Improving and Optimizing the Detection Method for Flow Injection Analysis Using Calibration Extension and External Data Comparison

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Abstract

Flow Injection Analysis is the method used by the National Atmospheric Deposition Program/Central Analytical Laboratory (NADP/CAL) to detect and quantify ammonium and orthophosphate in collected National Trends Network (NTN) and Atmospheric Integrated Research Monitoring Network (AIRMoN) precipitation samples. This quantification is determined through the use of a Beer's law plot, in which standard solutions of known concentration are analyzed and the resulting peak areas are plotted linearly against the concentrations. By calculating the equation of the line running through these points, one can accurately determine the concentration of unknown samples based on peak areas. This method is only valid, however, within the range of the known standard concentrations. By adding additional standards throughout the curve, the range of detection can be extended and the accuracy of the extrapolated line can be improved as well.

Setting up a second FIA and reproducing the exact same run properties and conditions is another valid tool used to produce confidence in a detection method. Data comparisons can then be used to determine the reproducibility and validity of collected site data. This poster shows the results and procedures used to extend the FIA's calibration range and to set up and use a second FIA for data comparison.

Objective

The National Atmospheric Deposition Program/Central Analytical Laboratories currently uses a Lachet Quickchem 8000 Flow Injection Analyzer for use for detection of Ammonium and Orthophosphate. We also own a second Quickchem 8000, which could theoretically be used as either a backup for our current FIA, or as a research instrument. Before samples can be run on the second FIA, test need to carried out to determine whether the results obtained from this new instrument are accurate and consistent with our current detection methods. By running both instruments simultaneously, using identical samples, manifolds, system parameters, standard solutions, and reagents, we should be able to easily see whether there is a significant difference in the data between the two instruments.

Experimental

Great care was taken to ensure that there would be minimal outside variables affecting the data. Samples from the National Trends Network were analyzed on the same day on both the current FIA as well as the new FIA. A total of two hundred NTN samples were analyzed in this fashion. External samples from various laboratory comparison studies were also ran to further ensure that there were no internal biases or influences. All standards used for calibration were made fresh the week of analysis, and were again used to calibrate both instruments. Reagents used for analysis were used on both instruments and were taken from the same batch. Both instruments were placed in the same lab to ensure that environmental differences would not contribute to data variations. Both instruments were set up using the same system parameters, software, and materials.

Instrument parameters (For Ammonium Detection)

Load Period: 25s

Inject Perio
d: 31s

Time to Valve: 24s

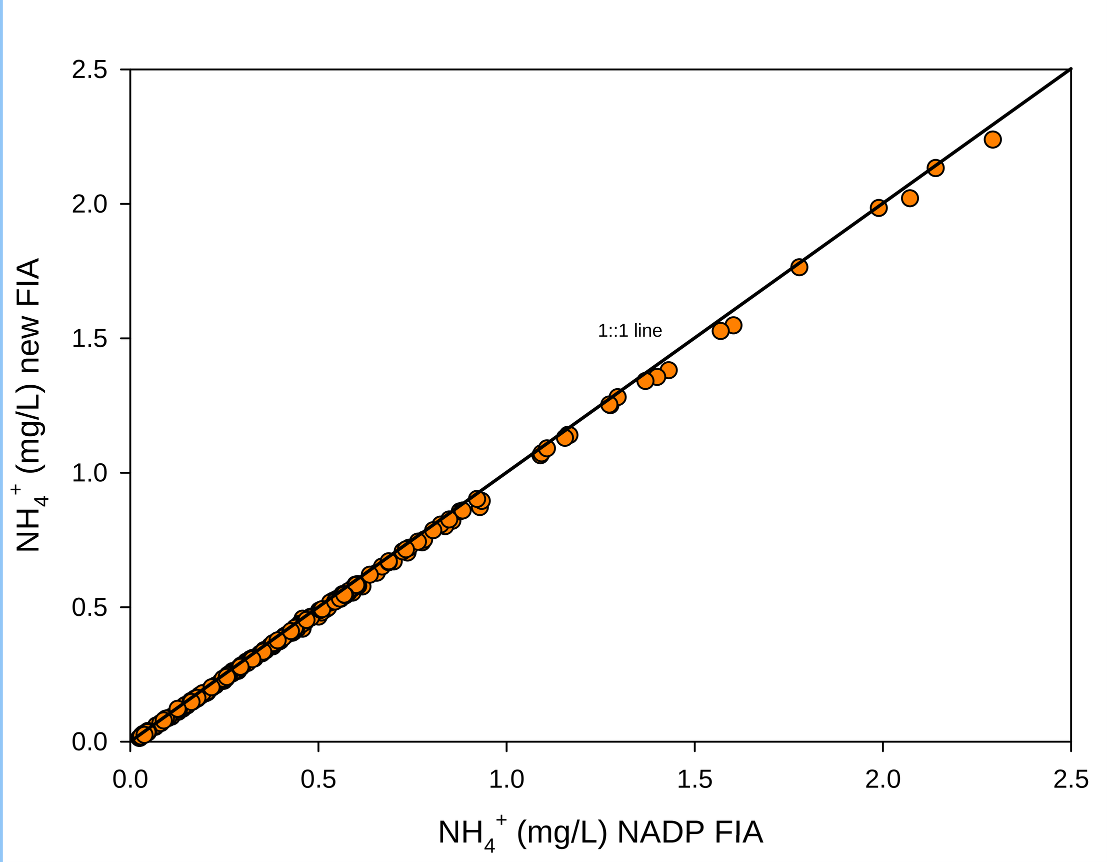
Expected Inject to Peak Start: 24s

Expected Peak Base Width: 52s

Calibration Fit Type: First Order

Force Through Zero: Yes

New FIA vs. Existing FIA



Statistical Data

Paired t-test

Number of Samples	195	Critical t Value for 90%	± 1.64
Average Difference	-13.92	Critical t Value for 95%	± 1.96
Standard Deviation	97.66	Critical t Value for 99%	± 2.58
Degrees of Freedom	194	Critical t Value for 99.5%	± 2.81
Experimental t value	-1.99		

Conclusion

Statistical analysis using a paired student t-test produced an experimental t-value of -1.99. The critical limit for $t_{0.05,\,194}$ = ± 1.96. Since our experimental t value exceeds this critical limit, we must say that the difference seen between the two sets of data is more than 95% likely be statistically significant. However, $t_{0.01,\,194}$ = ± 2.58, meaning that chance that the difference is statistically significant is less than 99%. When analyzing the raw data, an obvious bias can be seen, as shown by the average difference of -13.92. In fact, there was not a single case in which the difference between the old data and the new data was positive. This would suggest that, despite the results of the paired t-test, there is quite obviously a bias between the two instruments.

Future Work

Run additional external standards to further isolate the cause of the bias.

Extend the linear range of the calibration curve.

Exchange the valves on the two instruments to see if they might be causing a variation.

Continue to run comparison samples throughout the year to monitor the bias over time.

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