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 ($E_{el} = 18$ eV) and for the measurement of the calibration gases CH₄ and Ne ($E_{el} = 70$ eV) has resulted in the underestimation of the O atom densities by a factor of 2.9. The O₃ signal and the signal of its calibration gas have been both measured at 70 eV electron energy and O₂ density stays, therefore, unaffected. Updated figures with rescaled O densities 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 \( n^\text{mixture}_i \) according to the formula [2, 3]:

\[
S_{\text{detector}} = n^\text{mixture}_i F^\text{sampling}_i \sigma_i(E_i) I^\text{emission}_i L^\text{ionizer}_i \beta^\text{extraction}_i T(m_i),
\]

where \( n^\text{mixture}_i F^\text{sampling}_i = n^\text{ionizer}_i F^\text{sampling}_i \) 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, \( \sigma_i(E_i) \) is the ionization cross section at the used electron energy, \( I^\text{emission}_i \) is the electron emission current through the ionizer, \( L^\text{ionizer}_i \) the effective ionizer length, \( \beta^\text{extraction}_i \) the ion extraction efficiency from the ionizer, and \( T(m_i) \) 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 \( n^\text{cal}_i \). By dividing formula (1) for species \( i \) with the same formula for calibration species, we obtain:

\[
n^\text{mixture}_i = \frac{n^\text{cal}_i F^\text{sampling}_i \sigma^\text{cal}_i(E^\text{cal}_i) n^\text{cal}_i T(m^\text{cal}_i) S^\text{detector}}{F^\text{sampling}_i \sigma_i(E_i) T(m_i)} S^\text{detector} \sim S^\text{detector},
\]

where the same \( I^\text{emission}_i \) has been used for both measurements and where we have assumed that \( \beta^\text{extraction}_i \) and \( L^\text{ionizer}_i \) are the same for both \( i \) and calibration species. Expression (2) simplifies further for non-collisional sampling (species mean free path > 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:

\[
F^\text{sampling}_i \left| _{\text{collisionless}} = \frac{1}{4} \left( \frac{r}{x} \right)^2, \right.
\]

with \( r \) is the sampling orifice radius and \( x \) 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 ion 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 $z \leq 1$ [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-APPI) 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 CH4 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 CH4 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 O2 or O3 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 $S_{\text{cal}}(E_{\text{cal}})/S_{\text{detector}}$ ratio in the formula (1), independent of electron energy. However, higher electron energy influences the real 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 and recalibrated. We performed a test comparing the $S_{\text{cal}}(E_{\text{cal}})/S_{\text{detector}}$ 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 O2 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 O2 admixture between 0 and 0.6%. The applied rms voltage has to be increased at higher O2 admixtures, to keep the absorbed power constant. This increase explains the larger O and O3 densities obtained from the new measurements (more power absorbed) and the fact that the plasma can be sustained at much larger O2.
concentrations. The original and newly measured O₃ densities overlaps in the 0%–0.6% O₂ 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 μ-APPJ in He/O₂ 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: 5 mm distance, 0.6% O₂ admixture and 1.4 slm helium flow.