

Supplementary Materials: Part A

1 Correction for measured electron densities

In equation (48), the effective width of the plasma is arbitrary, but the definition of plasma width based on the FWHM value of the spontaneous emission profile in the direction of beam propagation is a reasonable value which has previously been applied for comparable electron density measurements in CO₂ microwave plasmas [1, 2].

The narrow H₂O plasma diameters, which go down to 1.5 mm at certain high power conditions may lead to deviations from the infinite slab approximation. In practice the diagnostic beam (which has a beam waist of 4.5 mm at the location of the plasma, will only partially overlap with the plasma in the radial direction and lead to an underestimation of the phase shift of the portion of the beam that passes through the plasma region. As the measured phase shift through the plasma represents an average of the beam power propagate through the plasma over the total beam power, a correction factor for the electron density in a finite H₂O in the infinite slab calculation can be obtained by considering the overlap integral of the plasma with the power density profile of the beam.

The power density pattern of a beam with power P with Gaussian distributions in x and y directions perpendicular to its direction of propagation may be expressed as

$$f(x, y) = \frac{2P}{s_x s_y \pi} \exp \left(-2 \left(\frac{x^2}{s_x^2} + \frac{y^2}{s_y^2} \right) \right), \quad (1)$$

where $s_x = s_y$ are the spot radii in the x and y direction (defined based on the $\frac{1}{e}$ width of the power).

The fraction of power that propagates through the plasma column with radius s_p (defined based on the $\frac{1}{e}$ width of the emission intensity) and length L is

$$\begin{aligned} \frac{P_{\text{through plasma}}}{P_{\text{total}}} &= \\ \frac{\int_{-L/2}^{L/2} \int_{-s_p}^{s_p} \frac{2P}{s_x s_y \pi} \exp \left(-2 \left(\frac{x^2}{s_x^2} + \frac{y^2}{s_y^2} \right) \right) dx dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{2P}{s_x s_y \pi} \exp \left(-2 \left(\frac{x^2}{s_x^2} + \frac{y^2}{s_y^2} \right) \right) dx dy} & \quad (2) \\ &= \int_{-L/2}^{L/2} \int_{-s_p}^{s_p} \frac{2P}{s_x s_y \pi} \exp \left(-2 \left(\frac{x^2}{s_x^2} + \frac{y^2}{s_y^2} \right) \right) dx dy. \end{aligned}$$

As previously noted, the beam propagation calculations show that the diagnostic beam spot radius is 4.5 mm (in both x and y direction) at the location of the plasma. Figure 1 shows the phase shift correction required to account for the finite plasma width (expressed as the FWHM of the emission profile) in infinite slab approximation calculation. Here the plasma radius is taken as the $\frac{1}{e}$ value of the full intensity – ($\frac{1}{e}$ radius values can be calculated by $\frac{FWHM * 1.21}{2}$). As the plasma length always greatly exceeds the beam size, plasma length variations have a negligible influence on the calculation outcome.

2 Hydrogen production through H₂O plasmolysis in a microwave plasma

The direct plasma-assisted H₂O splitting is investigated as an approach to plasma-chemical generation of H₂. In this light, preparation work for H₂O plasma processing has been made and preliminary

