2023 Particulate Iron Comparison - Microwave Plasma Atomic Emission Spectrometer vs Atomic Absorption Spectrophotometer

Sonya Havens

October 11, 2023

Agilent Microwave Plasma Atomic Emission Spectrometer

The Agilent Microwave Plasma Atomic Emission Spectrometer (MPAES) was purchased from Agilent Canada, December 2022 and included the following parts:

- Agilent 4210 MP-AES elemental analyzer with a nitrogen plasma emission source.
- Nitrogen generator
- SPS 4 autosampler
- AVS 4 integrated switching valve

The MPAES was received March, 2023, installed in June 2023 by Yang Liu, and used to measure particulate iron in samples collected from 2019 to the end of 2022 ($n = 249$) from 9 August, 2023 to 7 September, 2023 that were also measured by Emily Van at the University of Winnipeg (UW) using an Atomic Absorption Spectrophotometer (AAS) in May 2023.

Filters with retained particulate matter are placed in 20-mL HDPE acid washed vials and digested with 2 mL of trace metal grade nitric acid. After a 48 hour digestion period the digested sample is diluted to 20 mL with ultrapure water. These digested samples were then analyzed on the AAS at UW and on the MPAES at IISD-ELA.

Detection limits

The detection limit (C_{dl}) is calculated for each run using equations 1 through 3:

Equation 1. $C_{dl} = (y_d - b)/m$

where b is the y-intercept, m is the slope, and y_d is the signal detection limit, which is calculated using equation 2.

Equation 2. $y_d = 3s_y + b$

where s_y is the residuals between the measured signal for each standard concentration and the calibration curve predicted response for each standard concentration and is calculated using equation 3.
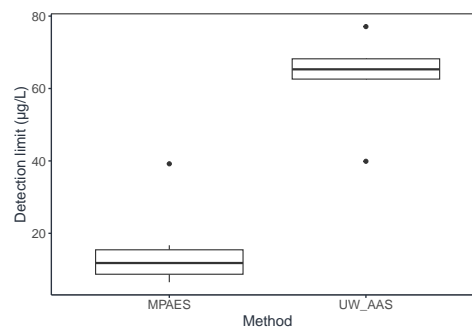
Equation 3. $s_y = \sqrt{((\sum d_i^2)/(n-2))}$

Figure 1: Limits of detection of the Atomic Absorption Spectrophotometer and the Microwave Plasma Atomic Emission Spectrometer

where n is the number of standards in the calibration curve, and d_i is the difference between the measured signal for each standard concentration and the calibration curve predicted response for each standard concentration.

The average detection limit over all of the analytical runs was 4.1 times lower on the MPAES (15.11 ± 11.24 µg/L, median = 11.8 µg/L) than on the AAS (62.62 ± 13.82 µg/L, median = 65.3 µg/L).

Duplicates

Sample duplicates are conducted every 15 to 20 samples. The average relative percent difference (RPD) of duplicated samples, calculated using equation 4, was $0.03 \pm 0.02\%$ (median $= 0.02\%$) and $11.04 \pm 44.31\%$ (median $= 2.9\%$) for samples analysed on the MPAES and on the AAS, respectively. The elevated average RPD of duplicates analysed on the AAS was due to the fact that 13 out of 35 (37%) of duplicate samples were filter blanks or method blanks. None of the duplicate samples ran on the MPAES were filter blanks or method blanks. RPD calculations are applicable when the concentrations of the duplicated samples are at least five times the detection limit. The average concentration of filter blanks (12.67 ± 51.05 µg/L) and method blanks (6.19 ± 21.27 µg/L) analysed on the AAS were lower than the AAS detection limit (62.62 ± 13.82 µg/L), and therefore are not applicable for RPD calculations. When these filter blanks and method blanks were removed, the average and median RPD's of duplicates analysed on the AAS were $3.23 \pm 3.11\%$ and 2.8%, respectively.

Equation 4. $RPD = ((C_1 - C_2)/((C_1 + C_2)/2))x100$

where C_1 and C_2 are the concentrations of the two replicates.

Blanks

Filter blanks, consisting of a GF/C filter, and method blanks, consisting of a GF/C filter with 100 mL of ultrapure water (Milli-Q type 1 water) filtered through it, were collected each time particulate iron samples were filtered.

Figure 2: Relative percent differences of duplicates analysed on the AAS and on the MPAES

Figure 3: Relative percent differences of duplicates analysed on the AAS and on the MPAES with filter blanks and method blanks removed

