Particle-Into-Liquid Sampler with Ion Chromatographs
Quality Assurance Report for Summer 2001 Campaign in Queens, NY

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Ion Chromatograph (IC) Operational Description

The liquid sample from the Particle Into Liquid Sampler (PILS) is injected into an IC column where the individual ionic species elude off separately. A conductivity detector measured the concentrations of each species. The conductivity response/concentration relationship is produced from injecting a range of known concentrations and producing a calibration curve.

Uncertainty

The ion liquid concentrations reported by IC software are converted into corresponding atmospheric concentrations. This conversion is dependent on the airflow rate, the liquid flow rate, and the liquid concentrations.

The airflow rate was measured daily with a Bios DryCal, which has a reported accuracy uncertainty of 1%. The precision of the DryCal is calculated from the thirty daily airflow measurements. the standard deviation is 0.15 LPM, or about 1% of the total 10.6 LPM flow rate.

The liquid flow rate pumped by the 8-channel IsmaTech peristaltic pump is dependent upon the condition of the flexible tubing used with the pump. The flow rate was measured with an Acculab portable scale with a stopwatch. The density of 1 g/ml was assumed for all liquids.   The accuracy uncertainty of this measurement was 2%. We report a liquid flow rate accuracy precision of 5% to account for the additional uncertainty related to the variability of the peristaltic pump flexible tubing. The peristaltic pump flow rate precision is not reported.

The dilution factor is the concentration of the lithium (Li) transport flow with steam divided by the concentration of the Li transport flow without the steam. The uncertainty of the dilution factor is 5%. The precision of the dilution factor measurements is 6%.

The Metrohm-IC calibration curves and the uncertainty associated with the conductivity detector result in a cumulative 3% accuracy uncertainty in the liquid concentrations. The precision of the Metrohm-IC was calculated as 1% from several measurements of the same standard solution.

Using the sum of the squares equation with these variables, the collective accuracy uncertainty of the PILS-IC measurements is 8%.

PILS Limits of Detection (LOD)

The LODs for each reported species from the PILS-IC system are based on the signal to noise ratio from chromatographs produced by the Metrohm-Peak IC software. Figure 1 shows a chromatograph baseline with an insert illustrating the noise. Figure 2 shows a chromatograph from the PMTACS-NY PILS-IC data. Each integrated peak area represents the integrated conductivity response from the baseline for each corresponding ion. The LOD is determined to be the concentration where the signal is three times the standard deviation of the noise.
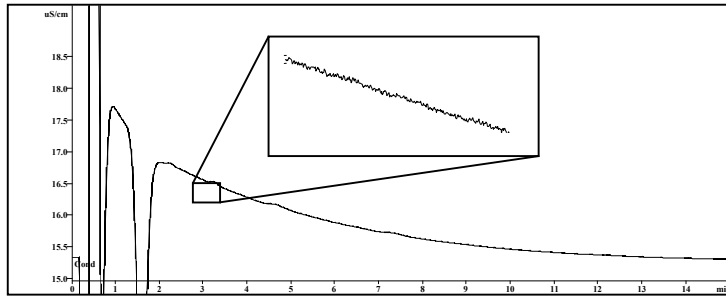

Figure 1. Chromatogram baseline with insert illustrating baseline noise found with Metrohm-Peak IC software.
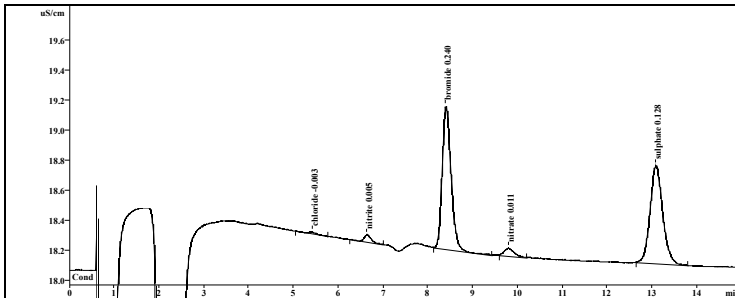

Figure 2. Typical anion chromatogram taken from the PMTACSNY PILS-IC data from Summer 2001. Numbers indicate the concentration in mg/L before conversion to $\mu g/m^3$.

