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abstract

# Improving single particle ICP–TOFMS using a desolvation sample introduction system and collision cell technology

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## Motivation

- Aerosol species are emitted from various sources, including deserts, vegetation, volcanic activity, and oceans, and are transported over long distances by atmospheric circulation (Figure 1). During transport, aerosols such as mineral dust can be wet or dry-deposited en route and onto the ice sheet where they are preserved in ice layers. By measuring the impurities in the ice layers, the history of climate changes, such as alteration in atmospheric circulation or climate conditions in the source regions, can be reconstructed.

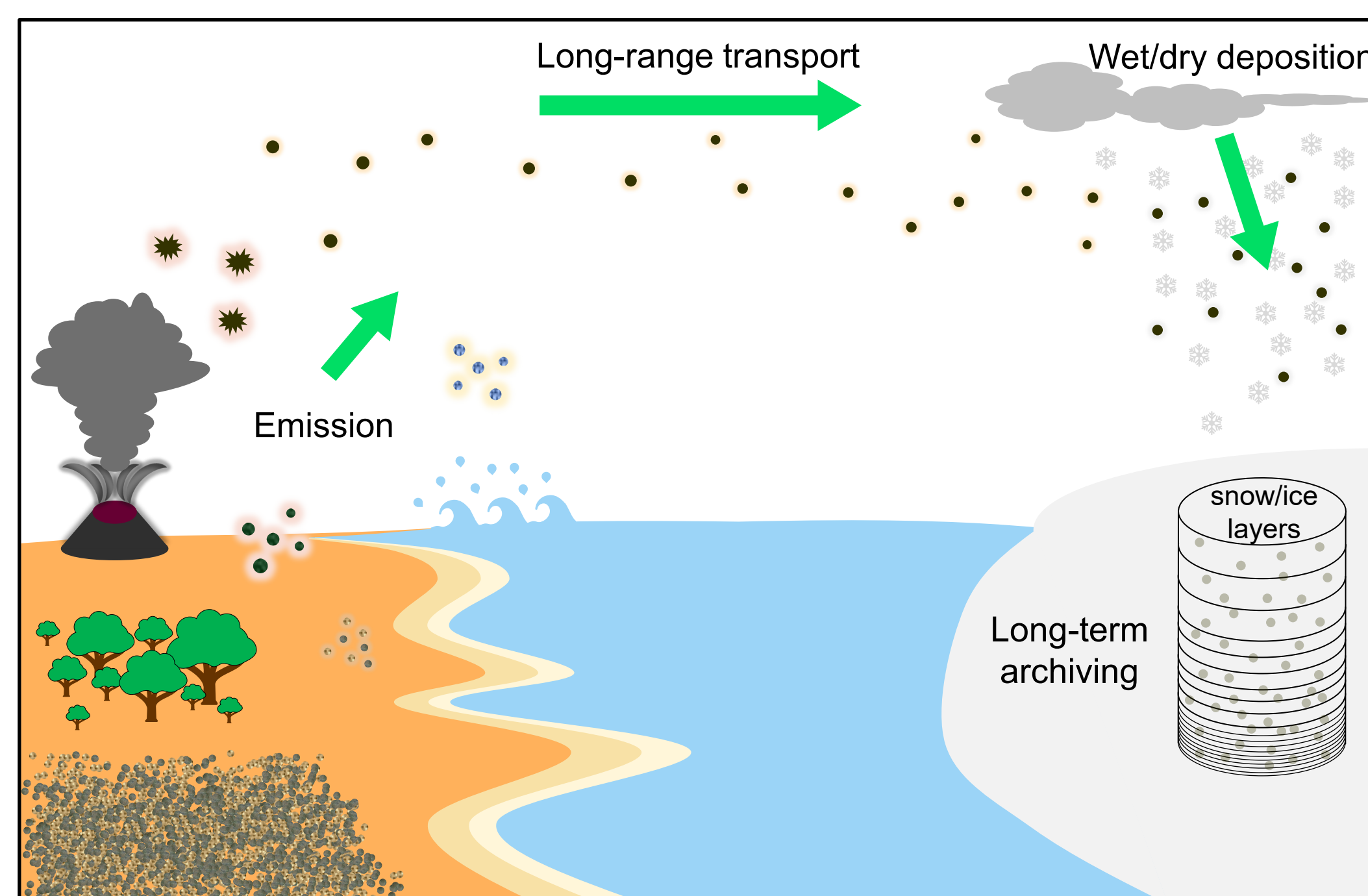


Figure 1. Life cycle of aerosol components archived in ice cores.

