Molecular beam sampling system with very high beam-to-background ratio: The rotating skimmer concept

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(Received 17 February 2009; accepted 22 April 2009; published online 20 May 2009)

A novel method of reducing the background pressure in a vacuum system used for sampling a molecular beam from a high pressure region is presented. A triple differential pumping stage is constructed with a chopper with rotating skimmer within the first pumping stage, which serves effectively as a valve separating periodically the vacuum system from the ambient environment. The mass spectrometry measurement of the species in the molecular beam show an excellent beam-to-background ratio of 14 and a detection limit below 1 ppm. The potential of this method for detection of low density reactive species in atmospheric pressure plasmas is demonstrated for the detection of oxygen atoms generated in an atmospheric pressure microplasma source. © 2009 American Institute of Physics. [DOI: 10.1063/1.3133804]

The knowledge of reactive species densities in plasmas is of major importance, e.g., for the study of plasma chemistry and for the understanding of thin film growth. Radicals exhibit due to their reactivity of very low densities and advanced detection techniques have to be applied. The detection of radical species is even more complex, when the plasma is operated at atmospheric pressures. One possible diagnostics is molecular beam mass spectrometry (MBMS). In MBMS, the plasma composition is measured by sampling a gas through a small orifice into a differentially pumped vacuum system (usually with two or three pumping stages) containing a mass spectrometer (MS).\(^1\)\(^-\)\(^5\) The sampling orifice is in line of sight with the ionizer of the MS and therefore even reactive species with high surface reactivity can be detected. MBMS provides, when properly designed and calibrated, absolute densities; a very important information for the identification of growth precursors. When used for the analysis of atmospheric pressure plasmas or gas mixtures, the diameter of the sampling orifice is much larger than the mean free path and a supersonic free jet is formed on the vacuum side of this orifice.\(^6\) The particle flux into the first pumping stage is rather large and at least three differentially pumped stages have to be used to reach a sufficiently low pressure in the last pumping stage housing the MS. Contrary to the sampling from a low pressure system, where no collisions take place, the pressure in the first pumping stage also plays an important role. It has to be low enough to prevent collisions of the collected particles in the free jet with the background particles in this pumping stage. This condition sets bounds to e.g., the size of the sampling orifice and impose high demands on the pumping speed in the first pumping stage. Additionally, the species concentrations in the molecular beam (MB) differ from that in the sampled gas. Several composition distortions occur e.g., due to large density gradients in the free jet and different radial velocity distributions of different species in the beam.\(^7\) These composition distortions have to be taken into account in any calibration procedure.

An important issue in both low and high pressure MBMS is a proper substraction of the background signal. The species density in the ionizer is a combination of the species density in the MB passing the ionizer and the background density (resulting in additional background signal) due to the background pressure in the MS pumping stage. The beam-to-background density ratio is typically close to unity\(^1\)\(^-\)\(^4\) for triply differentially pumped systems. The background signal can be measured with the help of a beam chopper in front of the ionizer, which can block the MB and allows hence the measurement of the background signal. This background signal has to be subtracted from the measured signal.

It would be beneficial to increase the density in the MB and at the same time to reduce the background density. However, both these densities are closely related. When a more intense MB is realized (e.g., by selecting a larger sampling orifice), more gas enters the MS pumping stage resulting in a larger background density. Additionally, the background pressure in the first pumping stage would increase and disturb the free jet. This problem can be resolved by combining a valve and a chopper in a special pulsed sampling unit, which can close and open the sampling orifice without disturbing the free jet in the open phase. When the sampling orifice is periodically closed on a time scale shorter than the residence time of the species in the MS pumping stage (approximately several hundred microseconds), the time-averaged particle flux into the MS is effectively reduced, resulting in a lower background density. However, the density in the MB remains the same during the time period when the sampling orifice is open. This MB density can then be measured in a time resolved manner. Here, we report on such a design of a sampling unit based on a rotating skimmer. This is explained in the following.

The scheme of the differential pumping system and a simplified technical drawing are shown in Figs. 1 and 2. The species of interest enter the first pumping stage via a sampling orifice (A) with a diameter of 100 \(\mu\)m. The orifice (B) to the second stage has a diameter of 6 mm. The skimmer
The arrows show the position of the bigger O-ring. PD stands for photodiode.

**FIG. 2.** (Color online) Simplified technical drawing of differential pumping system. The arrows show the position of the bigger O-ring, PD stands for photodiode.

