 0.6%. The applied rms voltage has to be increased at higher O$_2$ admixtures, to keep the absorbed power constant. This increase explains the larger O and O$_3$ densities obtained from the new measurements (more power absorbed) and the fact that the plasma can be sustained at much larger O$_2$.
concentrations. The original and newly measured O\textsubscript{3} densities overlaps in the 0%–0.6% O\textsubscript{2} admixtures, where the applied voltage is the same.

Figures 3 and 4 represent the figures with densities as a function of distance to the jet and applied voltage from the original publication with rescaled O densities. The rescaled MBMS densities, the TALIF densities or an average value of both should be used as representative for the analyzed jet. The higher O densities should be taken into account in our other publications, where the absolute O density has been used to analyze and interpret the experimental data [7–10].

Conclusions

An error in the O density calibration of the MBMS analysis of the $\mu$-APPJ in He/O\textsubscript{2} gas mixture has been identified in our publication. The explanation of the error and the updated figures from the original publication are provided. Much better agreement between MBMS and TALIF measurements is now obtained. The densities reported here should be used as representative values for this plasma jet under the studied conditions.
Figure 4. Original figure 6 from reference [1] with O densities scaled up by a factor of 2.9. Influence of the applied voltage (MBMS measurements, bottom axis) and the transceiver power (TALIF measurements, top axis) on the atomic oxygen and ozone density measured between points of ignition and arcing. Conditions: 3 mm distance, 0.6% O₂ admixture and 1.4 slm helium flow.

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Characterization of the effluent of a He/O\textsubscript{2} microscale atmospheric pressure plasma jet by quantitative molecular beam mass spectrometry

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Abstract. The effluent of a microscale atmospheric pressure plasma jet (\textmu-APPJ) operated in helium with a small admixture of molecular oxygen (<1.6%) has been analyzed by means of two independent diagnostics, quantitative molecular beam mass spectrometry (MBMS) and two-photon absorption laser-induced fluorescence spectroscopy (TALIF). The atomic oxygen density, the ozone density and the depletion of molecular oxygen have been measured by MBMS and the atomic oxygen density has been validated by TALIF. Absolute atomic oxygen densities in the effluent up to \(4.7 \times 10^{15} \text{ cm}^{-3}\) could be measured with a very good agreement between both diagnostics. In addition, ozone densities in the effluent up to \(1.4 \times 10^{15} \text{ cm}^{-3}\) and an O\textsubscript{2} depletion up to 10% could be measured by MBMS. The atomic oxygen density shows a maximum value at an O\textsubscript{2} admixture of 0.6%, whereas the ozone density continues to increase toward higher O\textsubscript{2} admixtures. With increasing distance from the jet, the atomic oxygen density decreases but is still detectable at a distance of 30 mm. The ozone density increases with distance, saturating at a distance of 40 mm. By applying higher powers to the \textmu-APPJ, the atomic oxygen density increases linearly whereas the ozone density exhibits a maximum.

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1. Introduction

Atmospheric pressure microplasmas correspond to non-equilibrium glow discharges operated at atmospheric pressure with an electrode separation from tens of \( \mu \text{m} \) to 1 mm. Microplasmas exhibit non-equilibrium character with high electron densities and low gas temperatures and require no expensive vacuum systems. These characteristics make them attractive for various applications such as treatment of temperature and vacuum sensitive materials, \textit{in vivo} sterilization of skin and wounds, or even localized material synthesis.