- Single-particle inductively coupled plasma time-of-flight mass spectrometry (sp-ICP–TOFMS) allows for the elemental composition analysis of individual particles without sacrificing analytical sensitivity, due to its simultaneous determination of composition over the full mass range and the high time-resolution. Erhardt et al. (2019) successfully measured the elemental composition of single dust particles in Greenland ice using the sp-ICP–TOFMS coupled to Continuous Flow Analysis (CFA) (Kaufmann et al., 2008). The first results support the origin of the particles from long-range transported clay minerals (Erhardt et al., 2019).
- However, the original sp-ICP–TOFMS system equipped with a cold spray chamber introduction only utilizes a small percentage (1 – 10%) of the total sample amount injected, limiting its ability to analyze trace elements in ice cores. To fully utilize sp-ICP–TOFMS for fingerprinting dust sources using trace elements such as Rare Earth Elements (REEs), it is necessary to increase the sample utilization efficiency and instrument sensitivity.

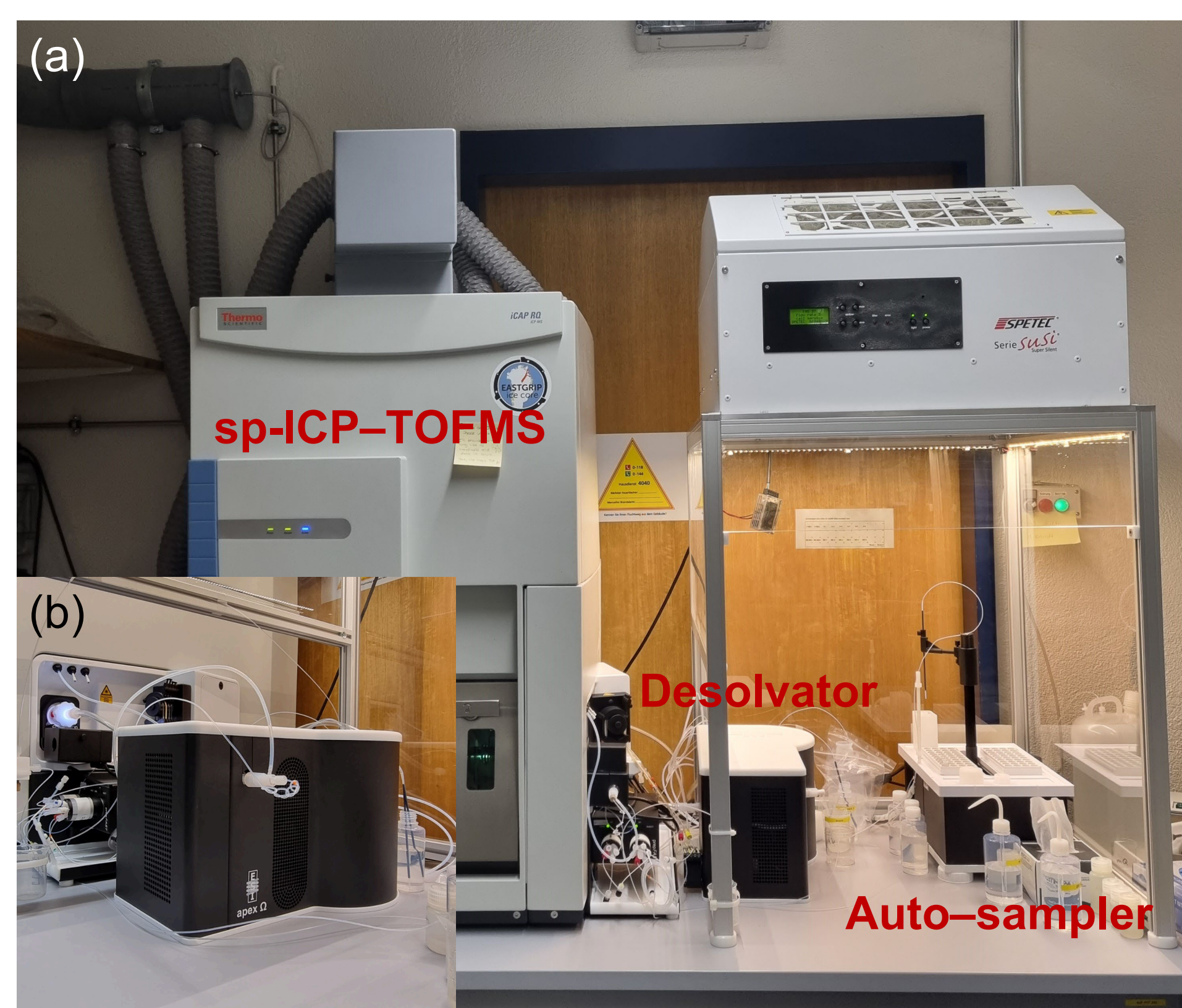


Figure 2. (a) Configuration of sp-ICP–TOFMS (icpTOF R, TOFWERK AG, Switzerland) coupled to a high-sensitivity desolvation sample introduction system (APEX Q Ω, ESI, USA) and an auto-sampler (SC-μ DX, ESI, USA). (b) Close-up view of the high-sensitivity desolvation sample introduction system.

- The sensitivity of ICP–TOFMS can be improved by increasing the sample transport efficiency (TE) using a desolvation sample introduction (DSI) and the detection efficiency (DE) using a collision cell technology (CCT) (Nelms, 2005).
- Although CCT and high-sensitivity DSI have been applied to ICP–MS systems to overcome analytical limitations in spectral interferences and sensitivity (Burger et al., 2019; Lin et al., 2019), their combined effects on single-particle analysis of natural mineral dust aerosols in ice cores, unlike bulk analysis, are still not sufficiently quantified.
- In this study, we investigated the effects of CCT and high-sensitivity DSI system (individually and in combination) on the capability of sp-ICP–TOFMS, including sensitivity, TE, and DE for ionic solutions and nanoparticle (NP) standards. Additionally, the applicability of the DSI system to analysis of natural mineral dust was tested by measuring μm-size natural mineral dust samples.

