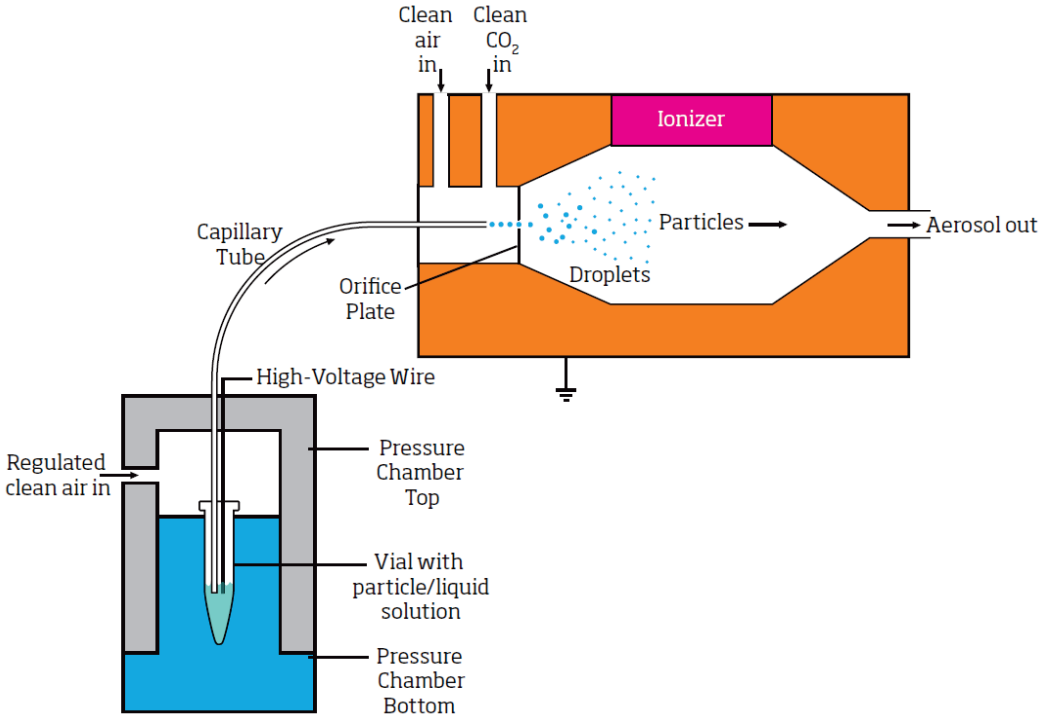
# ELECTROSPRAY OPERATION USING NITROGEN IN PLACE OF AIR

APPLICATION NOTE 3480-002

## Electrospray Aerosol Generator

The Electrospray Aerosol Generator (EAG) Model 3480 is used to generate monodisperse aerosol particles as small as 3 nm in diameter. The EAG pushes a charged liquid solution or suspension through a capillary tube and exerts an electrical field on the liquid at the capillary tip. Typical EAG operation uses a mixed flow of air and carbon dioxide ($CO_2$) to evaporate the liquid and transport the dried aerosol particles.




The EAG is used to generate a variety of nanoparticle and macromolecular aerosols for calibration, research, and quality-control applications. The use of air and $CO_2$ may not be suitable for air-sensitive samples. Therefore, the EAG was operated using nitrogen ($N_2$) in place of air, and the $CO_2$ flow was varied, to determine the limits of EAG operation using $N_2$ and $CO_2$.

## Methods

The EAG was used as part of the LiquiScan-ES (Model 3980), which combines the EAG with a Scanning Mobility Particle Sizer™ Spectrometer (Model 3936) to measure particle size distributions. Dry, filtered air and high-purity (>99.999%) $N_2$ and $CO_2$ gases were used. A silicon dioxide ($SiO_2$) nanoparticle standard material (30 nm ± 5%; TSI, P/N 6005269) was electrosprayed at ~0.05 wt% in 20 mM ammonium acetate; the $SiO_2$ standard is known to contain dissolved residue. The particle size distribution of the standard was measured using air and $N_2$ mixed with $CO_2$.