In recent years, a variety of microplasma jets has been developed \cite{1, 2}. These microplasma jets are capable of delivering reactive species (neutrals, metastables, ions, (V)UV photons) to a treated surface resulting in, for example, inactivation of pathogens \cite{3}–\cite{6}, deposition of thin films \cite{7, 8}, generation of nanoparticles \cite{9} or etching of surface material \cite{10}. Most of these microplasma jets are operated with a noble gas with an addition of a small amount of a molecular gas. In particular, reactive oxygen species (ROS) are believed to be responsible for surface modification and deactivation of bacteria \cite{5}. To understand and optimize these processes, the absolute densities of ROS must be known. With this knowledge, the plasma chemistry can be understood and existing plasma models can be validated. However, the experimental characterization of atmospheric pressure microplasmas is a challenging task due to the high pressure and their small dimensions. Atomic oxygen densities can already be determined by several diagnostics like titration, actinometry or catalytic probes but all of them exhibit weak points \cite{23}. Here, we report on quantitative measurements of ground state atomic oxygen, of ozone molecules, and of \( \text{O}_2 \) depletion by means of molecular beam mass spectrometry (MBMS) in the effluent of a microscale atmospheric pressure plasma jet (\( \mu \)-APPJ) operated in helium with a small admixture of molecular oxygen. The measurements of O atoms are compared to two-photon absorption laser-induced fluorescence spectroscopy (TALIF) measurements. O and \( \text{O}_3 \) densities and \( \text{O}_2 \) depletion are reported as function of \( \text{O}_2 \) admixture, applied voltage (power) and distance from the jet.
These absolute densities can be used to identify the crucial reactive species, e.g. deactivation of bacteria. Thus, an optimization of sterilization processes is possible. Furthermore, absolute densities are necessary as input parameters for new models and for the validation of existing models. In contrast to other diagnostics, MBMS offers a time-saving method to analyze the composition of an effluent of a μ-APPJ.

2. Experimental setup

2.1. μ-APPJ

The μ-APPJ is a capacitively coupled microplasma jet consisting of two stainless steel electrodes (length 30 mm and width 1 mm) with a 1 mm gap in between (cf figure 1). The plasma is ignited in this gap filling a volume of $1 \times 1 \times 30 \text{ mm}^3$. The plasma volume is confined on two sides by glass plates. The μ-APPJ used here is the same as the μ-APPJ described elsewhere [11] except for the position of the glass plates. In the previous version, the glass plates end 3 mm upstream from the μ-APPJ’s nozzle, so that the plasma volume is not entirely confined by glass. In this study, the glass plates cover the entire electrode length (cf figure 1) to allow MBMS measurements. One electrode is connected to a power supply (13.56 MHz, <30 W) through a matching network and the other one is grounded.

The gas flow through the μ-APPJ is 1.4 slm helium with a small admixture of molecular oxygen (< 1.6%). Both the helium flow and the O$_2$ flow, are controlled by mass flow controllers. It has been shown that this microplasma jet is a typical $\alpha$-mode discharge [12].

2.2. Molecular beam mass spectrometry

The effluent of this μ-APPJ has been analyzed by the MBMS system shown in figure 2. Since this MBMS system is described in detail elsewhere [13], only a brief overview is provided here. It consists of three pumping stages interconnected via small orifices (all grounded). The first sampling orifice (100 $\mu$m diameter) is used to extract the gas mixture to be analyzed and is placed in this case on the axis of the jet. The 100 $\mu$m diameter of the sampling orifice results
in a gas flow of approx. 0.1 slm in the MBMS system which is well below the gas flow of the µ-APPJ, thus ensuring a stagnation of the flow. The ionizer of the mass spectrometer (MS) is in line-of-sight with this sampling orifice. In contrast to traditional gas sampling methods, only a pulsed gas flow from the atmosphere into the pumping system is allowed. This pulsing is realized with a rotating skimmer, which is installed in the first pumping stage. The rotating skimmer consists of a stainless steel disk with small embedded skimmers. Only when the small skimmer is aligned with the sampling orifice, the molecular beam (MB) can directly penetrate the second pumping stage without disturbance. As long as the rotating skimmer is in the blocking position, the MB is blocked by the metal disk and a gas flow into the second stage is prevented. The background density in the MS pumping stage can be reduced in this way while the density in the MB stays constant (or even increases by enlarging the sampling orifice). This results in a very high beam-to-background ratio of 14 [13]. We have used four small embedded skimmers instead of one in this study to reduce the required sampling time by a factor of four. The background density in the third stage increases in this case only by a factor of two.