## Methods and instrumentation

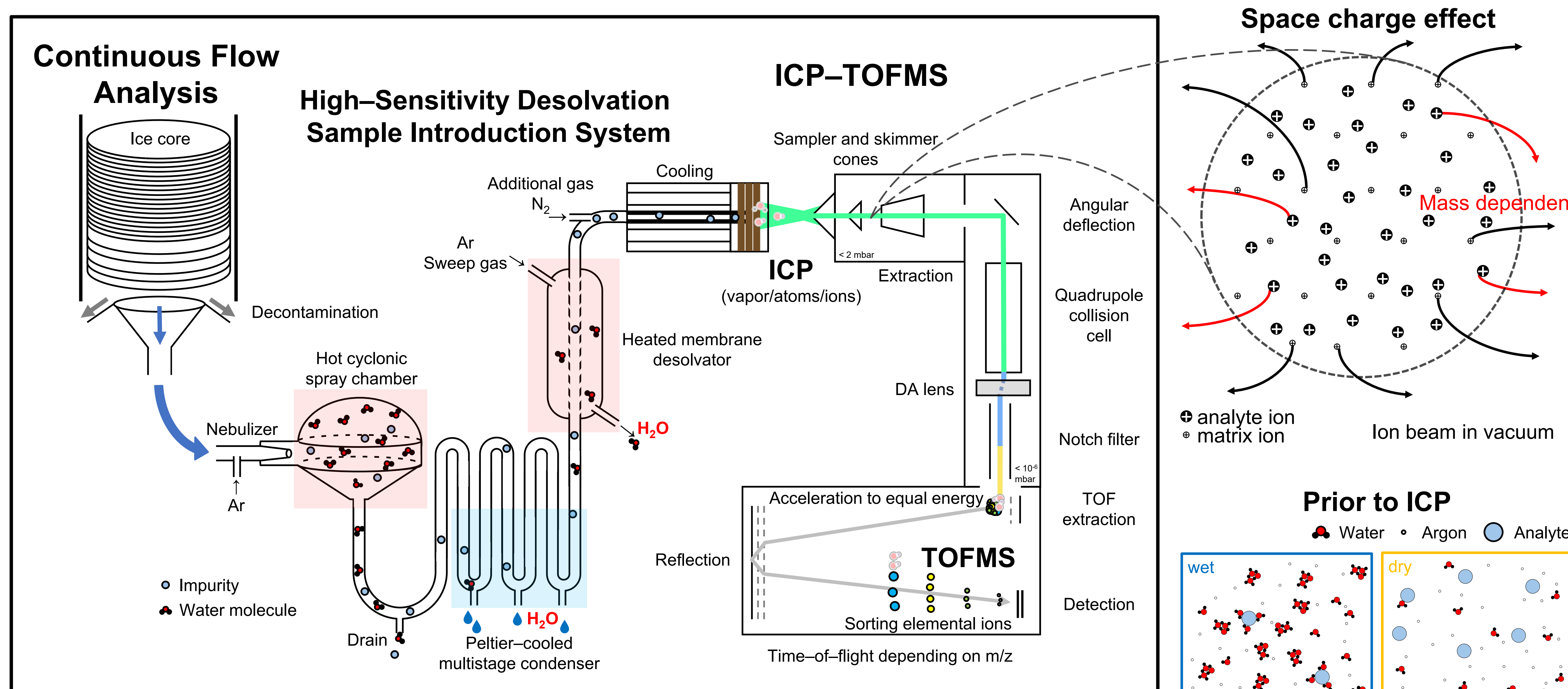


Figure 3. Schematic diagram of CFA–sp-ICP–TOFMS with a high-sensitivity DSI system. The meltwater sample from the CFA flows into the sp-ICP–TOFMS and undergoes a drying process through heating, condensation, and membrane diffusion during sample introduction. The ions reaching the TOFMS can be analyzed over the full mass range and due to the high time-resolution of sp-ICP–TOFMS, individual dust particles can be detected in addition to the dissolved background.

- To compare the capability of sp-ICP–TOFMS in different measurement conditions, we analyzed a tuning solution B (INORGANIC VENTURES, USA) and an ionic gold solution (INORGANIC VENTURES, USA) at a concentration of 1 ppb to evaluate sensitivity and spectral interferences, and to estimate the DE for ions originating from the dissolved analytes.
- Additionally, we analyzed 60 nm gold NPs (60 nm Gold Nanospheres, PVP, NanoXact™, nanoComposix, USA) at a concentration of 20,000 particles/mL to estimate the TE using the particle frequency method (Pace et al., 2011) and the DE for ions originating from the particles.
- The TE is defined as the ratio of amount of sample reaching the ICP to the amount of sample aspirated into spray chamber.
- The DE is defined as the ratio of number of ions detected to the number of atoms reaching the ICP.
- The TE and the DE were calculated as follows:

$$\text{Transport efficiency}[\%] = \frac{NPS_{\text{detected}} [\text{particles sec}^{-1}]}{NPS_{\text{aspirated into spray chamber}} [\text{particles sec}^{-1}]}$$

$$\text{Detection efficiency}[\text{counts atom}^{-1}, \%] = \frac{I_{\text{analyte}} [\text{counts sec}^{-1}]}{A_{\text{introduced into plasma}} [\text{atoms sec}^{-1}]} \text{ or } \frac{I_{NPS} [\text{counts particle}^{-1}]}{M_{NPS} [\text{g particle}^{-1}]} \times \frac{M_{ME} [\text{g mol}^{-1}]}{N_A [\text{atoms mol}^{-1}]}$$

$$NPS_{\text{detected}} [\text{particles sec}^{-1}] = \frac{PF [\text{particles}]}{T_{\text{measurement}} [\text{sec}]}$$

$$NPS_{\text{aspirated into spray chamber}} [\text{particles sec}^{-1}] = PNC_{\text{standard}} [\text{counts mL}^{-1}] \times UR [\mu\text{L min}^{-1}]$$

