DESCRIPTION OF THE THERMOSPRAY FORMED AT LOW FLOW RATE IN TS-FF-AAS BASED ON HIGH-SPEED IMAGES

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ABSTRACT. The mechanism of the thermospray formed at low flow rates using peristaltic pump in thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is here described for the first time. The study was based on magnified images of the thermospray formed inside the hot tube furnace by using a high-speed CMOS camera. For this purpose different image acquisition speeds were used (from 1000 to 18000 frames/s), revealing that the thermospray obtained under such conditions is quite different from those already reported. The frames of the thermospray evolution allow us to purpose a mechanism for its formation, indicating that the Leindenfrost effect plays an important role. The analysis of the images contributed to calculate parameters related to thermospray formation, such as pulse incidence average (110 ± 10, 320 ± 50 and 1200 ± 150 pulses per second) and pulse speed (6 ± 1, 10 ± 1 and 14 ± 2 m s^{-1}) for 0.1, 0.4 and 1.0 mL min^{-1} flow rate, respectively for both parameters. Additionally, the evaporation constant (λ) of 10^{-4} m^2 s^{-1} was esteemed and the present thermospray was

correlated to the conventional sprays using the Sauter mean diameter (SMD) parameter, which ranged from *ca*. 2 to 44 µm. In order to correlate the information obtained through images with analytical parameters employing the thermospray, the sensitivities for cadmium determination at each condition (0.12, 0.11 and 0.069 s L µg^{-1} for 0.1, 0.4 and 1.0 mL min^{-1} flow rate, respectively) were taken into account.

Figure S-1. Images of the liquid jet evolutions during thermospray formation using water at 0.4 mL min^{-1} flow rate, obtained at 1000 **(a)**, 3000 **(b)**, 6000 **(c)**, 10000 **(d)** and 18000 fps **(e)**.

