## Supplemental Information for: A rapid method for the determination of methylmercury and inorganic mercury species in whole blood by Liquid Chromatography with detection using Vapor Generation ICP-MS/MS

Emily J. Pacer, <sup>a,b</sup> Christopher D. Palmer <sup>a,b</sup> and Patrick J. Parsons <sup>a,b</sup>

<sup>a</sup> Wadsworth Center, New York State Department of Health, Empire State Plaza Albany, NY 12237 USA.

<sup>b</sup> Department of Environmental Health Sciences, University at Albany, Rensselaer, NY 12144.



Supplemental Figure 1: LC-ICP-MS chromatograms of NIST SRM 955c (Level 4) showing a 15-cm C18 column (used in development work) comparing different TMAH concentrations: 0.01% (v/v) (orange); 0.1% (v/v) (green); 1% (v/v) (blue); and 5% (v/v) (purple). The final TMAH concentration of 0.1% (v/v) was selected based on the optimal sensitivity and agreement between found and SRM assigned values for Hg species.



Supplemental Figure 2: LC-ICP-MS chromatograms of three Hg standards at 1, 10, and 20 µg/L eluting a C8 column. Two different filtration techniques were used in sample preparation: PES syringe filters (black); and UCT Refine<sup>™</sup> columns (red). Similar chromatographic performance was evident with both filtration techniques.



Supplemental Figure 3: Sample preparation flow path for processing whole blood for Hg speciation by LC-ICP-MS.



Supplemental Figure 4: LC-ICP-MS chromatograms of an 18  $\mu$ g/L Hg species with different spike injection volumes: 80  $\mu$ L (blue); 60  $\mu$ L (red); and 40  $\mu$ L (black). A 60- $\mu$ L injection volume was chosen based on sensitivity and good resolution between the Hg species.



Supplemental Figure 5: LC-ICP-MS chromatograms of Hg species in NIST SRM 955c Level 4 comparing a 15-cm C18 (blue) column with a 15-cm C8 (red) column without VG during method development work.



Supplemental Figure 6A: Typical LC-VG-ICP-MS/MS calibration curves for three different Hg species (B) LC-VG-ICP-MS/MS chromatograms for 5 calibration standards containing three Hg species.



Supplemental Figure 7: Stability of three Hg species in THAH extracts of NIST SRM 955c Level 2 over a 3-day period.



Supplemental Figure 8: Difference plots showing deviation from the assigned value for various archived proficiency testing materials from the NYSDOH, QMEQAS, and PCI programs comparing method performance for total Hg (calculated as the sum of species) by (A) LC-ICP-MS and (B), LC-VG-ICP-MS/MS. The black dashed lines denote the NYSDOH PT quality specifications for total blood Hg:  $\pm 3 \mu g/L$  or  $\pm 30\%$  around target value, whichever is greater; it is fixed at  $\pm 3 \mu g/L$  at concentrations less than or equal to 10  $\mu g/L$ .