All µ-APPJ measurements have been done on-axis in a controlled helium atmosphere to avoid admixture of ambient air into the effluent. The distance between the sampling orifice and the µ-APPJ nozzle was 3 mm, so no additional plasma was visible between the jet and the metal sampling orifice under most of the conditions used. Only for very high applied electrode voltages and low O$_2$ admixtures does a small additional plasma appear there.

**Figure 2.** Sketch of the differential pumping system.
2.3. Calibration procedure of the MBMS signal

The signal of the MS is calibrated by comparing the signal of species with known density with that of species with unknown density [14, 15]. However, special care has to be taken when sampling from atmospheric pressure is considered. When a gas flows through a nozzle from high pressure to vacuum, the gas expands forming a supersonic free jet [16]. By placing a skimmer in this free jet the central region is extracted and the resulting MB is analyzed by the MS downstream.

The composition of the gas mixture in the MB changes compared to the composition in front of the sampling orifice due to collisions in the beam. This effect is called composition distortion in MBMS sampling and has been described by Knuth [17] in detail. One of the major effects is radial diffusion in the free jet depending on the mass of the particles and on the mean molecular weight of the gas mixture. A general trend can be recognized with lighter particles diffusing more easily out of the beam axis and hence being discriminated against heavier particles at the measuring point (ionizer). We have observed this effect in measurements of different He/Ar mixtures (not shown here): the measured helium/argon concentrations were always lower/higher compared to their true concentrations in front of the sampling orifice.

The composition distortion depends on the collision partners. The mixture contains only 1.6% of O$_2$ and, therefore, the main collision partner is helium. We calibrated the density of the unknown species by adding a small amount of gas with the same or similar mass and known density to helium. We then compared the measured signals of these calibration species to those of the unknown species. We used a mixture of helium with a small amount of neon (mass 20 amu) or methane (mass 16 amu) for calibration of atomic oxygen (mass 16 amu). Two calibration gases were used to monitor possible effects due to inherent differences in the elastic collision cross sections of Ne, CH$_4$ and O with He atoms and to identify the difference due to mass of Ne and O. The measured calibration factors differed by only 10% from each other, indicating that the systematic error due to these differences is small. For the calibration of the ozone signal (mass 48 amu) argon (mass 40 amu) was used.

Corresponding electron impact ionization cross sections and the known mass dependence of the transmission function of the MS [18] have been taken into account during all calibration and plasma measurements.

The atomic oxygen MBMS measurements were performed with an electron energy in the ionizer of about 15 eV to prevent dissociative ionization of molecular O$_2$ with threshold at 18 eV [19]. Such dissociative ionization is irrelevant for ozone and molecular oxygen measurements. Therefore, an electron energy of 70 eV is used for O and O$_3$ detection.

Considering errors of available ionization cross sections (typically 5–10%), inaccuracy of calibration of mass-dependent transmission function of the MS, drifts in the electronics and age of the detector, the MBMS should provide absolute densities with systematic errors within a factor of two. Additional systematic error can arise due to different composition distortions for measured and calibrated gas. We have already argued that this error is probably small. However, to verify our calibration procedure we have also compared our results to O densities measured by TALIF described in the following.

2.4. TALIF

Another well-established diagnostic for measuring atomic oxygen is TALIF: ground-state oxygen atoms are excited into a higher state by simultaneous absorption of two photons. The
fluorescence radiation emitted from that higher energy state is proportional to the ground state atomic oxygen density. Results of TALIF measurements of a similar µ-APPJ’s effluent are already reported [11]. However, since we used a modified geometry of the µ-APPJ in order to allow MBMS measurements, TALIF measurements of this modified jet are performed and reported here.

The overall reliability of the TALIF measurements is stated to be 50%. This is based on uncertainties in the values of the ratios of the two-photon excitation cross sections, the detection sensitivity of the photomultiplier at the respective wavelengths and the effective branching ratios of the observed fluorescence transitions including collisional quenching. More information about TALIF measurements, the calibration procedure and the experimental setup can be found elsewhere [11], [20]–[22].