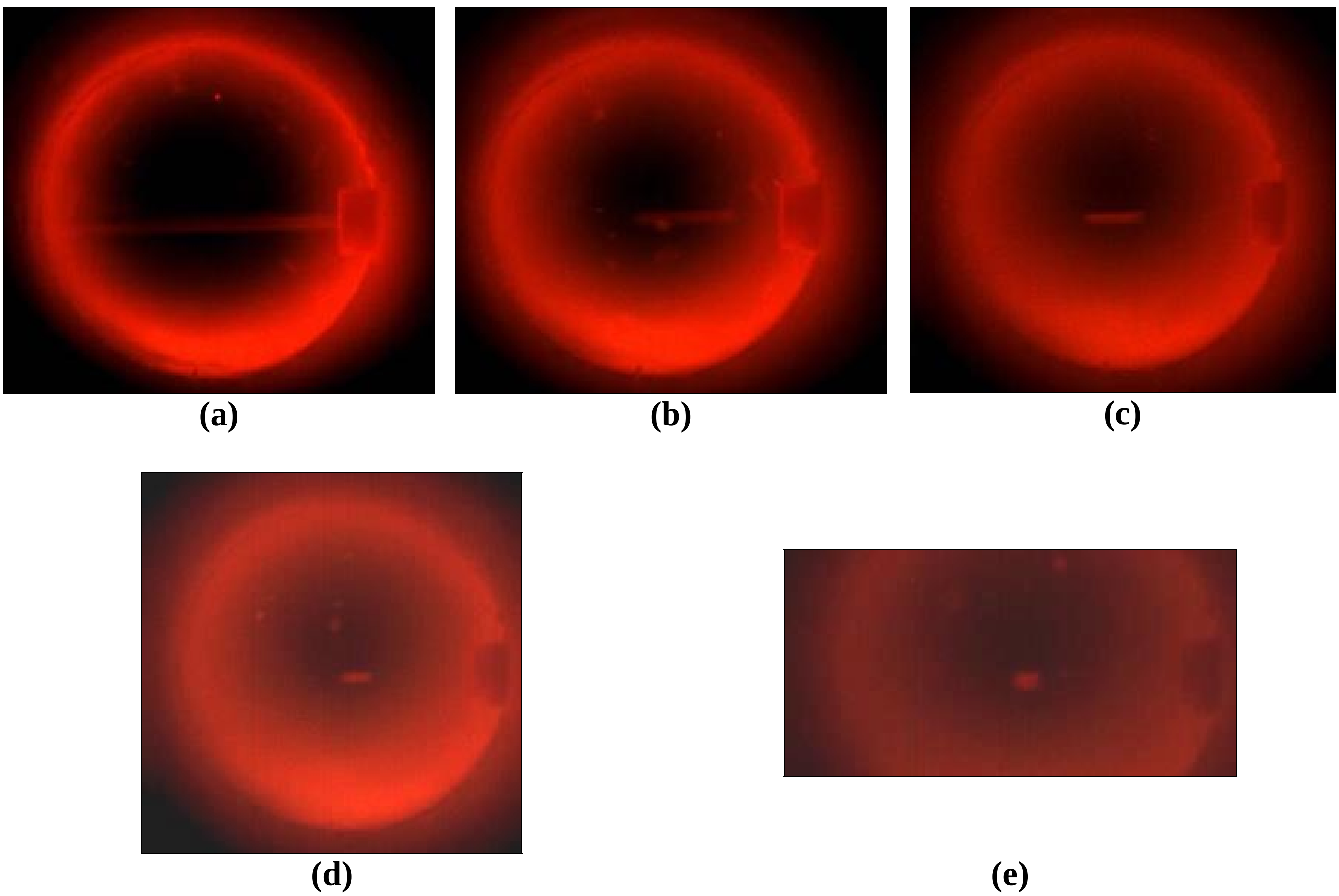
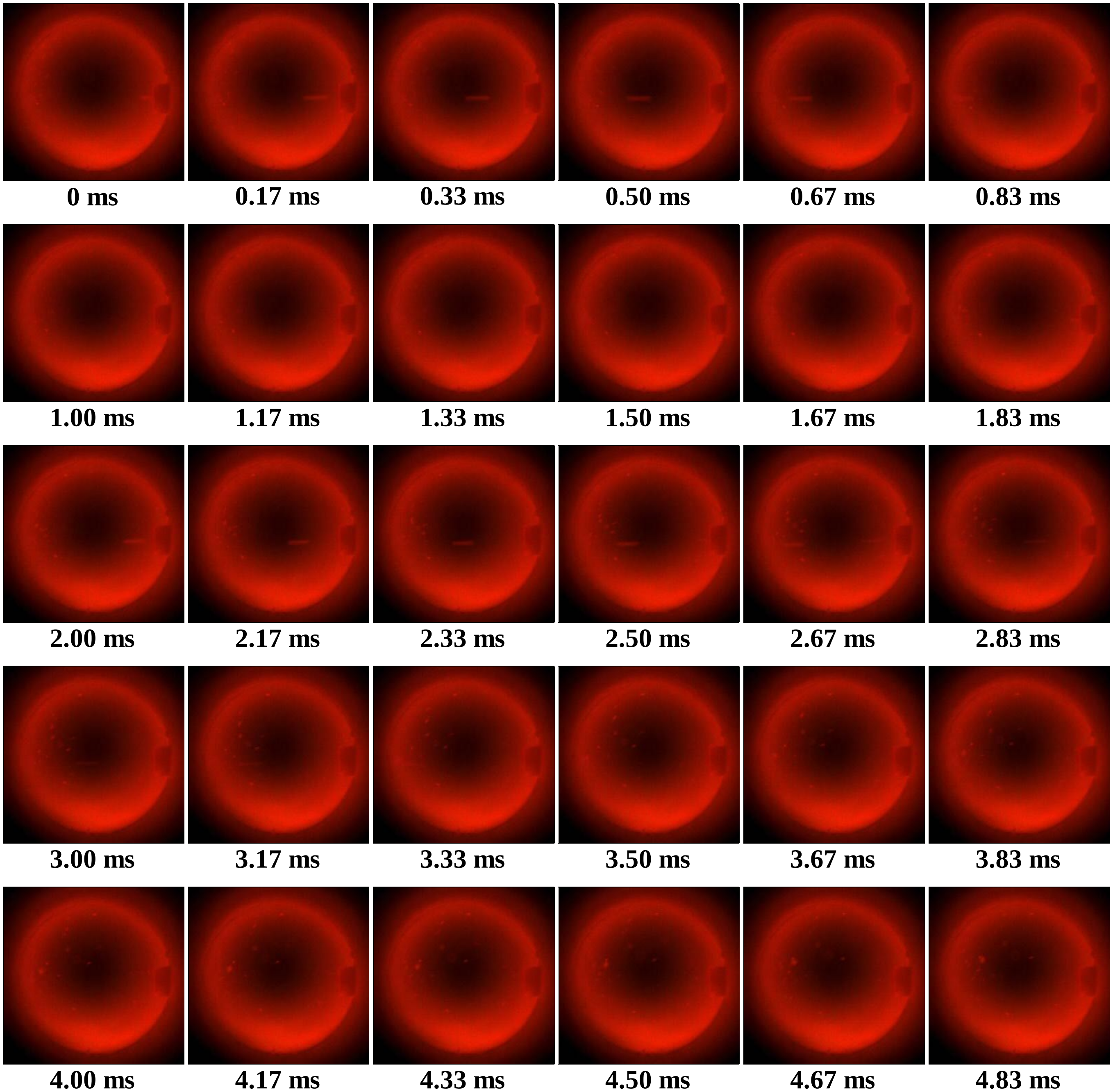
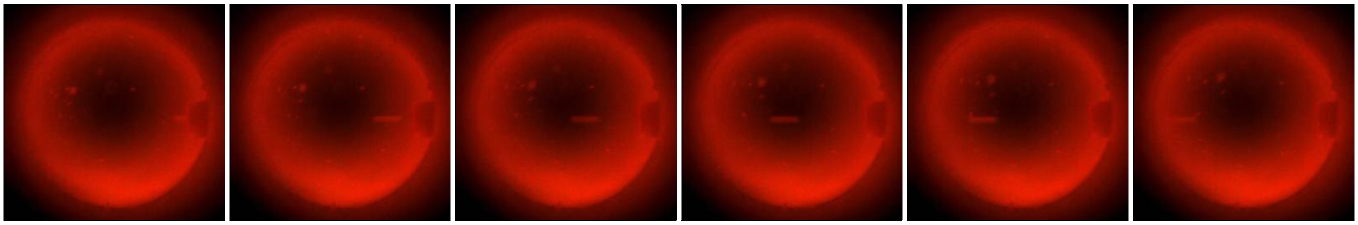
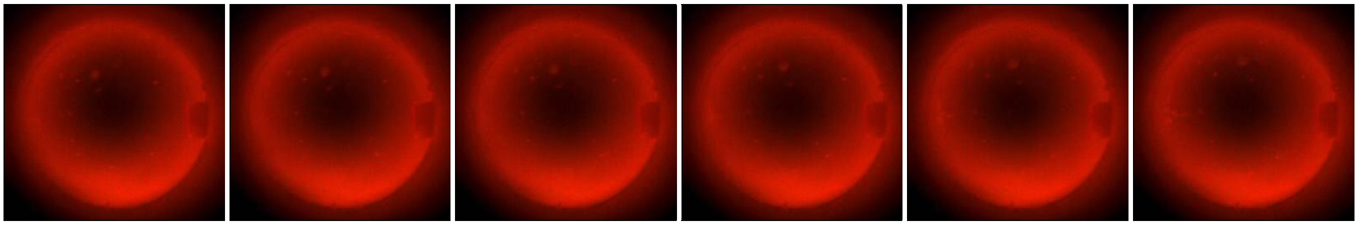