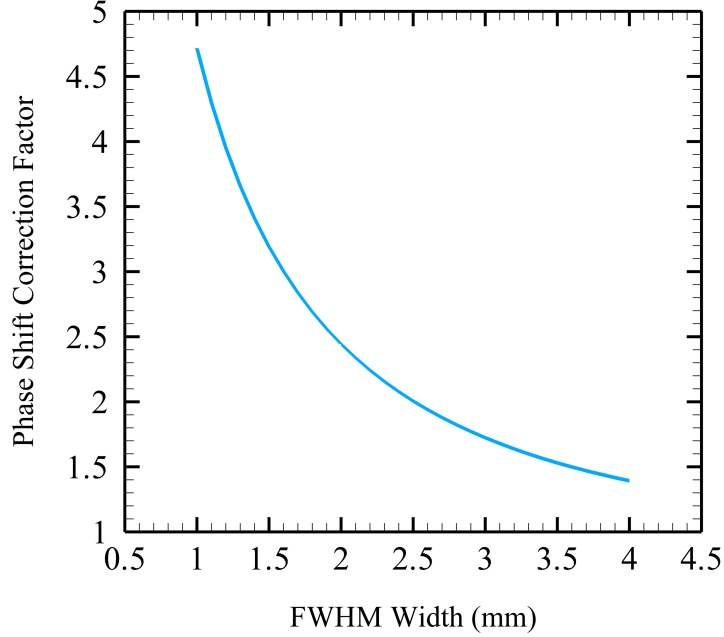


Figure 1: Calculated correction factors for measured phased shift versus assumed width of the plasma (FWHM of the spontaneous emission profile).

performance measurements have been done on pure water plasmolysis in a microwave plasma reactor as described in the main part of the paper.

The conversion of H_2O can be defined based on a mole fractions x_i of products and reactants in the exhaust gas mixture

$$\alpha = \frac{x_{\text{H}_2}}{x_{\text{H}_2} + x_{\text{H}_2\text{O}}}. \quad (3)$$

The efficiency of a conversion process is defined based on the ratio of energy input and reaction enthalpy for dissociation, similar to (50).

$$\eta = \alpha \frac{\Delta H}{E_v}, \quad (4)$$

where E_v is the specific energy input, or average energy absorbed in the plasma process per injected H_2O molecule. The efficiency of this process in the H_2O microwave plasma is determined based on measurements of effluent composition using a 3-channel gas chromatograph (GC) (InterScience CompactGC 4.0). The effluent is sampled and analysed downstream from the plasma. Individual components of interest (N_2 , O_2 , H_2 , CO_2 and He) are quantified based on response factors determined from external standards. The gas chromatograph and sampling system are designed to accept gas samples with high water concentrations at sub-atmospheric pressure conditions dictated by the plasma process. Limitations apply, particularly in the lower limit of sampling pressure the current approach permits of approximately 100 mbar.

The water flow (administered by a Bronkhorst El-Flow liquid mass flow controller and ASteam DV4 evaporator) is injected in the reactor as steam at a temperature of 180°C . Despite heating of critical components in the sampling line, condensation of water vapor could not be fully prevented. Therefore, the concentration of plasma products in the gaseous mixture in the sampling lines is corrected in the composition analysis by means of an internal standard of Helium. The He component admixed prior

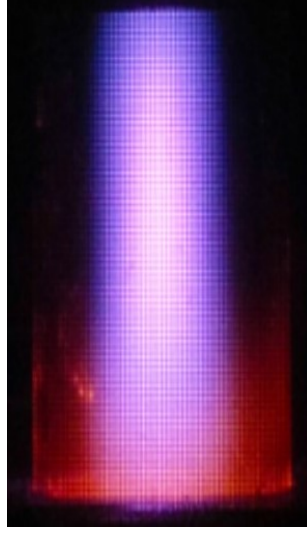


Figure 2: Plasma discharge appearance in 98.70% H_2O in a trace of He at 190 mbar microwave induced plasma.

to injection with known proportion to the steam flow rate, is used to quantify the magnitude of the condensation effect between plasma and GC sample by evaluating the change in its concentration in the measured analyte. Since the trace gas does not react, the factor of concentration increase C of the components in the measured sample (superscript S) with respect to the exhaust composition (superscript ex) due to the partial loss of water from the sample by condensation in the sampling line. C is determined from known and measured mole fractions of He

$$C = \frac{x_{He}^S}{x_{He}^{ex}} = x_{He}^S \frac{\Gamma_{H_2O}^{in} (1 + \frac{1}{2}\alpha) + \Gamma_{He}^{in}}{\Gamma_{He}^{in}}. \quad (5)$$