(C) to the third stage has an opening diameter of 0.8 mm and is at the distance of 44 mm from the sampling orifice (A). The vacuum in stage 1 is generated using a rotary oil pump and the volume of this stage is approximately 1 l. Turbomolecular pumps are used in stages 2 (500 l/s) and 3 (100 l/s) and volumes of these stages are \( V_2 \sim 6.5 \) l and \( V_3 \sim 2 \) l. The third stage houses a HiQuad quadrupole MS with the ionizer at 125 mm distance from the sampling orifice. The housing of vacuum stages has a cylindrical form with orifices and the ionizer on its symmetry axis, cf. Fig. 2. Within the first pumping stage, a chopper is placed consisting of a stainless steel disk with a conical hole. Two different chopper designs have been tested: Design (1) with a conical hole in a 2 mm thick metal disk and design (2) with a 2 mm long conical skimmer (D) embedded in a 1.5 mm thick metal disk, providing a larger gap between the chopper disk and the front plate with the sampling orifice (A) (cf. insets in Fig. 1). Both the hole (a) and the skimmer (b) have a diameter of 1 mm on the narrow side, an opening angle of 90° and a diameter of 5 mm on the wide side. The chopper is rotated by an ultrahigh vacuum stepper motor at arbitrarily chosen frequency of 14.3 Hz. At a specific position of the chopper (open position), the hole or the skimmer (D) aligns in line of sight with the orifices (A) and (B) and allows the formation of the free jet and the direct penetration of the sampled species into stage two, where the good vacuum assures molecular flow conditions. The MS signal is measured time resolved with a multichannel scaler card with a time resolution of 1 \( \mu \)s. This measurement is synchronized with the chopper revolutions by means of a photodiode signal. Appearance of the MB signal over the background signal can be observed in this way at the open position of the chopper, whereas only background signal is measured at time when the chopper is closed.

Special care has to be taken regarding the chopper design. The chopper, when open, should not disturb the formation of free jet. Therefore, it is important that the edge of the conical hole (D) moves as close as possible to the sampling orifice (A). This distance is \( \sim 100 \) \( \mu \)m in our case and it is adjusted by controlling the position of the front plate by four distance screws at its circumference. The bigger O-ring used there enables this movement without compromising good sealing of the first pumping stage from the atmosphere, cf. Fig. 2. However, when the chopper disk is too close to the plate with the sampling orifice (A), pressure stays high in the narrow gap between them, which disturbs the measurement. Curve (a) in Fig. 3 shows a time dependent \( N_2 \) signal at mass 28 amu as measured from laboratory air with the chopper design (1). The chopper is open only for \( \sim 270 \) \( \mu \)s in the time interval indicated by two dashed lines. However, a broad peak with several substructures is observed even before the chopper has reached the open position. These substructures appear at the moment, when the conical hole (D) overlaps for the first time with the orifice (B) (cf. inset in Fig. 3) and the gas from the narrow gap between chopper and front plate can enter the pumping stages 2 and 3. The gas in this narrow gap should be pumped as efficiently as possible to reduce high pressure in this region and to avoid the additional signal. This is achieved by embedding a skimmer into a thinner chopper disk. The gap between the chopper and the plate with the sampling orifice is large enough to...
enable effective pumping of this region, when the chopper is blocking the MB. At the same time, the edge of the skimmer (D) is very close to the plane with the sampling orifice and therefore does not disturb the free jet when the chopper is in open position. Curve b) in Fig. 3 shows a time dependent \( N_2 \) signal at mass 28 amu as measured with the chopper design (2). The additional structures are significantly reduced and only one single well defined peak is observed. Moreover, the background signal is reduced more than a factor of two.

The chopper disk is mounted very close (100–200 \( \mu \)m) to the plane with the large orifice (B), resulting in a very small conductance between stages 1 and 2 when the chopper is blocking the orifice (B). Consequently, very low pressures can be sustained in pumping stages 2 and 3 even if only a rotary oil pump is used to pump the first stage resulting in a pressure as high as 50 Pa. When the chopper is not rotating and it is at the blocking position, the pressures in the stages 2 and 3 are only \( p_2=1 \times 10^{-2} \text{ Pa} \) and \( p_3=2 \times 10^{-3} \text{ Pa} \), respectively. Pressure \( p_2 \) is 0.5 Pa and \( p_3=7 \times 10^{-4} \text{ Pa} \) when the chopper is not moving and at open position with the skimmer aligned with the sampling orifice. When the chopper is rotating, the pressures decreases to \( p_2=1 \times 10^{-2} \text{ Pa} \) and \( p_3=2 \times 10^{-5} \text{ Pa} \), because the chopper is for \( \sim 99.6\% \) of the time in the blocking position.

The resulting beam-to-background ratio achieved in Fig. 3 is approximately 14. This is factor 5–10 better than in systems with continual gas sampling. This superior beam-to-background ratio, however, requires longer measurement times because the chopper is \( \sim 99.6\% \) of the time blocking the MB. It is important to note that this time does not have to be 250 time longer (1/0.004) to get the same count rates, since the density in MB can be much higher now.