Figure S-2. Extensive milliseconds sequence (33 ms) of the thermospray formation of water at 0.4 mL min^{-1} flow rate, obtained with a CMOS camera operating at 6000 fps and 1/6000 s. Images show liquid jets issuing from the ceramic capillary tip, fling across the nickel furnace and impacting on the opposite wall, until total vaporization process, guided by Leidenfrost effect.

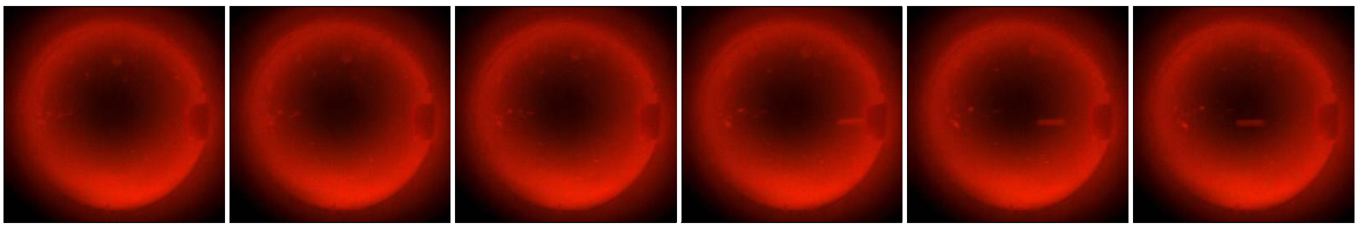




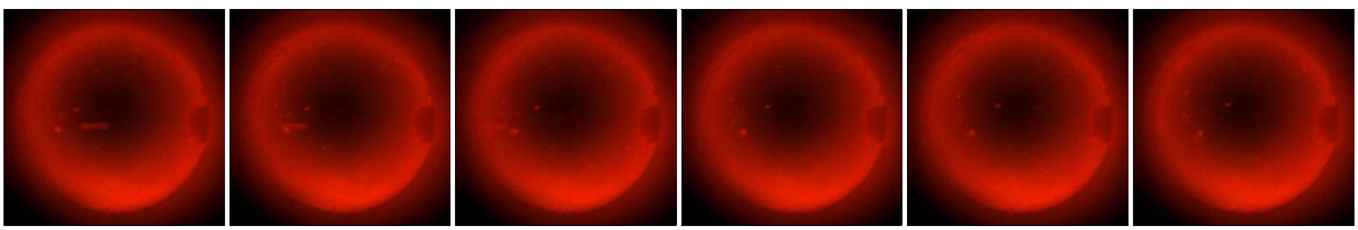
5.00 ms | 5.17 ms | 5.33 ms | 5.50 ms | 5.67 ms | 5.83 ms



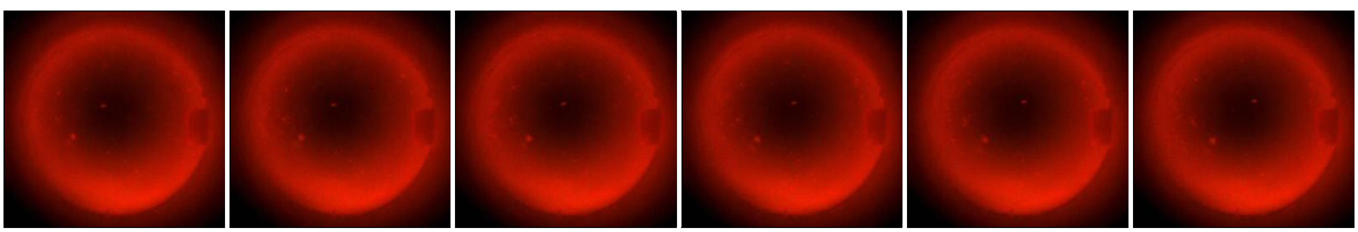
6.00 ms | 6.17 ms | 6.33 ms | 6.50 ms | 6.67 ms | 6.83 ms



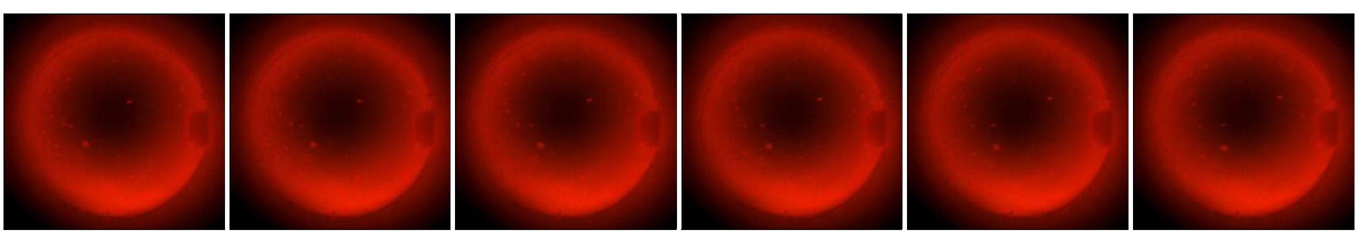
7.00 ms | 7.17 ms | 7.33 ms | 7.50 ms | 7.67 ms | 7.83 ms