The value of C also links the measured mole fractions of H_2 and O_2 in the sample to their original respective mole fractions in the exhaust gas

$$x_{H_2}^{ex} = \frac{x_{H_2}^S}{C}, \quad (6)$$

$$x_{O_2}^{ex} = \frac{x_{O_2}^S}{C}. \quad (7)$$

Lastly, by definition, the sum of mole fractions of the exhaust gas mixture should equate to unity

$$x_{H_2O}^{ex} + x_{O_2}^{ex} + x_{H_2}^{ex} + x_{He}^{ex} = 1. \quad (8)$$

By substitution of equation eqs. (5) to (8) into equation (3) we obtain an expression of α in terms of the sampled concentration values

$$\alpha = \frac{x_{H_2}^S}{C - x_{O_2}^S - x_{He}^S}, \quad (9)$$

which for small values of $\alpha \ll 1$ simplifies to

$$\alpha \approx \frac{x_{H_2}^S}{x_{He}^S \left(\frac{\Gamma_{H_2O}^{in}}{\Gamma_{He}^{in}} \right) - x_{O_2}^S}, \quad (10)$$

where $\left(\frac{\Gamma_{H_2O}^{in}}{\Gamma_{He}^{in}}\right)$ represents the known ratio of volumetric flow rates of H_2O and He in the input gas mixture.

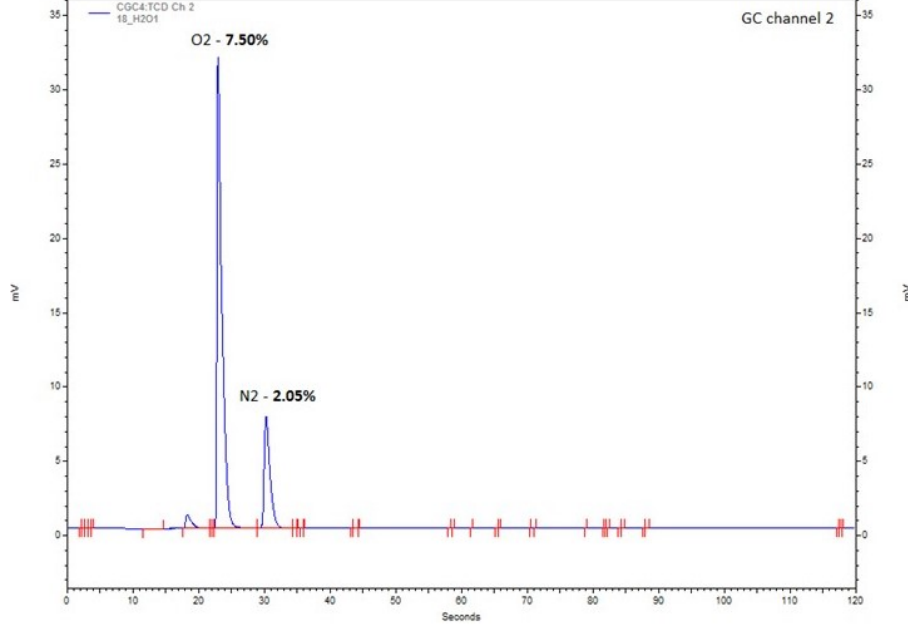


Figure 3: Chromatogram channel 2 in 98.70% H_2O in a trace of He at 190 mbar microwave induced plasma.

The experimental operating conditions of the plasma experiment are described in the main part of the paper 6.1. The visual appearance of the discharge is shown in figure 2. Here gas flows from top to bottom. The plasma has a diffuse appearance. The downstream portion of the plasma (lower side of the discharge) shows a red-hot glow of the containing quartz tube, indicating the rapid exothermic recombination of plasma products to H_2O in that region.