In order to test the detection limit of our MB sampling system, laboratory air has been measured as follows: the time resolved signals at parent masses of He (mass 4), \( N_2(28) \), \( O_2(32) \), argon (36, 38, and 40), \( \text{CO}_2(44) \), and \( \text{Kr} \) (84) have been measured with 100–10 000 chopper revolutions and the sum of the counts in the peak (the counts within the dashed lines as indicated in Fig. 2) has been corrected for (i) the background signal measured out of the peak (average signal between 10 and 60 ms), (ii) the corresponding ionization cross section, and (iii) the known mass dependent transmission of the MS. The species concentrations from such corrected and revolution averaged signals are compared in Table I with literature values. It is demonstrated that even Krypton atoms with only 0.65 ppm can be detected (21 counts in the peak compared to six counts in background in 10 000 revolutions), showing the sensitivity limit of this setup. Additionally, the composition distortion mentioned above can be seen with lighter particles being more discriminated than heavier particles. This discrimination is typical for free jets and we omit for the moment detailed discussion of this phenomenon.

In order to check the capabilities of our sampling system for radical detection, atomic oxygen is measured in a \( \text{He}/O_2 \) atmospheric pressure microplasma jet. The plasma is generated between two metal electrodes 1 mm apart, 1 mm wide and 30 mm long at atmospheric pressure in \( \text{He} \) gas (flow 1.4 slm) with addition of up to 2% of \( O_2 \). The effluent of this jet contains \( O \) atoms up to the distance of several millimeters. More details can be found elsewhere. An electron energy of 15 eV is selected in the MS ionizer in order to avoid dissociative ionization of \( O_2 \) molecules. The applied power was 20 W, the \( \text{He} \) flow 1.4 slm, and the exit of the microplasma jet was at 2 mm distance from the sampling orifice. Figure 4 shows the time resolved \( O \) signal at 0.6% of \( O_2 \) in \( \text{He} \) with 76 counts in the peak and on average 0–9 counts in the background measured in 3147 revolutions. The \( \text{He} \) signal measured under the same conditions is shown for comparison. The inset in Fig. 4 shows the \( O \) count rates (counts in the peak corrected for the averaged background counts) per 1000 revolutions as a function of the \( O_2 \) flow. The same trend has been measured by two-photon laser induced fluorescence revealing a maximum \( O \) density of \( 1.4 \times 10^{14} \text{ m}^{-3} \) (\( \sim 5 \) ppm) at 0.6% of \( O_2 \) addition. Our preliminary estimation of the \( O \) density based on calibration measurements with known amount of Neon gas in the jet gives the density approximately ten times higher. This is most likely due to small differences in the microplasma jet design.

### Table I. Composition of the air.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Measured</th>
<th>Literature</th>
<th>Gas</th>
<th>Measured</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.79 ppm</td>
<td>5.24 ppm</td>
<td>(^{36}\text{Ar})</td>
<td>0.0006%</td>
<td>0.0006%</td>
</tr>
<tr>
<td>(N_2)</td>
<td>68.71%</td>
<td>78.08%</td>
<td>(^{40}\text{Ar})</td>
<td>1.10%</td>
<td>0.93%</td>
</tr>
<tr>
<td>(O_2)</td>
<td>30.11%</td>
<td>20.94%</td>
<td>(\text{CO}_2)</td>
<td>0.073%</td>
<td>0.038%</td>
</tr>
<tr>
<td>(^{36}\text{Ar})</td>
<td>0.0054%</td>
<td>0.0031%</td>
<td>(^{84}\text{Kr})</td>
<td>1.62 ppm</td>
<td>0.65 ppm</td>
</tr>
</tbody>
</table>
and the measurement in a stagnation flow configuration. More details will be given elsewhere.\textsuperscript{11}

To conclude, the MBMS sampling system employing a rotating skimmer which acts as a closable sampling orifice has been developed and tested. The measurement of the composition of laboratory air has shown, that species with concentrations down to subppm levels can be detected. When applied to a He/O\textsubscript{2} atmospheric pressure microplasma jet, O atoms have been detected.

The authors thank V. Schulz-von der Gathen and N. Knake for fruitful discussions and the assistance with the microplasma jet.

\begin{thebibliography}{9}
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\end{thebibliography}

FIG. 4. (Color online) He (mass 4, 26 eV electron energy, 1038 revolutions) and O (mass 16, 15 eV electron energy, 3147 revolutions) signals as measured from the He/O\textsubscript{2} plasma jet. Time resolution of x-axis is 20 s. The inset shows the count rates of O at different O\textsubscript{2} flows.