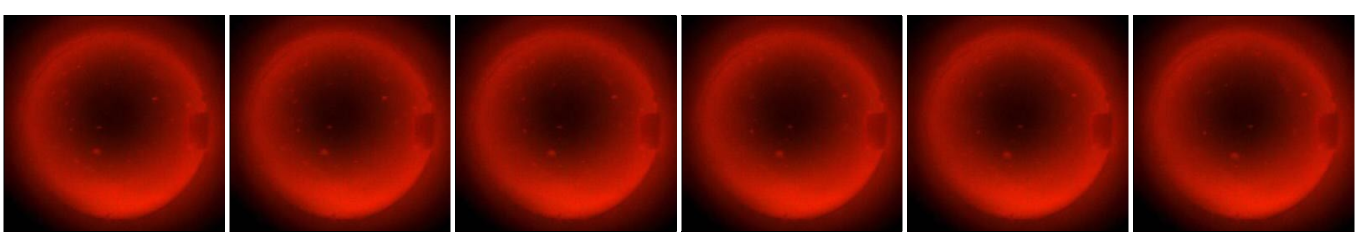
8.00 ms | 8.17 ms | 8.33 ms | 8.50 ms | 8.67 ms | 8.83 ms



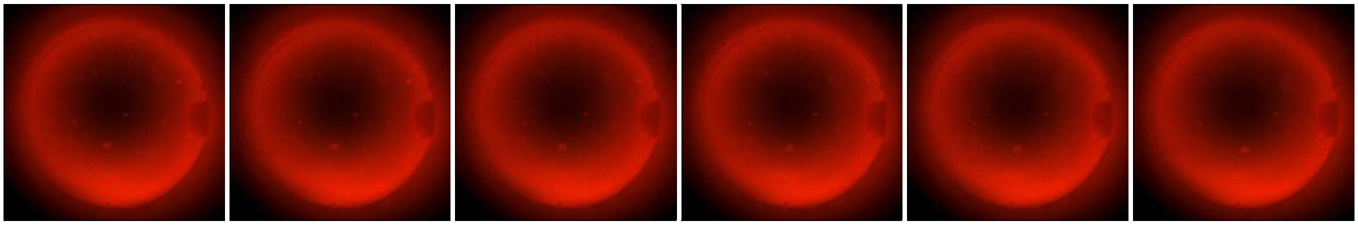
9.00 ms | 9.17 ms | 9.33 ms | 9.50 ms | 9.67 ms | 9.83 ms



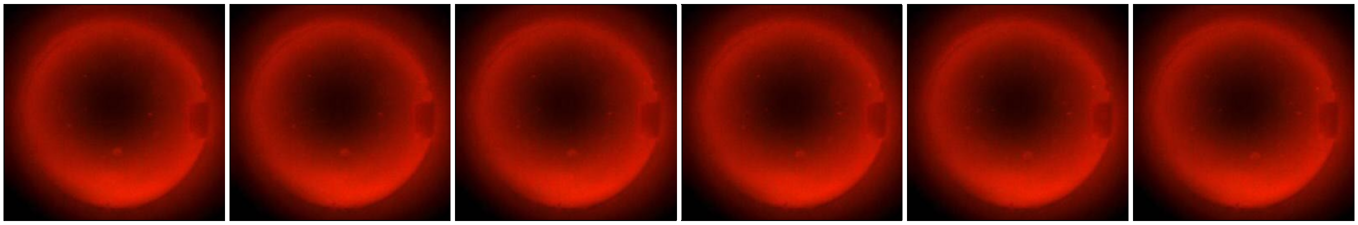
10.00 ms | 10.17 ms | 10.33 ms | 10.50 ms | 10.67 ms | 10.83 ms



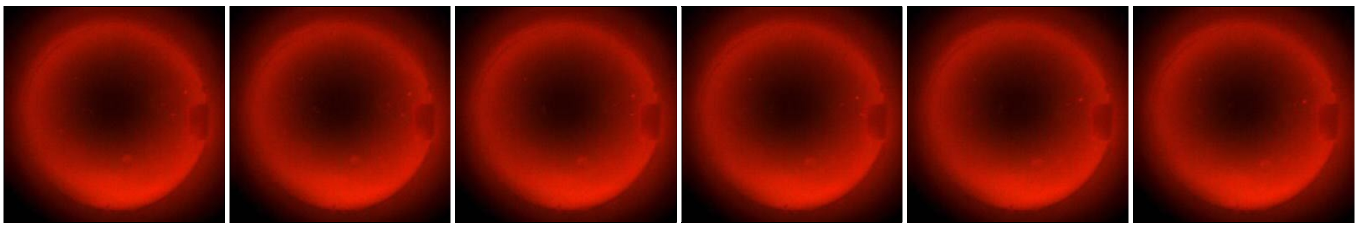
11.00 ms | 11.17 ms | 11.33 ms | 11.50 ms | 11.67 ms | 11.83 ms



