SUPPORTING INFORMATION

HIGH-SENSITIVITY AND HIGH-SPEED SINGLE-PARTICLE INDUCTIVELY COUPLED PLASMA SPECTROMETRY WITH THE CONICAL TORCH

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S1. Description of the Particle Introduction System

Since the droplets generated by the microdrop generator were relatively large (i.e., 50 µm), their associated Stokes number was much larger than one. This meant that a carrier gas could not be typically used to transfer the droplets to the torch. Since the torch was operated horizontally, without the necessary arrangements, it proved to be almost impossible to carry the droplets within the injector tube. Naturally, the droplets would fall under the effect of gravity and hit the inner wall of the injector tube at some point before reaching the plasma. Therefore, the ultimate purpose of the designed particle introduction system, as schematically shown in **Figure S1**, was to facilitate the transport of droplets by desolvating them, and make sure the resulting particles reached the plasma.

Several different designs and/or strategies were iterated. For example, increasing the carrier gas velocity was tried, but proved to be ineffective. It was decided to desolvate the droplets to make them light enough such that the carrier gas could carry them. One common method would be to use heat to desolvate the droplets as shown by many researchers. For example, Olesik et al. used a furnace for this purpose.[1-2] They reported good stability and precision (better than 5%) with relatively high furnace temperatures of around 500°C when the device was operated vertically. However, if the device was to be operated horizontally, the temperature of the furnace had to be increased to as high as 800 – 900°C in order to ensure successful transfer of droplets to the plasma, while the precision would be compromised (e.g., 10% – 20%).[3-4] Aside from the high temperature, several other components such as heater, insulation, spray chamber, electrical circuitry, etc., was needed. As a simpler alternative, helium-assisted desolvation has been proposed based on the fact that the binary diffusion coefficient of water vapor in helium is higher than in argon. Since diffusion coefficient in a binary gas system is proportional to the square root of the reduced mass, using helium as desolvation gas would lead to a higher evaporation rate for the droplets.[5-6] Additionally, thermal conductivity of He is more than 8 times higher than that of argon which enhances the desolvation process. In fact, it was shown that using helium instead of argon would lead to three times faster desolvation for the droplets at room temperature.