## Results

Table 1 shows the operating conditions of the EAG during stable cone-jet spraying using air and $N_2$ at 1.5 L/min and different $CO_2$ flow rates. Operating voltage and current were similar using air with and without $CO_2$. For EAG operation using $N_2$, voltage was decreased slightly to maintain a stable current of approximately -230 nA as $CO_2$ flow decreased from the nominal value of 0.1 L/min. At $CO_2$ flow rates less than 0.05 L/min, stable operation was not possible using $N_2$.

**Table 1.** Electrospray Aerosol Generator Operation Using Air and $N_2$ Mixed with $CO_2$

| | Air | | Nitrogen | | | |
|---|---|---|---|---|---|---|
| $CO_2$ flow rate (L/min) | 0.1 (nominal) | 0 | 0.1 (nominal) | 0.075 | 0.05 | < 0.05 |
| EAG voltage (kV) | 2.04 | 2.04 | 2.00 | 1.92 | 1.80 | — |
| Current (nA) | -230 ± 1 | -238 ± 2 | -232 ± 1 | -231 ± 1 | -228 ± 2[1] | — |

[1]Infrequent spikes in current were observed, up to -260 nA

For all particle size measurements, a 25-µm capillary was used, and a stable cone-jet spraying mode was achieved. All particle size distributions are the average of three scans. No adjustments were made to the gas viscosity, density, and pressure in Aerosol Instrument Manager® software.

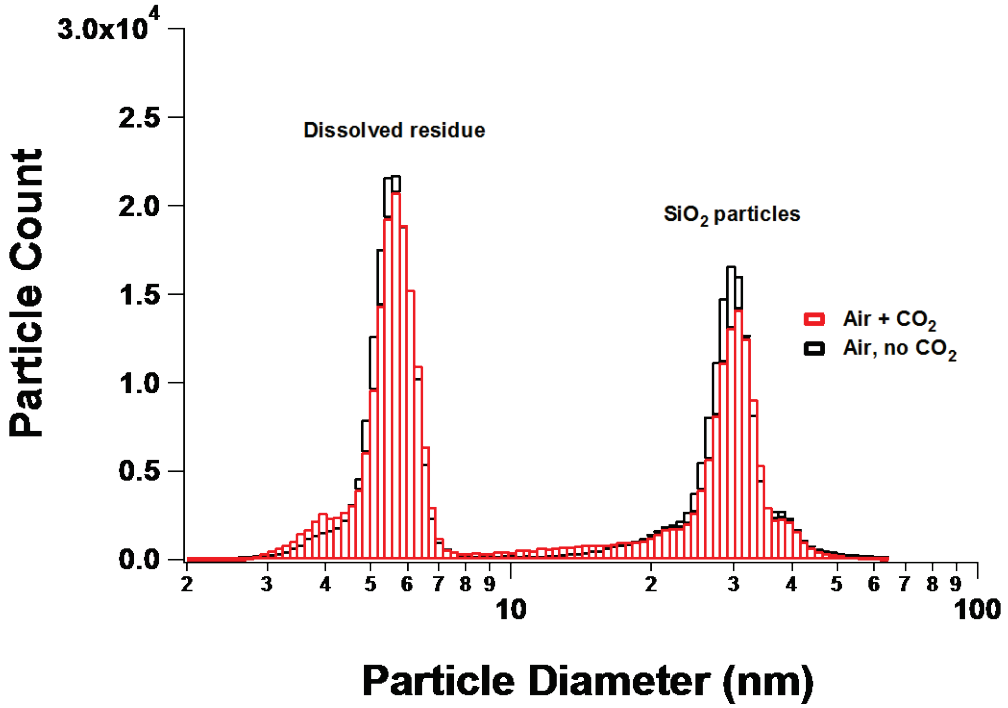



**Figure 1.** Particle size distribution of $SiO_2$ standard using air with and without $CO_2$. The $SiO_2$ particles were accurately sized at 28.9 nm. A residue peak was observed at 5.5 nm due to soluble impurities. The results with and without $CO_2$ were similar.
(Air flow = 1.5 L/min; $CO_2$ flow = 0.1 or 0 L/min).