The following table reports the LOD's for the reported PILS-IC species:

Anions	LOD ($\mu g/m^3$)
chloride	0.05
nitrite	0.05
nitrate	0.05
sulfate	0.05
Cations	LOD ($\mu g/m^3$)
sodium	0.10
ammonium	0.60
potassium	0.10
calcium	0.10
magnesium	0.10

The cation LODs are larger than the anion LODs due to the greater noise amplitude of the cation chromatograph baseline. The anion IC includes a suppressor to decrease background noise due to interfering ions, such as carbonate. Other than ammonium, these LODs are identical to those reported for the PILS-IC setup for the Texas Supersite in Texas, and the Atlanta Supersite in Georgia. The ammonium LOD is explained in the next section. Examining several chromatograms throughout the summer dataset revealed a relatively constant level of noise found in flat sections of the baselines. Therefore, the LODs are held constant for the entire dataset.

Ammonium

Ammonium is the primary aerosol base for the PILS-IC data set, comprising 91% of all recorded cations by mass. The charge balance for the PMTACS-NY PILS-IC data appears to have an apparent offset from neutrality, suggesting a possible systematic error or correction factor. This feature is also found in data sets from other recent PILS-IC field studies where the PILS was operated in a similar manner.

Linear regression of the recorded versus calculated NH_4, as shown in Figure 3, produces a y-intercept of 0.0313 $\mu mol/m^3$ (0.56 $\mu g/m^3$), suggesting that adding 0.0313 $\mu mol/m^3$ to the recorded ammonium would make the apparent isolated neutral data set neutral.
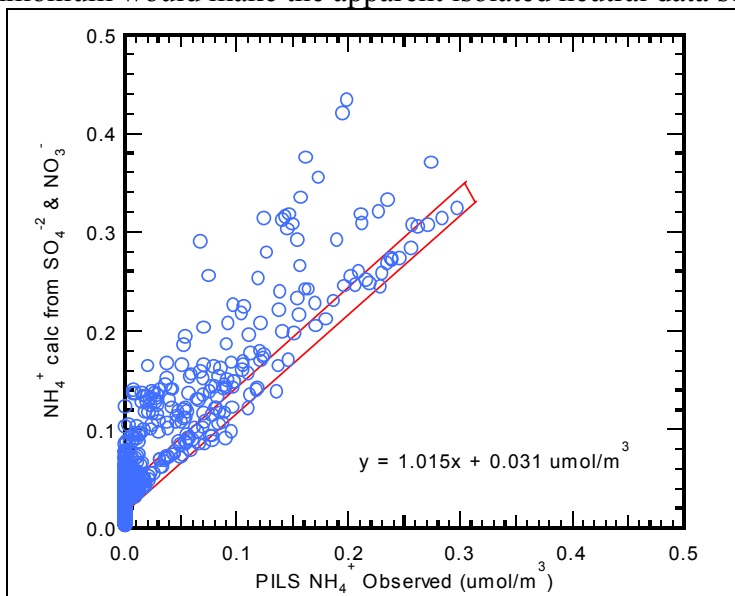

Figure 3. Observed versus calculated NH_4.