While the filter blank and method blank results obtained on the AAS and the MPAES were correlated ($R^2 = 0.62$, $p < 0.001$), the MPAES results were consistently biased high (fig 4).
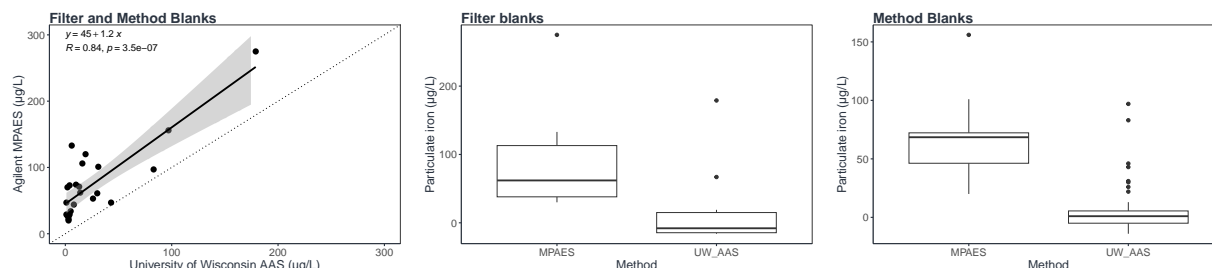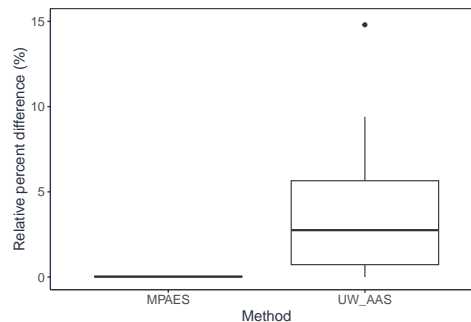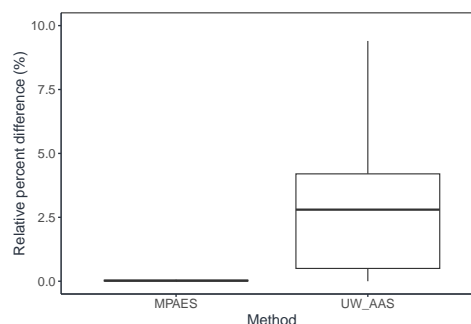

Figure 4: Filter blanks and method blanks analysed on the AAS and MPAES

The blanks were reran to assess whether the elevated concentrations of particulate iron in blanks analysed with MPAES were due to increased storage time.

The rerun results were higher than those obtained in the original run, indicating that increasing the storage time of digested samples may lead to elevated particulate iron concentrations. It is unclear as to why this is the case. It is possible that iron could be leaching from the plastic, but the vials were acid washed to remove iron from the plastic, prior to use.
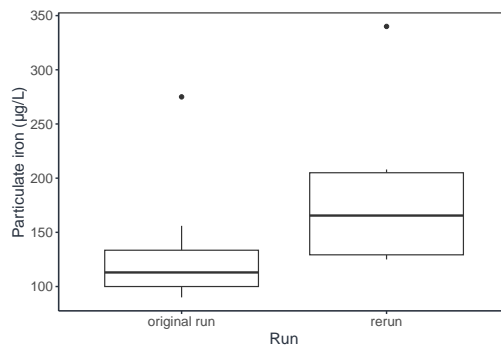
2

Figure 5: Particulate iron concentrations of filter blanks and method blanks in original run and rerun

Comparison with UW AAS results

Particulate iron concentrations analysed on the AAS and MPAES were significantly correlated ($R^2 = 0.89$, $p < 0.001$) and the 95% confidence interval for the slope of the AAS versus MPAES linear model for particulate iron was between 1.11 and 1.19. This bias (slope > 1) was likely due to the fact that samples out of range of the standard curve were not diluted and rerun at the UW.

When samples that required dilution (>775 µg/L) were removed from the comparison, the particulate iron concentrations analysed on the AAS and the MPAES were still significantly correlated ($R^2 = 0.96$, $p < 0.001$) and the 95% confidence interval for the slope of the AAS versus MPAES linear model was between 0.95 and 1.
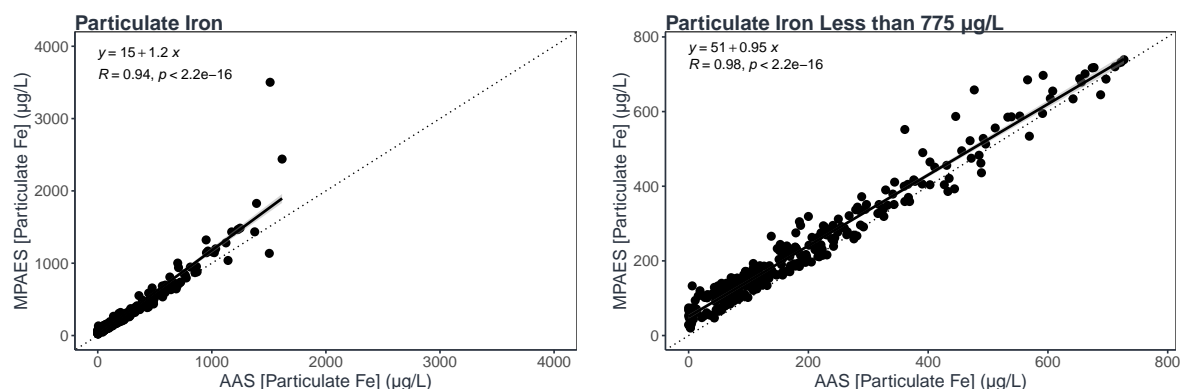

Figure 6: Comparison of particulate iron concentrations of samples analysed on the AAS and on the MPAES

Conclusions

The MPAES performed well for the analysis of particulate iron, with lower detection limits than the AAS and excellent precision. The MPAES and AAS particulate iron results were highly correlated with a slope of 1.0 falling within the 95% confidence interval, indicating that the migration from AAS to MPAES will not induce a step change in the long-term data. Long-term (>2 months) storage of digested samples could lead to elevated concentrations in samples, as witnessed by the reruns of filter blanks and method blanks, though the cause is unknown. To address the potential affect of long-term storage of digested samples on particulate iron concentrations, a storage holding time limit of 14 days will be applied to digested samples.

```
## [1] "This report was created on 2023-10-11"
```