$$NPS: \text{number of particles per a second} [\text{particles sec}^{-1}]$$

$$T: \text{time} [\text{sec}]$$

$$PF: \text{particle pulse frequency} [\text{particles}]$$

$$UR: \text{uptake rate} [\mu\text{L min}^{-1}]$$

$$PNC: \text{particle number concentration of solution} [\text{particles mL}^{-1}]$$

$$I_{\text{analyte}} [\text{counts sec}^{-1}] = \frac{\Sigma I_{\text{background-corrected}} [\text{counts}]}{T_{\text{measurement}} [\text{sec}]}$$

$$A_{\text{introduced into plasma}} [\text{atoms sec}^{-1}] = \text{Mass Conc} [\text{ng mL}^{-1}] \times IF [\%] \times UR [\mu\text{L min}^{-1}] \times TE [\%] \times N_A [\text{atoms mol}^{-1}] \times M_{ME}^{-1} [\text{mol g}^{-1}]$$

$$I: \text{intensity of analyte signals} [\text{counts sec}^{-1}]$$

$$N_A: \text{number of atoms per a second} [\text{atoms sec}^{-1}]$$

$$N_A: \text{Avogadro's number} [6.022 \times 10^{23} \text{ atoms mol}^{-1}]$$

$$I_{NPS}: \text{intensity of nanoparticles} [\text{counts particle}^{-1}]$$

$$M_{NPS}: \text{mass of nanoparticles} [\text{g particle}^{-1}]$$

$$M_{ME}: \text{molar mass of ME} [\text{g mol}^{-1}]$$

$$IF: \text{isotopic fraction} [\%]$$

$$TE: \text{transport efficiency} [\%]$$

- The applicability of the DSI system was tested by measuring the reference material for natural mineral dust, ultra fine test dust (UFTD, RM8632, PTI, USA).