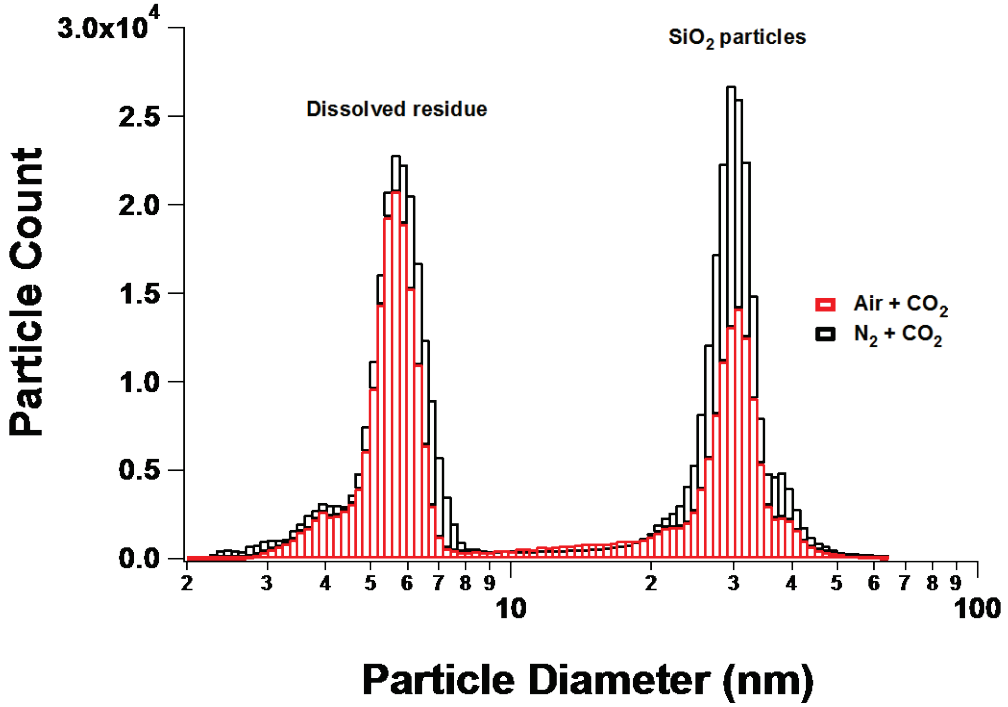



**Figure 2.** Particle size distribution of $SiO_2$ standard using air and $N_2$ with $CO_2$ at the nominal flow rate. The $SiO_2$ particles were accurately sized at 28.9 nm in both gases. The size of the residue particles was consistent in both gases. The $SiO_2$ particle count was higher using $N_2$, while the particle count for the residue was similar in both gases.
(Air flow = $N_2$ flow = 1.5 L/min; $CO_2$ flow = 0.1 L/min).

