## **Supporting Information**

Selective measurement of Cl<sub>2</sub> and HCl based on Dopant-assisted negative photoionization Ion mobility spectrometer Combined with the Semiconductor Cooling

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This supporting information provides additional information on the following aspects:

Schematic diagram of the online dilution system for obtaining different concentrations of Cl<sub>2</sub> or HCl (Fig.S1); Schematic diagram of the online dilution and humidification system for obtaining different concentrations of Cl<sub>2</sub> or HCl (Fig.S2); The work sequence of the DANP-IMS coupled semiconductor cooling pre-processing method (Fig.S3); The comparison of Cl<sub>2</sub> signal intensity passing through the cold trap and not passing through the cold trap at different concentrations (Fig.S4).

S1. Schematic diagram of the online dilution system for obtaining different concentrations of Cl<sub>2</sub> or HCl.



Fig S1. Schematic diagram of the online dilution system.

As shown in Fig S1, the online dilution system included four mass flow meters for two dilutions. Mass flow meter 1 was used to control the standard  $Cl_2$  or HCl gas flow rate. At the same time, mass flow meter 2 was used to control the flow rate of clean air as the dilution gas. By adjusting the two flow meters, a lower-concentration standard  $Cl_2$  or HCl gas was obtained after the first dilution. Then, mass flow meter 3 was used to control the  $Cl_2$  or HCl flow rate obtained after the first dilution and excess gas was discharged. The mass flow meter 4 was used to control the clean air flow rate for the second dilution, and the desired target concentration of  $Cl_2$  or HCl was obtained. Finally, a triple quick connector adapter was used to connect the DANP-IMS for sampling and discharging of excess gas.

S2. Schematic diagram of the online dilution and humidification system for obtaining different concentrations of Cl<sub>2</sub> or HCl.



Fig S2. Schematic diagram of the online dilution and humidification system.

On the basis of the secondary online dilution in S1, a bubbling bottle was added after the secondary dilution gas to humidify the sample and obtain samples at different humidities.

## S3. The work sequence of the DANP-IMS coupled semiconductor cooling pre-processing method.



Fig S3. Working sequence of DANP-IMS coupled semiconductor cooling pre-processing method.

The process is divided into two phases: the  $Cl_2$  (T0-T3) phase and the total chlorine (T4-T6) phase. The  $Cl_2$  phase includes trap pre-cooling, sample injection at -30 degrees Celsius, purging with drift gas, and trap purging. The pre-cooling phase lasted for one minute, and during the injection phase, the  $Cl_2$  injection volume was 350 ml min<sup>-1</sup> for four minutes. Purging with drift gas stage was performed simultaneously with the trap purge. During purging with drift gas, the drift gas flow rate is set to 2000 mL min<sup>-1</sup> for 2 minutes. At the same time, the inbuilt pump of the trap purged the aqueous portion of the trap, with the thermal purge lasting for 3 minutes and the room temperature purge lasting for 2 minutes.

The total chlorine phase consists of an injection and a purge. During the injection phase, total chlorine was injected at a volume of 400 ml min<sup>-1</sup> for 30 seconds. During the purge phase, the drift gas flow rate was adjusted to 2,000 ml/min for 2 minutes.

S4. The comparison of Cl<sub>2</sub> signal intensity passing through the cold trap and not passing through the cold trap at different concentrations.



Fig S4. Comparison of signal intensity of Cl<sub>2</sub> passing through the cold trap and not passing

through the cold trap at different concentrations.

Due to the trap removing a portion of  $Cl_2$ , the signal intensity of  $Cl_2$  passing through the trap needs to be compared to the signal intensity of total chlorine without passing through the trap to maintain consistency. By comparing the signal intensities under both conditions at the same concentration, the ratio of the signal intensity for  $Cl_2$  passing through the trap to that without passing through the trap is found to be 1:1.2.