The TALIF measurements were performed in an undisturbed effluent, whereas the MBMS necessarily disturbs the effluent by the presence of the front metal plate with the sampling orifice. Consequently, a stagnation of the gas flow occurs and radicals recombine at the metal surface. But this is not necessarily a disadvantage of the MBMS concept because during all microplasma applications a surface, which should be treated, is placed in the effluent. Therefore, an MBMS is especially suited for microplasma measurements, because it determines densities at the vicinity of this surface.

3. Results

Atomic oxygen and ozone densities in the effluent of the µ-APPJ are measured. Whereas the ozone and O₂ densities could only be measured by MBMS, the atomic oxygen measurements are performed by both MBMS and TALIF. The O and O₃ densities were observed for a variation of the O₂ admixture, of the applied electrode voltage and of the distance between the µ-APPJ and the sampling orifice. During MBMS and TALIF measurements, the µ-APPJ was placed in a helium atmosphere at 1 bar so no reactions between ROS and air molecules can take place. Additionally, the depletion of molecular oxygen was also measured by means of MBMS.

The error bars shown in the following graphs are calculated by the standard deviation of the noise \( \sqrt{\text{detected particles}} \).

3.1. O₂ depletion

O₂ depletion was determined with the MBMS by measuring the O₂ signal during the plasma on and off phase. The difference between these signals corresponds to O₂ depletion. Upon changing the O₂ admixture between 0 and 1%, the relative O₂ depletion decreases slightly from 5 to 3% at a distance of 2 mm and an electrode voltage of 230 V \(_{\text{rms}}\) (not shown here). A variation of the electrode voltage (at a distance of 2 mm and an O₂ admixture of 0.6%) reveals a linear correlation between the applied voltage and the O₂ depletion with a maximum value of about 10% at a voltage of 340 V \(_{\text{rms}}\) (cf figure 3). The dissociation degree of molecular oxygen in the discharge core of the µ-APPJ measured by TALIF is up to 20% [23] and corresponds approximately with our value in the effluent obtained by MBMS. The O₂ depletion is probably lower in the effluent due to neutral recombination of atomic oxygen leading again to the formation of molecular oxygen.
Figure 3. O$_2$ depletion dependence on the applied electrode voltage (0.6% O$_2$ admixture, 1.4 slm helium flow and 2 mm distance).

Figure 4. Influence of the O$_2$ admixture on the atomic oxygen (●, ○) and ozone (■) density at 230 V$_{rms}$ applied voltage, 3 mm distance and a helium flow of 1.4 slm. The O density obtained by TALIF is scaled by a factor of 0.27.

3.2. Variation of O$_2$ admixture

Figure 4 shows the densities of atomic oxygen and ozone with varying molecular oxygen admixture at a constant helium flow of 1.4 slm and an applied electrode voltage of 230 V$_{rms}$. The distance between the µ-APPJ’s nozzle and sampling orifice is 3 mm. The atomic oxygen density increases with raising O$_2$ admixtures, peaking at about 0.6%. Beyond this point the O density decreases again until the plasma extinguishes at high O$_2$ admixtures. Both MBMS and TALIF yield an almost identical dependence of the O density on the O$_2$ flow. However, the absolute O density measured by MBMS is about 0.27 times smaller than the value measured by TALIF.
The maximum measured O density is about $8.5 \times 10^{14}$ cm$^{-3}$ (MBMS) or $3.2 \times 10^{15}$ cm$^{-3}$ (TALIF). Considering the fact that both measurements are performed under different conditions (undisturbed effluent versus stagnation of the flow and recombination at the front plate of the MS) this result can still be regarded as a very good agreement. The recombination of O atoms at the metal surface and longer residence time in the effluent due to stagnation flow can also explain the lower densities measured by MBMS. This comparison shows that our MBMS system is suitable for measuring absolute densities of reactive species in atmospheric pressure microplasma jets.

The O$_3$ density does not show, in contrast to the O density, a maximum and increases until the plasma extinguishes at high O$_2$ admixtures. A maximum value of about $1 \times 10^{15}$ cm$^{-3}$ is found at an admixture of 1% O$_2$. The MBMS measurements could only be performed up to an O$_2$ admixture of 1%. With higher admixtures, the plasma could no longer be ignited.