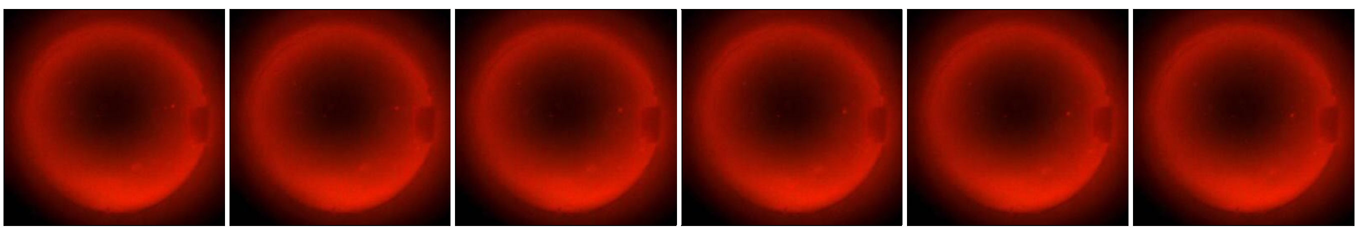
12.00 ms **12.17 ms** **12.33 ms** **12.50 ms** **12.67 ms** **12.83 ms**



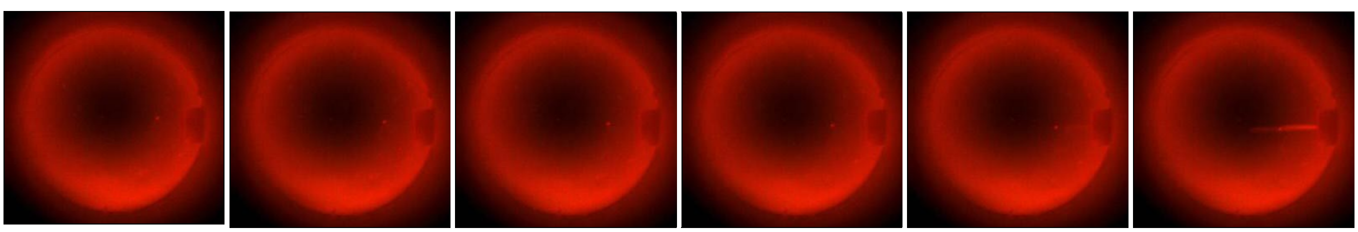
13.00 ms **13.17 ms** **13.33 ms** **13.50 ms** **13.67 ms** **13.83 ms**



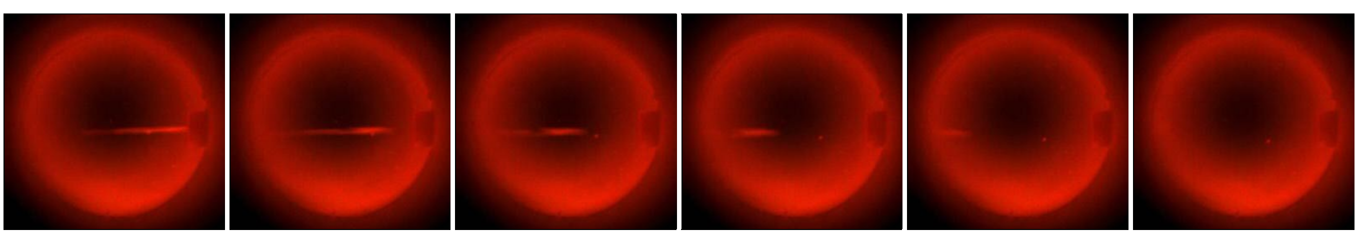
14.00 ms **14.17 ms** **14.33 ms** **14.50 ms** **14.67 ms** **14.83 ms**



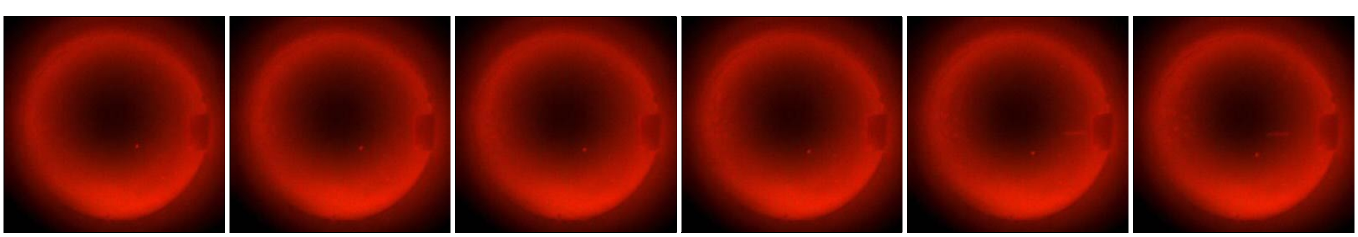
15.00 ms **15.17 ms** **15.33 ms** **15.50 ms** **15.67 ms** **15.83 ms**



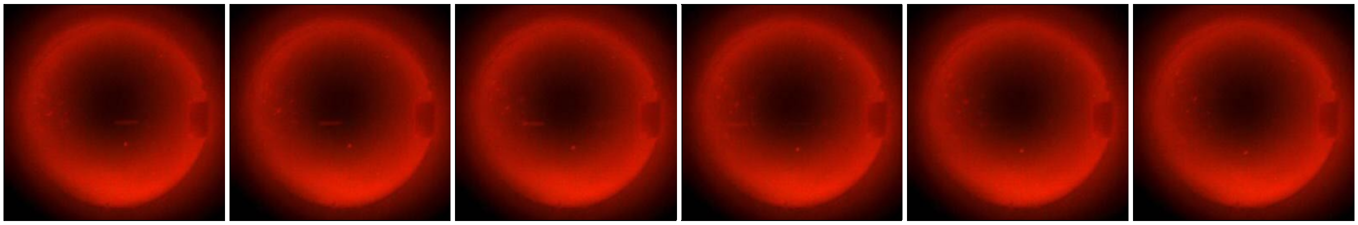
16.00 ms **16.17 ms** **16.33 ms** **16.50 ms** **16.67 ms** **16.83 ms**