## Results and discussion

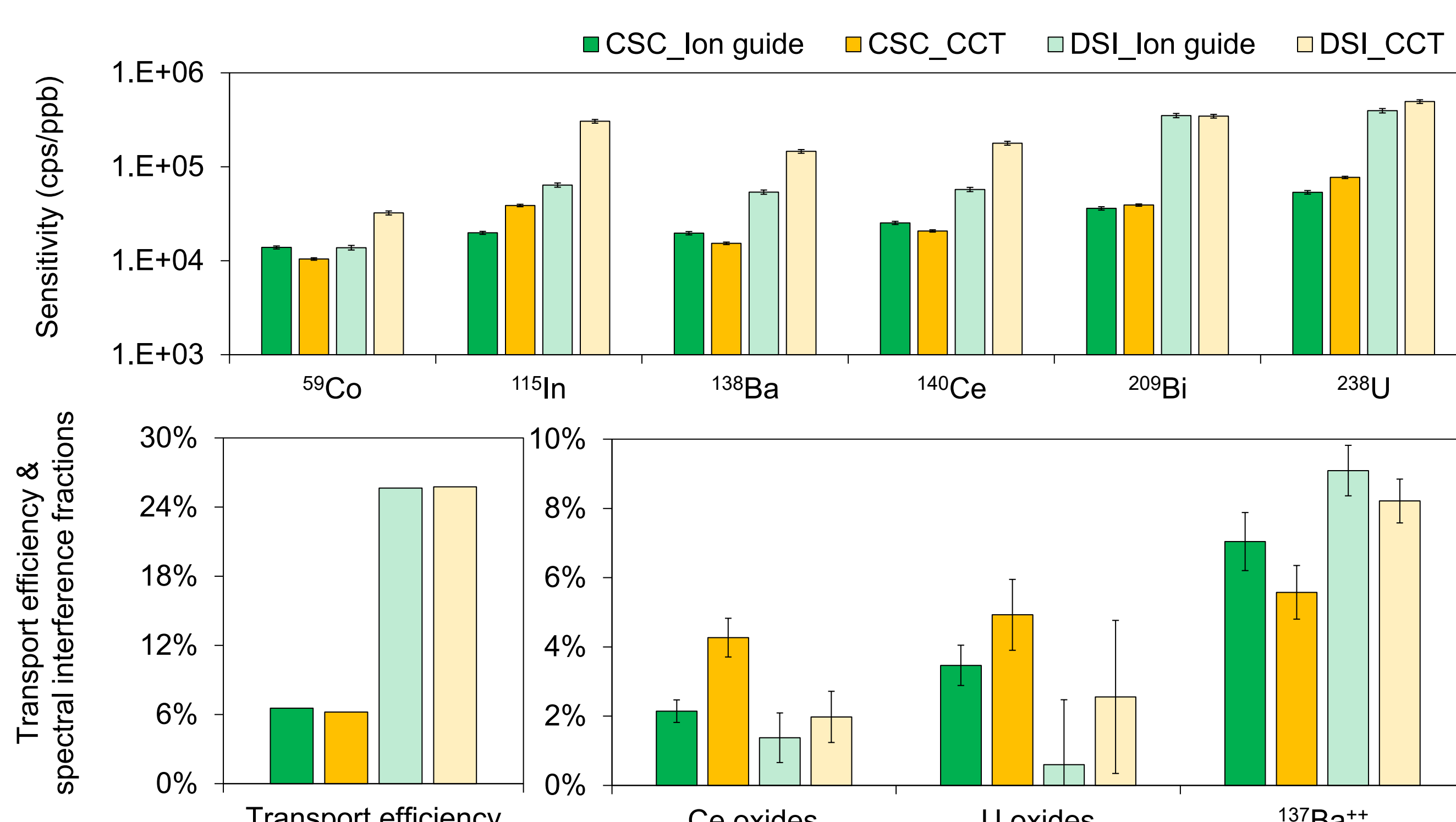


Figure 4. Instrumental sensitivity, TE, and spectral interference fractions of sp-ICP–TOFMS without (CSC) and with a high-sensitivity DSI system in ion guide (unpressurized collision cell) and CCT (pressurized collision cell) modes. Error bars in sensitivity are presented as a standard deviation of the intensity in a 5-min measurement. The fractions of Ce oxides, U oxides, and  $^{137}\text{Ba}^{++}$  were estimated using  $^{140}\text{Ce}^{16}\text{O}^{+}/(^{140}\text{Ce}^{+} + ^{140}\text{Ce}^{16}\text{O}^{+})$ ,  $^{238}\text{U}^{16}\text{O}^{+}/(^{238}\text{U}^{+} + ^{238}\text{U}^{16}\text{O}^{+})$ , and  $^{137}\text{Ba}^{++}/(^{137}\text{Ba}^{+} + ^{137}\text{Ba}^{++})$ , respectively. The error bars in the spectral interference fractions are presented as a standard deviation of the intensity of the numerator divided by the mean of the denominator in a 5-min measurement.

- The use of a DSI system improved sensitivity for most analyte ions originating from dissolved analytes by a factor of about 2 to 10, with roughly a four-fold improvement in TE compared to the cooled spray chamber (CSC), except for  $^{59}\text{Co}$  due to its low kinetic energy (Figure 4).