Very similar relative O and O$_3$ trends have been obtained in a zero-dimensional global model of a He/O$_2$ atmospheric pressure plasmas by Park et al [25].

A possible explanation for the observed trends is given as follows. Assuming that atomic oxygen is produced in the plasma core via the reaction $e^- + O_2 \rightarrow 2O$, the O density increases with increasing O$_2$ admixture, but is limited by the plasma (i.e. electron density). A competing process is the three-body reaction $O + O_2 + M \rightarrow O_3 + M$ consuming atomic oxygen and producing ozone. The O$_3$ production (and therefore the O consumption) becomes more effective at higher O$_2$ ratios, thus the O$_3$ density increases and the O density decreases. Additionally, the electron density decreases with rising O$_2$ concentration due to the electronegativity of the O$_2$ molecule. The dissociation rates of O$_2$ and of O$_3$, and therefore the atomic oxygen density, also decrease at high O$_2$ concentrations.

It has to be emphasized that the measurements are performed at a distance of 3 mm where no equilibrium has yet been reached (see the next section): the O density in the effluent begins to decrease with distance due to recombination with O$_2$, producing O$_3$. With higher O$_2$ ratios the recombination proceeds on shorter time scales. Therefore, an increase of the O$_3$ density with growing O$_2$ admixture is observed.

### 3.3. Variation of the distance

The distance between the $\mu$-APPJ and the MBMS sampling orifice was varied to monitor a spatial variation of the densities. Figure 5 shows the spatial O and O$_3$ density distribution in the effluent of the jet. The jet was operated with a helium flow of 1.4 slm and an addition of 0.6% O$_2$ at an electrode voltage of 230 V$_{\text{rms}}$. The atomic oxygen density decreased monotonically with increasing distance from the jet and could still be detected in a distance of 30 mm. Again, the absolute atomic oxygen density measured by MBMS was 0.27 times the density measured by TALIF. The highest O density obtained by TALIF was about $3.2 \times 10^{15}$ cm$^{-3}$ in contrast to $7.0 \times 10^{14}$ cm$^{-3}$ obtained by MBMS. A detection limit of our MBMS system of about 6 ppm could be estimated by the lowest detectable atomic oxygen signal at high distances.

In contrast to the atomic oxygen production, the ozone production mainly takes place in the effluent: directly at the nozzle the ozone density ($3.7 \times 10^{14}$ cm$^{-3}$) is lower than the atomic oxygen density. But with increasing distance the ozone density grows till it saturates beyond a distance of 40 mm at a density of about $1.4 \times 10^{15}$ cm$^{-3}$. This observation is consistent with the model of a larger He/O$_2$ atmospheric pressure plasma jet with a larger electrode distance of 1.6 mm, indicating similar O and O$_3$ trends [26].
3.4. Variation of the electrode voltage

The atomic oxygen and ozone density were measured at a distance of 3 mm in front the υ-APPJ’s nozzle while varying the electrode voltage between the point of plasma ignition and arcing, corresponding to 185 and 315 V\textsubscript{rms}. The helium flow through the jet was 1.4 slm with 0.6\% O\textsubscript{2} admixture. For technical reasons, it was not possible to measure the electrode voltage during the TALIF measurements. Instead, the rf-transceiver power was recorded. Since it is difficult to compare voltage and power explicitly, the qualitative behavior in the interval from ignition to arcing was evaluated for both (cf figure 6). This corresponds to a power from 2 to 11 W. At the ignition point, an atomic oxygen density of 4.6 × 10\textsuperscript{14} and 1.3 × 10\textsuperscript{15} cm\textsuperscript{−3} could be measured by MBMS and TALIF, respectively. By increasing the applied voltage, the atomic oxygen production also increased linearly. At the highest possible power, before arcing, a density of 2.0 × 10\textsuperscript{15} cm\textsuperscript{−3} (MBMS) or 4.7 × 10\textsuperscript{15} cm\textsuperscript{−3} (TALIF) was reached, respectively. It is not, by implication, possible to compare the applied voltages with the applied power. Therefore it is not surprising that measured data were not, even with the factor of 0.27, in perfect agreement with each other. However, both diagnostics showed the same trend in the O density.