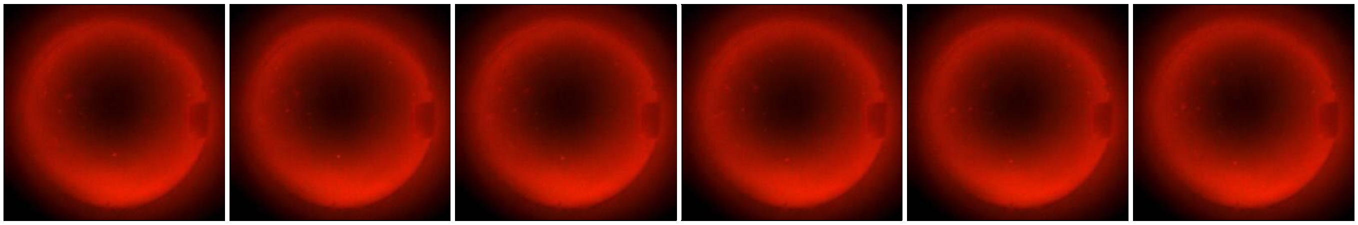
17.00 ms **17.17 ms** **17.33 ms** **17.50 ms** **17.67 ms** **17.83 ms**



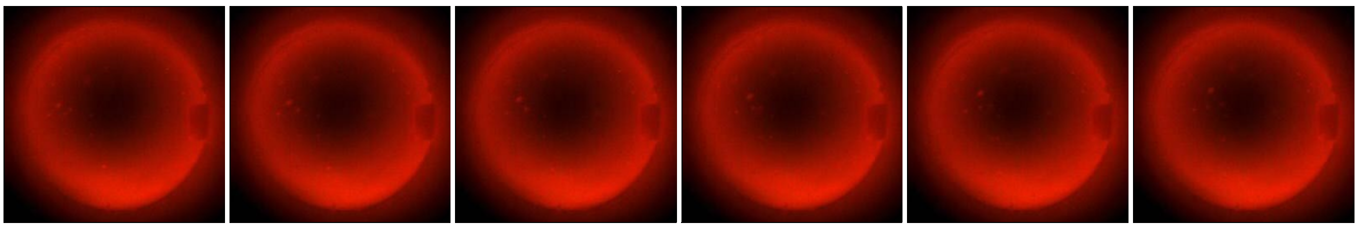
18.00 ms **18.17 ms** **18.33 ms** **18.50 ms** **18.67 ms** **18.83 ms**



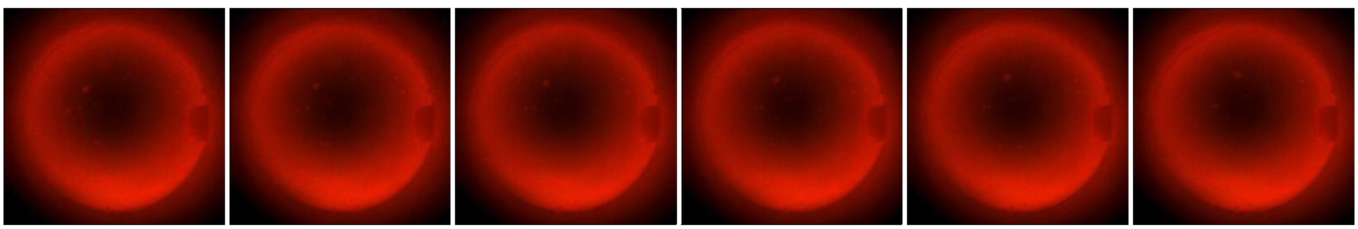
19.00 ms **19.17 ms** **19.33 ms** **19.50 ms** **19.67 ms** **19.83 ms**



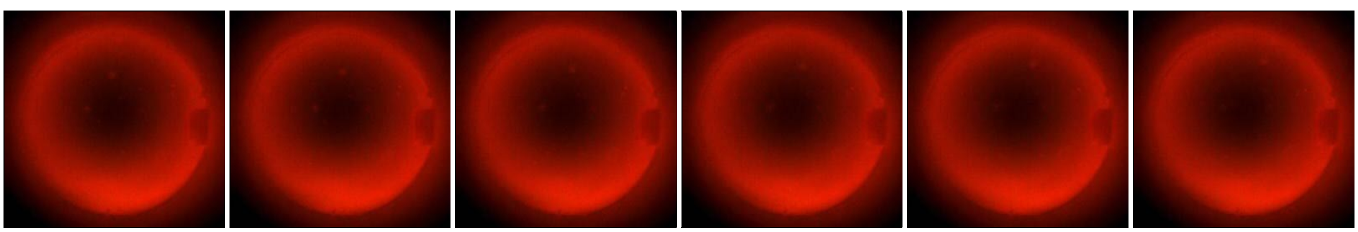
20.00 ms **20.17 ms** **20.33 ms** **20.50 ms** **20.67 ms** **20.83 ms**



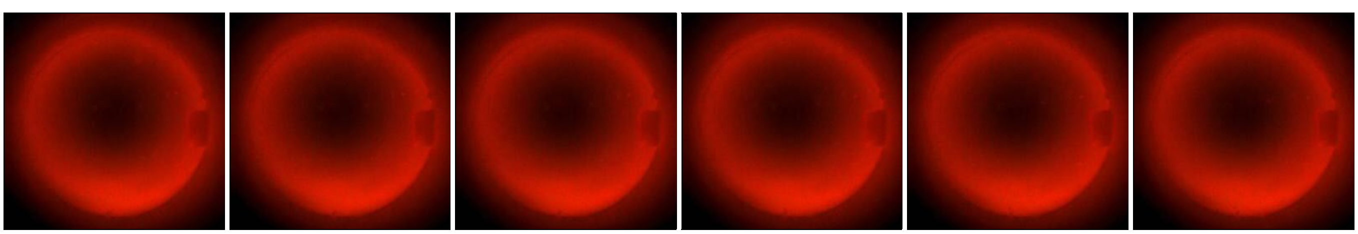
21.00 ms **21.17 ms** **21.33 ms** **21.50 ms** **21.67 ms** **21.83 ms**