- The collisional focusing effect, which is caused by the reduced ion kinetic energy due to collisions, enhanced the DE for  $^{59}\text{Co}$  in a DSI system, resulting in a three-fold improvement in sensitivity for  $^{59}\text{Co}$  compared to the unpressurized collision cell mode. As a result, the use of CCT in combination with the DSI system increased the sensitivity for analyte ions by a factor of 2 to 15.
- The DSI system significantly reduced the oxide contents, but there was a slight increase in the oxide contents again in CCT mode.
- The DSI system generated a dry plasma condition, resulting in more doubly charged ions (i.e.,  $^{137}\text{Ba}^{++}$ ). This effect could be adjusted by dedicated plasma tuning.
- The use of the DSI in combination with CCT improved sensitivity for the  $\text{Au}^{+}$  solution by a factor of three compared to the CSC in ion guide mode (Figure 5).
- However, the DE for  $\text{Au}^{+}$  originating from both the  $\text{Au}^{+}$  solution and AuNPs was reduced by 30 percentage using the DSI in ion guide mode.
- The loss of DE for  $\text{Au}^{+}$  from AuNPs by the DSI was more effectively recovered (33%) by CCT than that from the  $\text{Au}^{+}$  solution (17%). This difference could be because the collisional ion focusing is more pronounced for ion clouds under the high transport condition of dried samples of the high-sensitivity DSI system.