The fixed input volumetric flow of water and He gives $\left(\frac{\Gamma_{H_2O}^{in}}{\Gamma_{He}^{in}}\right) = 66.7$ under assumption of ideal gas conditions. The chromatograms of the effluent samples under these conditions are shown in figures 3 and 4. The mole fractions determined from the component peak areas are listed in table 1. Concentrations are calculated from response factors based on calibration gas mixtures (Linde HiQ) with accurately known concentrations. The relatively high uncertainty in the mole fraction of Helium results from its response factor, which, in contrast to the other gas components, was based on an external standard obtained from preset mass flow controllers rather than pre-mixed calibrated mixtures.

Table 1: Mole fraction of the sampled gas mixture.

Component	Mole fraction x_i^S	Note
N_2	0.0205	small air contents due to over-venting during pressure equilibration 0.0695 when corrected for air contents
O_2	0.075	
H_2	0.1421	
He	0.302 ± 0.040	

Note the presence of N_2 peak in the chromatograms, which indicates the penetration of a small

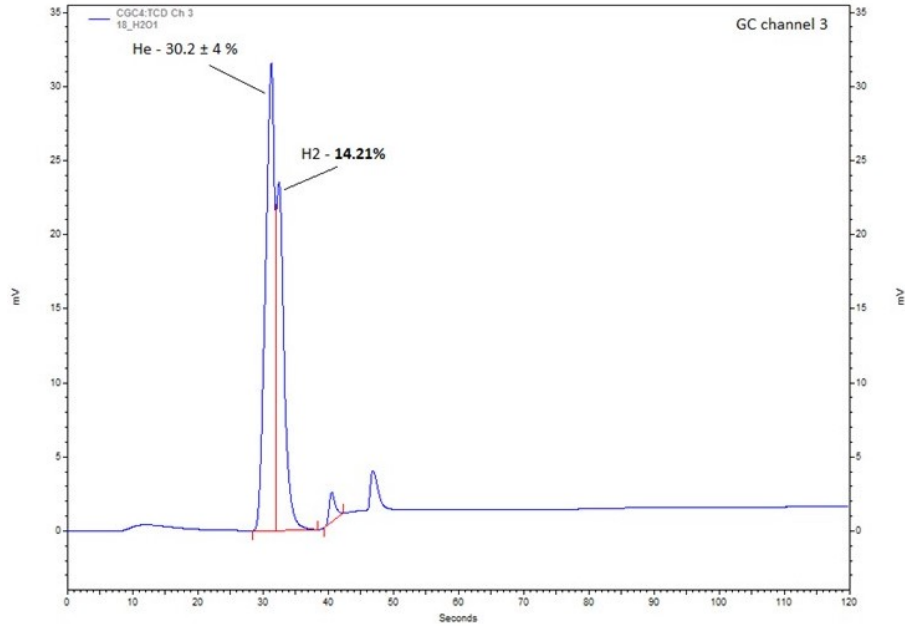


Figure 4: Chromatogram channel 3 in 98.70% H_2O in a trace of He at 190 mbar microwave induced plasma.

quantities of air during the ample pressure equalization to atmospheric conditions further condensation of H_2O . While this air contamination in the sample influences the O_2 concentration, this value can be corrected based on the known N_2/O_2 ratio in air. After correcting the O_2 concentration, the stoichiometric ratio of O_2 and H_2 of 1:2 is obtained as to be expected for the H_2O dissociation reaction.

Using equation (10) and (4), a conversion factor $\alpha = 0.75 \pm 0.15\%$ and energy efficiency $\eta = 1.2 \pm 2\%$ are obtained.

References

- [1] A.J. Wolf, T.W.H Righart, F.J.J Peeters, P.W.C Groen, M.C.M van de Sanden, and W A Bongers. Characterization of CO_2 microwave plasma based on the phenomenon of skin-depth-limited contraction. *Plasma Sources Science and Technology*, 28(11):115022, nov 2019.
- [2] A J Wolf, T W H Righart, F J J Peeters, W A Bongers, and M C M van de Sanden. Implications of thermo-chemical instability on the contracted modes in CO_2 microwave plasmas. *Plasma Sources Science and Technology*, 29(2):025005, feb 2020.