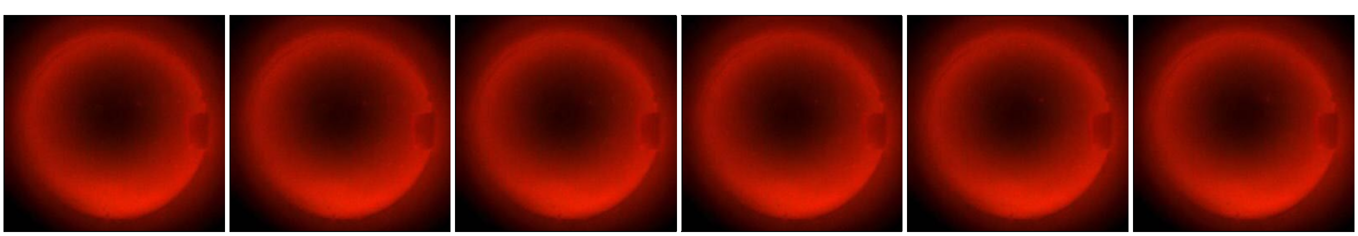
22.00 ms **22.17 ms** **22.33 ms** **22.50 ms** **22.67 ms** **22.83 ms**



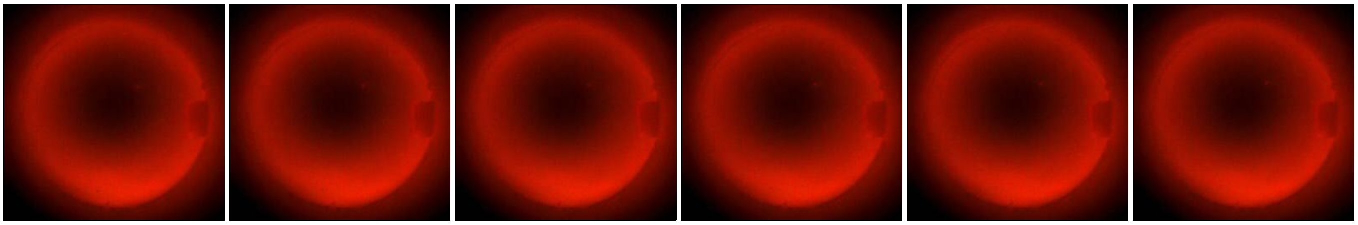
23.00 ms **23.17 ms** **23.33 ms** **23.50 ms** **23.67 ms** **23.83 ms**



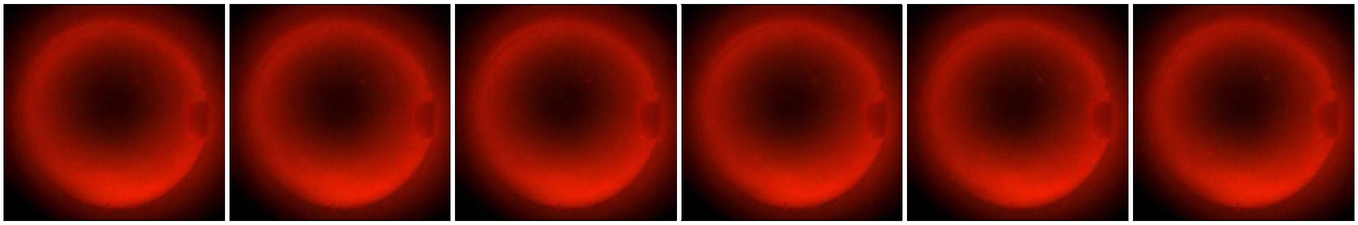
24.00 ms **24.17 ms** **24.33 ms** **24.50 ms** **24.67 ms** **24.83 ms**



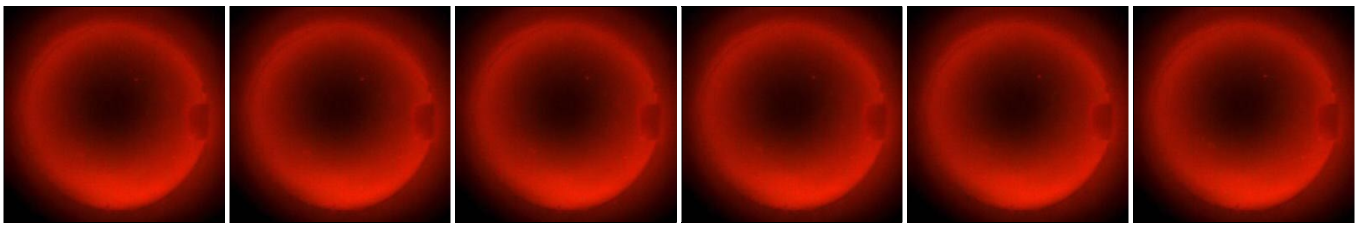
25.00 ms **25.17 ms** **25.33 ms** **25.50 ms** **25.67 ms** **25.83 ms**