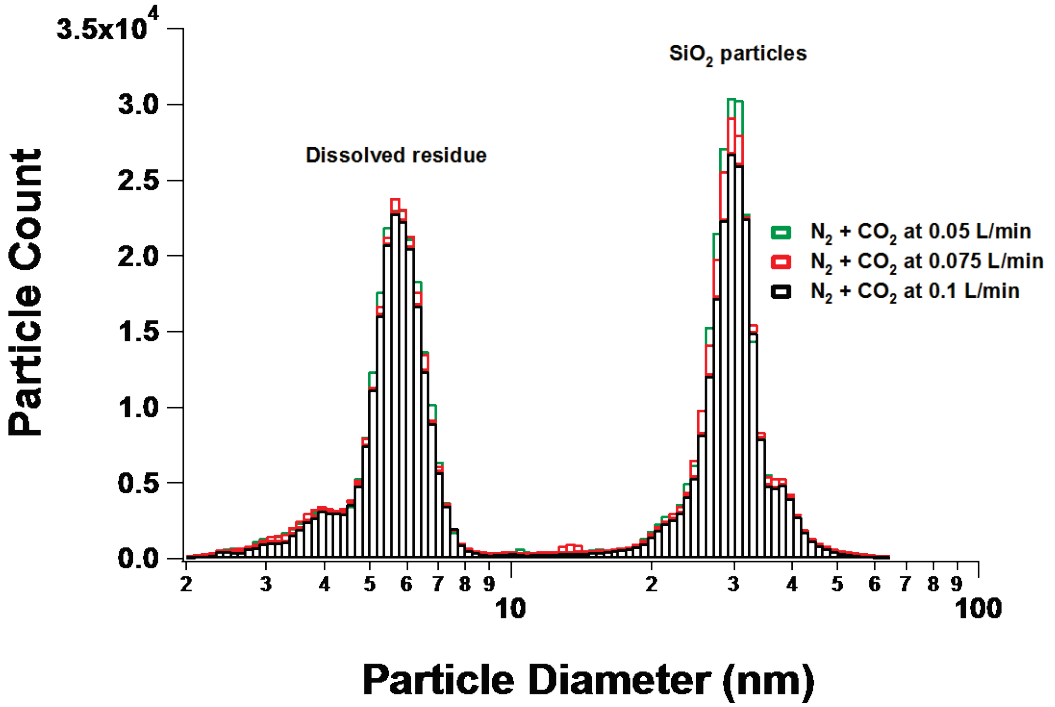



**Figure 3.** Particle size distribution of $SiO_2$ standard using $N_2$ with various $CO_2$ flow rates. The $SiO_2$ particles were accurately sized at 28.9 nm at $CO_2$ flow rates down to 0.05 L/min. The size of the residue particles was consistent in both gases. The $SiO_2$ particle count increased slightly as $CO_2$ flow rate decreased, while the residue particle count was similar at all $CO_2$ flow rates. At $CO_2$ flow <0.05 L/min, the sample could not be electrosprayed; a droplet was observed at the capillar tip, but the droplet was not drawn away from the tip at any voltage (0–3.5 kV). ($N_2$ flow = 1.5 L/min).

The gas used in an electrospray must be able to sustain the electric field required to achieve and maintain stable operation. Dielectric strength, an intrinsic property of gases, determines the maximum electric field strength that can be sustained before electrical breakdown occurs. As the voltage and electric field strength increase, the gas can become ionized and release free electrons that are accelerated by the electric field. As the electric field exceeds the dielectric strength of the gas, free electrons collide with molecules in the gas, releasing more electrons and forming a conductive path. This phenomenon is called corona discharge. The collision process can lead to a chain reaction, known as an electron avalanche or electrical breakdown. Stable electrospray operation cannot be sustained at voltages that induce corona discharge/electrical breakdown.

To prevent these phenomena, the gas or gas mixture used in an electrospray must be electrically insulating. That is, the gas molecules can remove electrons freed during ionization by attaching to the electrons during collisions. $N_2$ is a non-electron-attaching gas, due to its electronic structure, and has a lower electrical breakdown voltage ($V_B$) than air and $CO_2$. Thus, $N_2$ alone cannot sustain stable electrospray operation. On the other hand, $CO_2$ is an electron-attaching gas. Therefore, adding $CO_2$ to $N_2$, even at < 5%, allows stable electrospray operation at the nominal voltage setting of ~ 2 kV. The $V_B$ of air is significantly higher than that of $N_2$ because $O_2$ is also an electron-attaching gas, and its $V_B$ is much higher than that of $N_2$. Air and $CO_2$ can maintain stable electrospray operation at higher voltages than $N_2$ because they are able to control the acceleration of free electrons and thereby inhibit an electron avalanche.

## Conclusions

The EAG can be operated using $N_2$ in place of air, as long as $CO_2$ is supplied at $\geq$ 0.05 L/min. The sizing of particles using the LiquiScan-ES is not affected by replacing air with $N_2$. The addition of $CO_2$ is necessary to prevent electrical breakdown of the carrier gas during EAG operation using $N_2$.

## References

Meek, J.M. and Craggs, J.D. Electrical Breakdown of Gases, John Wiley, New York (1978).

Spencer, J.N., Bodner, G.M., and Rickard, L.H. Chemistry: Structure and Dynamics, 5th Ed., Wiley (2010)

UNDERSTANDING, ACCELERATED

**TSI Incorporated** – Visit our website **www.tsi.com** for more information.

| | | | |
|---|---|---|---|
| **USA** | **Tel:** +1 800 874 2811 | **India** | **Tel:** +91 80 67877200 |
| **UK** | **Tel:** +44 149 4 459200 | **China** | **Tel:** +86 10 8219 7688 |
| **France** | **Tel:** +33 4 91 11 87 64 | **Singapore** | **Tel:** +65 6595 6388 |
| **Germany** | **Tel:** +49 241 523030 | | |

3480-002 Rev. A (A4)  Printed in U.S.A.