The ozone density was about 3.4 × 10\textsuperscript{14} cm\textsuperscript{−3} at the ignition point and increased to 4.5 × 10\textsuperscript{14} cm\textsuperscript{−3} at a voltage of 200 V\textsubscript{rms}. Beyond this maximum, the O\textsubscript{3} density decreased slightly to a value of 3.0 × 10\textsuperscript{14} cm\textsuperscript{−3} at the highest possible voltage of 315 V\textsubscript{rms}.

By applying higher voltages to the electrodes, the O\textsubscript{2} dissociation degree increased (cf figure 3), possibly due to an increasing electron density \cite{11}, \cite{23}–\cite{25}. Therefore, it is reasonable that the atomic oxygen density increases in the same manner. The ozone density behaves differently. As already shown, ozone molecules are mainly produced in the effluent, but at a close distance of 3 mm we see mainly the end product of the ozone coming from plasma chemistry inside the plasma core. This explains the nearly unaffected ozone signal while increasing the applied voltage. Only a slight increase can be observed first, because more
atomic oxygen is available to produce ozone molecules. But with higher powers the dissociation rate of the ozone molecules also increases, and hence the ozone density decreases. Processes influencing the ozone production are manifold and complicated. So more detailed measurements and models are in preparation.

4. Conclusion and outlook

The knowledge of absolute densities of reactive species generated in atmospheric pressure plasma jets is a very important information for understanding their effects in, for example, treatment of living tissues or skin wounds. Additionally, it is important for validation of results of plasma models and for understanding and optimization of the performance of these jets in their different applications.

Here, we reported the atomic oxygen density measurements in the effluent of a μ-APPJ as measured by two independent diagnostics. A maximum atomic oxygen density of around $10^{15} \text{cm}^{-3}$ was found at a molecular oxygen admixture of 0.6%. It increases linearly with applied power and decreases almost linearly as the distance from the jet increases. However, O atoms are also detectable even at a distance of 30 mm from the jet. The discrepancy between TALIF and MBMS measurements is only a factor of 0.27, which can be explained by different jet configurations during measurements: TALIF measurements are performed in an undisturbed effluent, whereas the MBMS introduces a metal plate with a sampling orifice into the gas flow. This agreement shows that our design of the MBMS system using a rotating skimmer is suitable for measuring absolute densities of reactive species in atmospheric pressure microplasma jets.

Additionally, the O$_3$ density and O$_2$ depletion have been measured by MBMS. The ozone density increases by admixing more O$_2$ in the μ-APPJ and by increasing the distance from...
the jet. The influence of the applied power on the O$_3$ density is small, and stays almost constant. Overall, a maximum ozone density of about $10^{15}$ cm$^{-3}$ was found. By increasing the O$_2$ admixture only a slight decrease of the relative O$_2$ depletion could be observed. The O$_2$ depletion increases linearly with the applied power reaching a maximum of about 10%.

The measured O and O$_3$ densities are consistent with predictions of different models in the literature. Also, the determined O$_2$ depletion corresponds to the values obtained in the core of the plasma by TALIF.

MBMS and TALIF measurements may complement one another, leading to the understanding of plasma chemistry of microplasmas: TALIF can detect only selected species but therefore measurements are possible in the effluent as well as in the discharge core. With MBMS only the effluent can be analyzed but therefore almost all atoms and molecules can be detected.

MBMS measurements of the $\mu$-APPJ in ambient air are in preparation to analyze the influence of admixed air on the plasma chemistry. Furthermore, a disturbing surface will be placed in the effluent during TALIF measurements to ascertain the effect of the stagnation of the gas flow and surface recombination on the densities of atomic oxygen. The ozone density in the discharge core and in the effluent will be determined by UV absorption measurements.

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