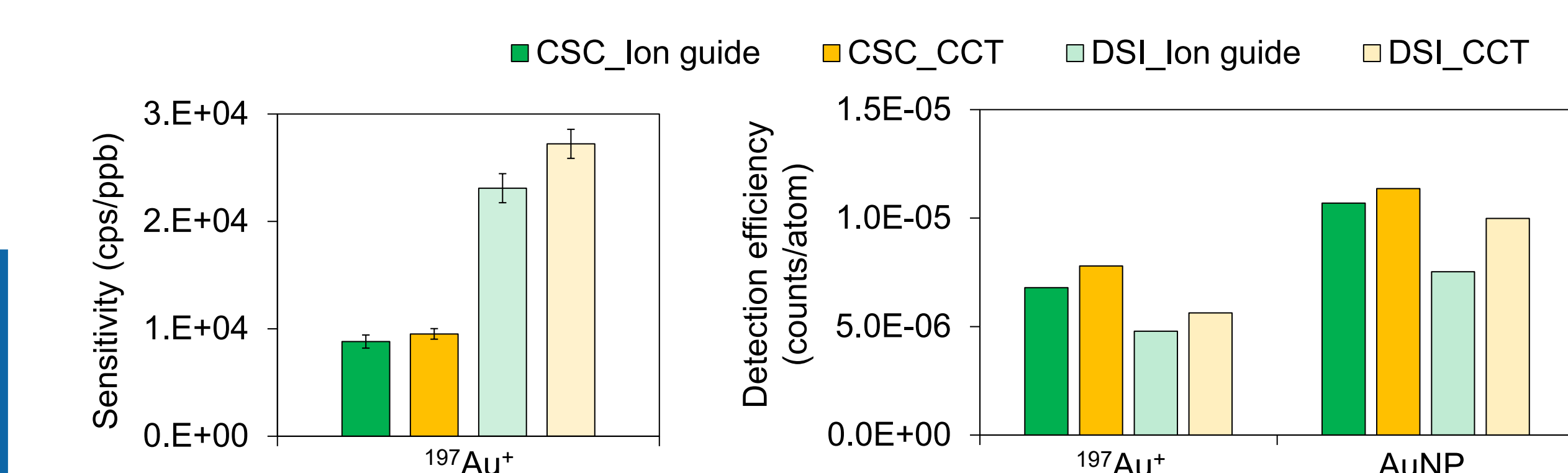


Figure 5. Sensitivity for the  $\text{Au}^{+}$  solution and DE for Au ions originating from dissolved  $\text{Au}^{+}$  and from AuNPs. Error bars in sensitivity for the  $\text{Au}^{+}$  solution represents a standard deviation of sensitivity in the 5-min measurement.