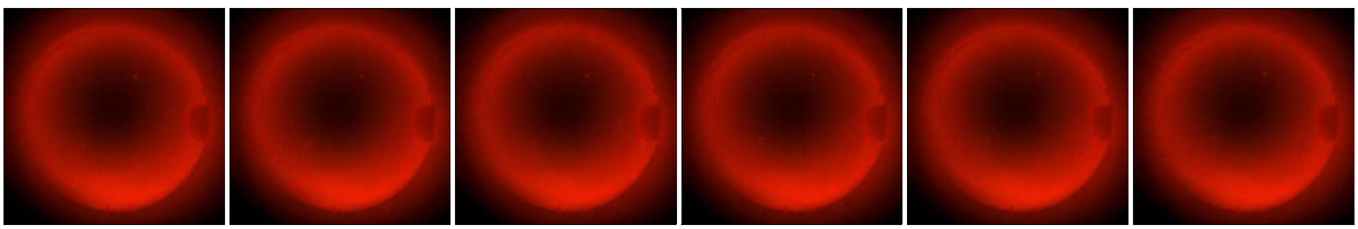
26.00 ms 26.17 ms 26.33 ms 26.50 ms 26.67 ms 26.83 ms



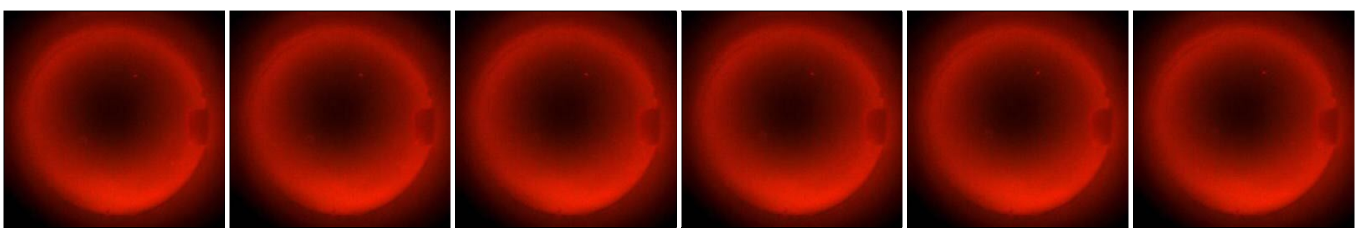
27.00 ms 27.17 ms 27.33 ms 27.50 ms 27.67 ms 27.83 ms



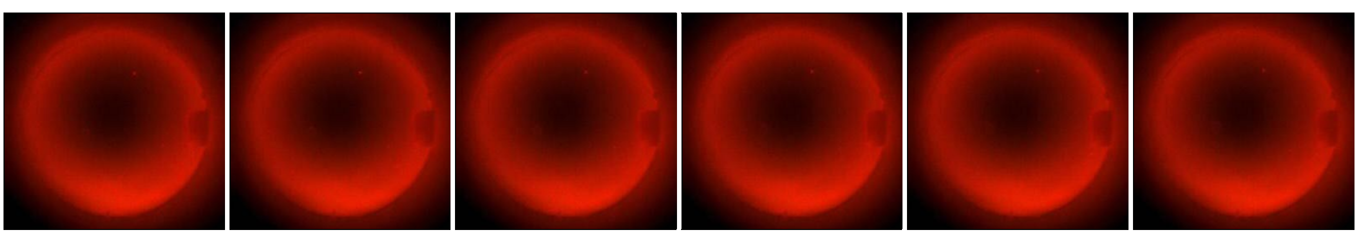
28.00 ms 28.17 ms 28.33 ms 28.50 ms 28.67 ms 28.83 ms



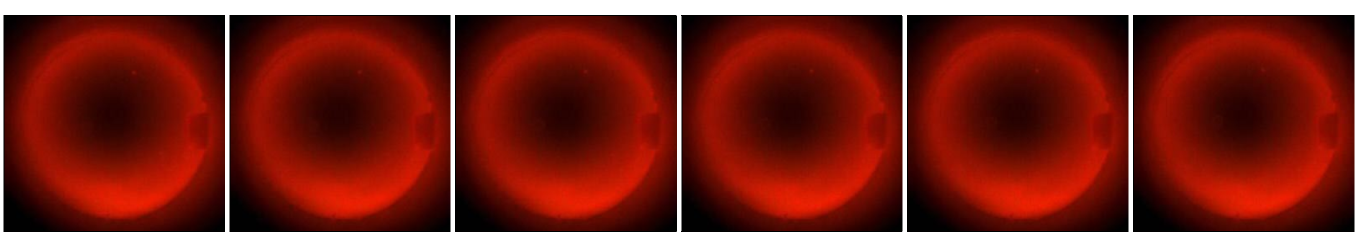
29.00 ms 29.17 ms 29.33 ms 29.50 ms 29.67 ms 29.83 ms



30.00 ms 30.17 ms 30.33 ms 30.50 ms 30.67 ms 30.83 ms



31.00 ms 31.17 ms 31.33 ms 31.50 ms 31.67 ms 31.83 ms



32.00 ms 32.17 ms 32.33 ms 32.50 ms 32.67 ms 32.83 ms

Figure S-3. Schematic representation of the thermospray formation. Water is carried towards the ceramic capillary edge (time t_0), which is heated in the flame. With fast heating, just a part of the water vaporizes and new gaseous phase “protects” the rest of the liquid from direct thermal conduction much probably due to the Leidenfrost effect (t_1). These liquid and gaseous phases are ejected inside the furnace (t_2) and the liquid pulse flies crossing the tube, until its impact on the opposite hot furnace wall (t_3). Then, a great amount of droplets are formed and they bounce back from the heated furnace wall, once again probably due to the Leidenfrost effect (t_4), followed by their vaporization (t_5). Then, a new liquid pulse is formed (t_6) and it is ejected inside the furnace (t_7).