

# Traceable calibration for ambient air GOM measurements using non- thermal plasma oxidation of elemental mercury

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Atmospheric mercury (Hg) predominantly exists in 0, and +2 oxidation states. However, they are operationally defined as gaseous elemental ( $\text{Hg}^0$ , GEM), oxidised ( $\text{Hg}^{\text{II}}$ , GOM), and particulate bound mercury ( $\text{Hg-p}$ , PBM). The exact chemical composition of  $\text{Hg}^{\text{II}}$  species in the ambient air is poorly understood due to several sampling limitations caused by their chemical behavior and lack of adequate measurement methods. Hence they are collectively quantified and reported as  $\text{Hg}^{\text{II}}$ . The automated Tekran Hg vapor analyzer coupled to the speciation unit is typically used for continuous atmospheric Hg measurements, where sampling of  $\text{Hg}^{\text{II}}$  is based on pre-concentration onto KCl coated annular denuders. The current speciation methods for  $\text{Hg}^{\text{II}}$  measurements are fraught with significant uncertainty, from sample collection to calibration. High reactivity of  $\text{Hg}^{\text{II}}$  and their presence at ultra-trace levels make it difficult to sample and calibrate. Given that improper calibration may lead to sampling biases, reliable and metrologically traceable calibration methods are required for quantifying  $\text{Hg}^{\text{II}}$  in the ambient air. In the present study, we tested the newly developed calibration method based on non-thermal plasma oxidation of elemental Hg, a unique method that is traceable to NIST SRM 3133. Trace amounts of  $\text{Hg}^{\text{II}}$  species such as  $\text{HgO}$ ,  $\text{HgCl}_2$ , and  $\text{HgBr}_2$  was produced with trace levels of reactant gases such as oxygen, and electrolytically produced chlorine, and bromine driven by plasma-assisted oxidation inside sorbent traps. The plasma oxidation efficiency of elemental Hg was  $98.5 \pm 7.5\%$  ( $k=2$ ),  $96.8 \pm 6.9\%$  ( $k=2$ ), and  $97.4 \pm 9.6\%$  ( $k=2$ ) when using  $\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{Br}_2$  as reaction gases, respectively. Calibration method was tested against the internal permeation source of Tekran 2537B Hg analyzer by loading known masses of  $\text{HgO}$  onto different KCl-coated denuders using plasma. Results have shown that the ambient air  $\text{Hg}^{\text{II}}$  measurements using Tekran 2537B are biased low. Average  $\text{Hg}^{\text{II}}$  concentration measured was  $45.0 \pm 16.5$  and  $47.3 \pm 6.5 \text{ pg m}^{-3}$  for Tekran and Plasma calibrations respectively. Measurement uncertainty due to calibration was 36.8% for Tekran internal calibration and 13.8% for plasma calibration method (expanded relative combined standard uncertainty reported as  $k=2$ ).