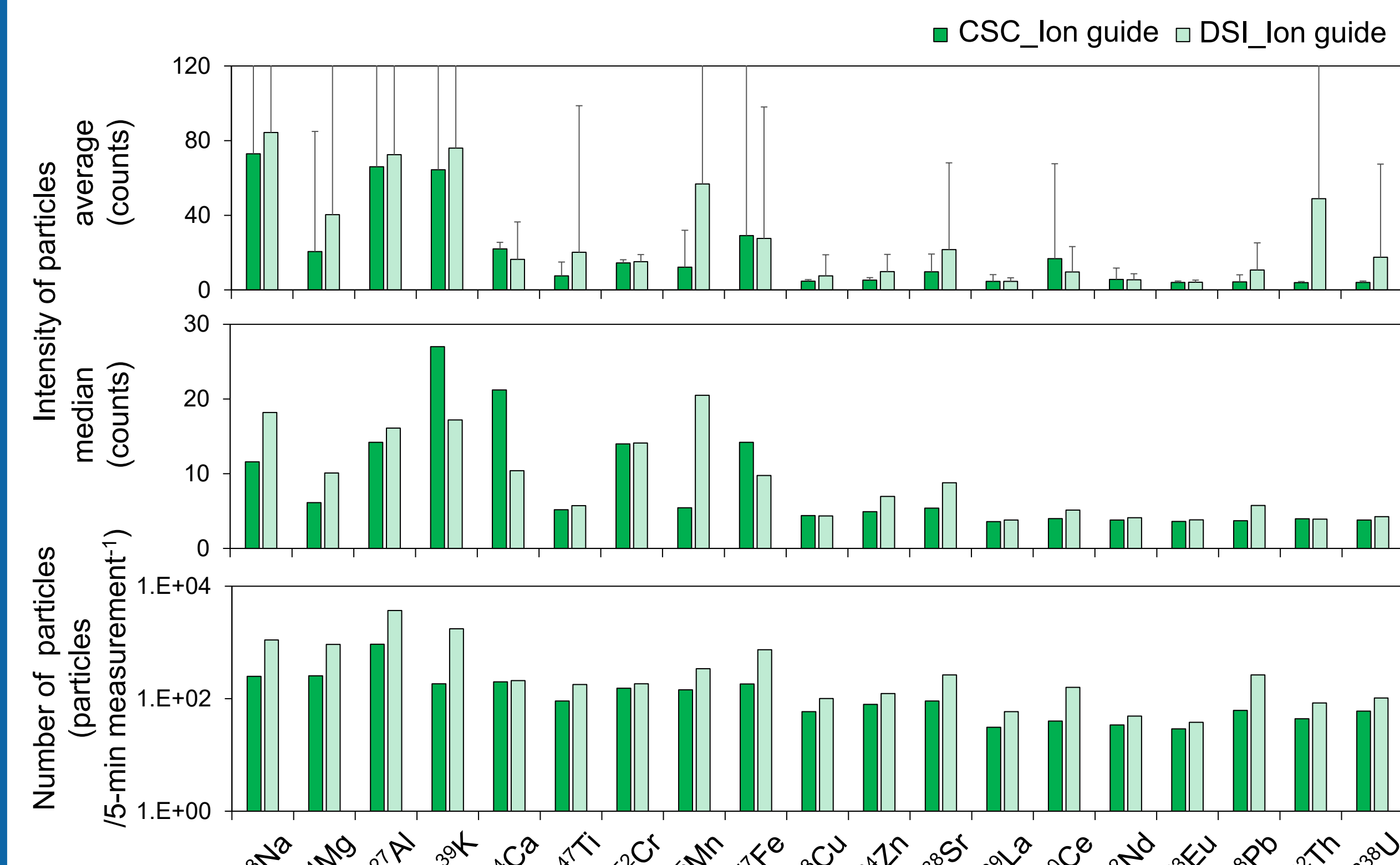


Figure 6. Signal intensity and the number of detected ultra fine test dust particles using two different sample introductions (i.e., CSC and DSI) in unpressurized cell mode. Error bars in average intensity of particle signals for each analyte represent a standard deviation of the intensity in the 5-min measurement.

- A higher number of UFTD particles was detected in both major crust elements and REEs using the DSI compared to CSC because of the increase in transport efficiency.
- The change in background intensity allowed the notch filter to be reduced. This reduced notch filter made some changes in the intensity of detected particles.
- To summarize, there was no significant loss of particles in the condenser or membrane desolvator in DSI compared to the CSC although the intensity of detected particles can be affected by the different notch filter setting and background intensity for certain mass channels.

## Conclusions

- A novel CFA–sp-ICP–TOFMS technique allows for the continuous elemental composition analysis of single dust particles in ice cores.
- However, the current sample utilization efficiency and sensitivity of sp-ICP–TOFMS using only a spray chamber limit its capability to determine trace elements that can be used for source identification (fingerprinting) of single mineral dust particles.
- The use of a DSI system improved the TE by a factor of about four, resulting in a gain in sensitivity for analytes by a factor of 2 to 15 in CCT mode.
- Especially, the collisional ion focusing effect of CCT on the ion clouds from AuNPs was more pronounced in high transport conditions of dried samples by DSI compared to the conventional CSC sample introduction.
- The use of the DSI system didn't cause significant loss of natural mineral dust particles according to the pilot testing using UFTD.
- These enhancements in TE, DE, and sensitivity of sp-ICP–TOFMS by a DSI in combination with CCT will help to analyze trace isotopes in individual mineral dust particles and to geochemically characterize the mineral dust in ice cores. Ultimately, this will allow for a more precise geochemical characterization of fingerprints of individual soil-derived aerosols preserved in ice cores, which can be used to reconstruct past climate change such as the alterations in atmospheric circulation.

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