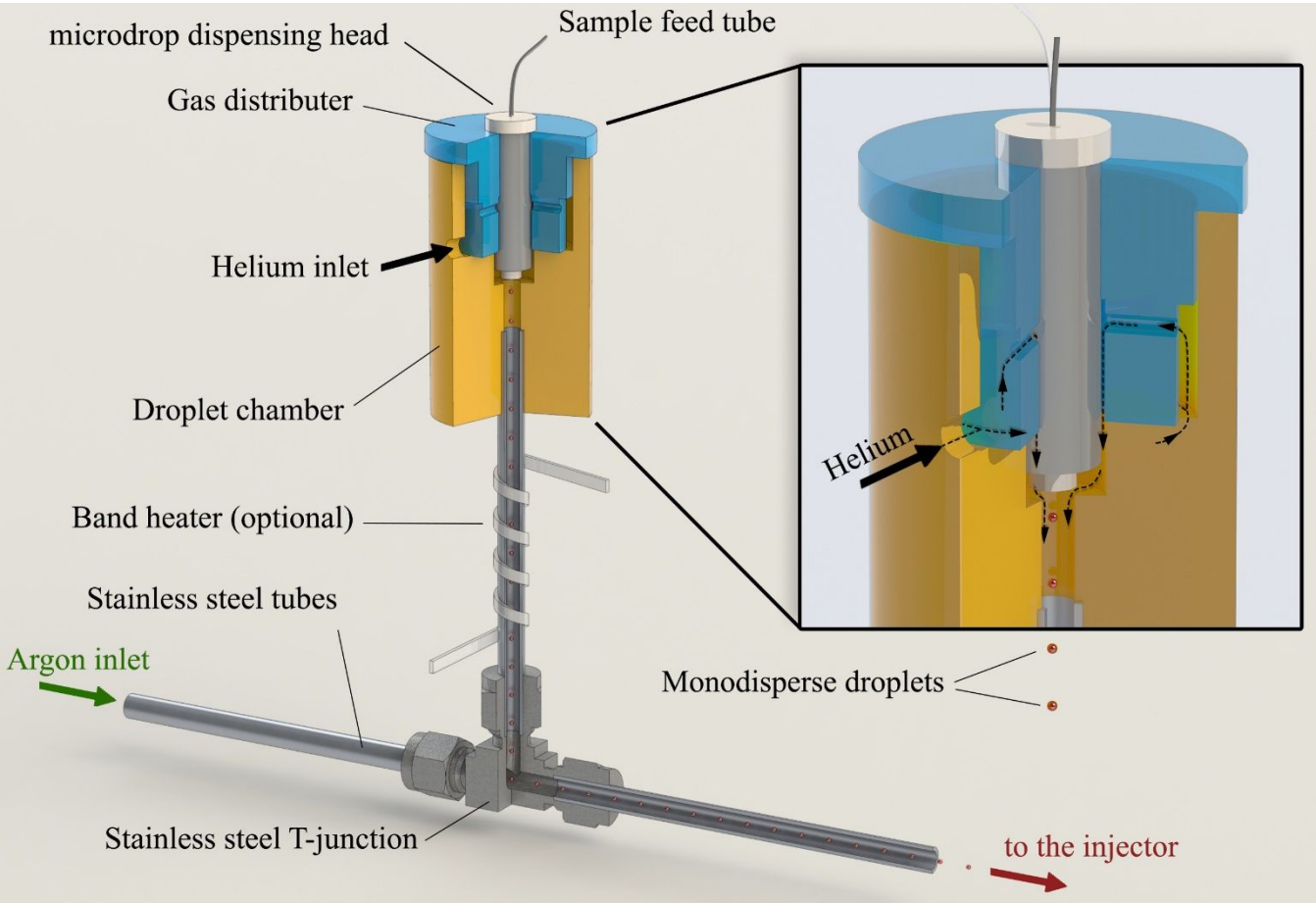

Figure S1. Sectioned view of the particle introduction system with its various components. The inset shows a magnified view of the droplet chamber, gas distributor, and dispenser head with the arrows showing the flow path of the helium desolvation gas.

In this work, after several iterations, we designed a new particle introduction system based on the idea of helium-assisted desolvation.[5-6] A 3D model of this system is shown in **Figure S1**. This system is mainly comprised of a chamber coupled with a gas distributer (both machined out of polycarbonate) which embraced the microdrop dispenser head. The purpose of the gas distributer is to form a laminar, uniform, thin layer of He flow around the tip of the dispenser head to smoothly carry the generated droplets throughout the tubes. Based on the direction arrows in **Figure S1,** helium first enters the chamber through a side inlet port and, after

being evenly distributed around the chamber, goes into the thin annular area between the dispenser head and the distributor through six straight holes. It then flows along the annular area, in strictly a non-swirling manner, toward the tip of the dispenser head for carrying the droplets. O-rings (not shown in **Figure S1**) were implemented at suitable positions between the chamber, distributor, and the dispenser head to prevent helium from leaking. This design proved to work reliably and smoothly deliver a train of droplets at its outlet (inset of **Figure S1**).

After emerging from the chamber, the droplets entered a ¼ inch stainless steel tube which was positioned vertically to serve as a vessel in which the droplets could desolvate. Different lengths were tested for this tube. When the length was too short, the droplets did not have enough time to desolvate and, therefore, deposited in the horizontal portion of the introduction path later on. On the other hand, too long a length made it difficult to align the tube in order to prevent the droplets from hitting the inner wall of the tube at some point. A length of about 30 cm was found to be appropriate. Also, aside from stainless steel, polycarbonate and PTFE tubes were tested as well, but failed to work satisfactorily due to being prone to static charge. In general, static electricity was found to be one of the major culprits in deflecting the droplets from their main path. For example, if the operator carried any static charge and approached the system within a few tens of centimeters, the droplets were seen to be deflected and hit the inner walls due to the electric field. For this reason, except for the chamber and gas distributer, all the other components of the introduction system were made out of stainless steel and properly grounded.

After the vertical path, the desolvated droplets entered a stainless steel T-junction to be directed toward the plasma (**Figure S1**). The T-junction was connected to the injector tube via another stainless steel tube which was coupled with a ball-joint terminal at its other end. To deflect and push the droplets in the horizontal direction, a make-up argon gas was also fed to the junction from the opposite side via another tube. The length of this tube was chosen long enough to allow for the gas flow to be fully developed and any possible flow circulations to dissipate. It was concluded that a slight mismatch in the inner diameters of these tubes and the T-junction would lead to formation of recirculation zones and fluctuations in the flow which deteriorated the stability of droplet transport. Therefore, we made sure that the inner diameters of the tubes throughout the whole system were identical. The advantage of using a make-up gas was threefold. First, without changing the He flow rate and the desolvation process of droplets, the Ar flow rate could be adjusted for signal optimization purposes. Second, it was observed that addition of argon led to improved signal intensities compared to when only helium was used as both make-up and desolvation gas. Third, when needed, it could be used to introduce aerosol by connecting a conventional nebulizer/spray chamber. An application of this last features is when nanoparticles or cells are nebulized into the plasma for analysis, and monodisperse desolvated particles can be employed for simultaneous calibration.[7]

The highest particle introduction rate that the system could achieve using He as desolvation gas was around 100 – 150 particles/s. Higher rates would cause the He gas in the vertical stainless steel tube to be saturated and lead to incomplete desolvation and unsuccessful transport of the particles. For this reason, an optional band heater was also wrapped around the vertical stainless steel tube connected to the droplet chamber (**Figure S1**). The heater was covered with alumina-silica blanket for insulation, and a thermocouple was inserted between the band heater and the stainless steel tube to control the temperature (not shown in **Figure S1**). The heater was only used when high particle introduction rates (i.e., 1000 – 2000 particles/s) were desired. With all the mentioned arrangements, the droplets could be desolvated (with or without the heater, depending on the particle introduction rate) and transported to the plasma in a consistent fashion. Unlike some other works wherein a small increase or decrease in the carrier gas flow rate was reported to cause instability and interruption in particle transport, [5-7] we could successfully change the make-up gas flow rate from 0.05 L/min to beyond 1 L/min as needed.

S2. References

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