Extrapolating this correction to the entire ammonium data set creates a corrected ammonium trace. Figure 4 shows the inorganic charge balance with the recorded ammonium in red (top trace), and the corrected ammonium in blue (bottom trace). The corrected charge balance still produces acidic events correlating to sulfate and PM events, but periods of neutrality now exist. With all of this in mind, the consensus for the LOD for ammonium is 0.60 ug/m^3.
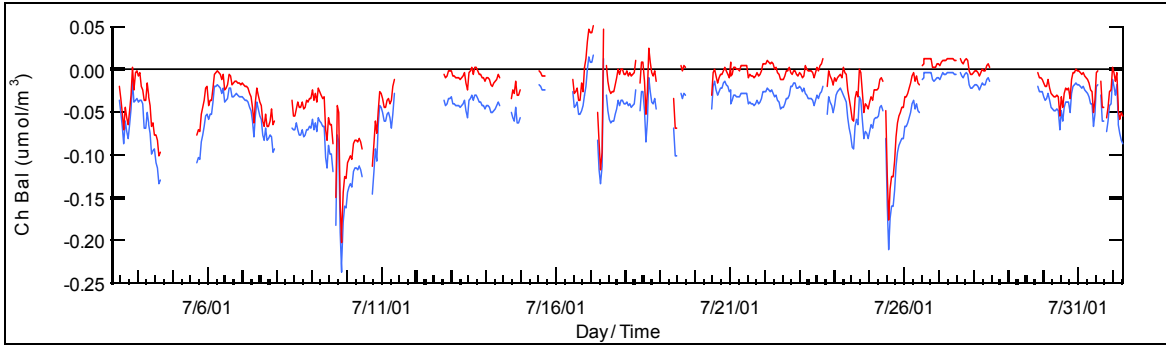
Figure 4. Charge balance with correction.

This theoretical correction is reclassified as an experimental error or sample loss due to supporting tubing experiments. Research conducted after the PMTACS-NY field intensive relates ammonium loss from the liquid sample to the tubing material used. Figure 5 illustrates several different solutions of ammonium run through the ICs with varying residence times to determine the effect. The solutions are denoted in the legend. With increased residence time, the measured ammonium decreased with the Teflon tubing. This did not occur with the polyetheretherketone (PEEK) tubing.
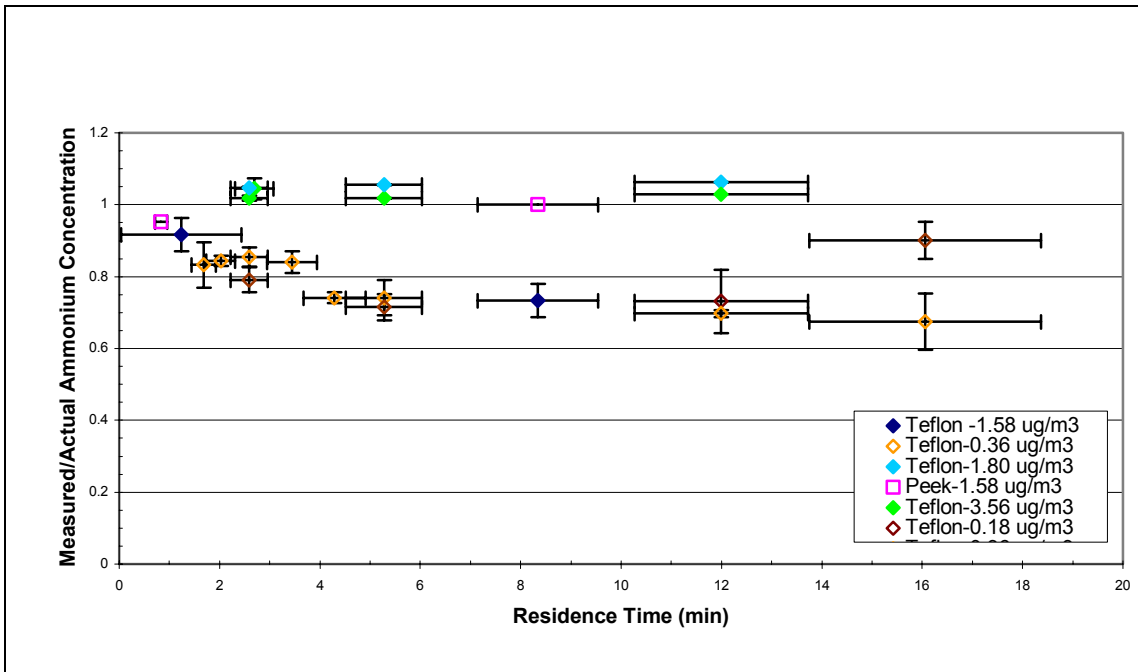

Figure 5. Residence time experiments run with Teflon and PEEK tubing. The legend indicates the concentrations of the ammonium solution injected into the ICs.

Figure 6 shows that this decrease in concentration with longer residence times did not occur for sulfate, except at very low concentrations.
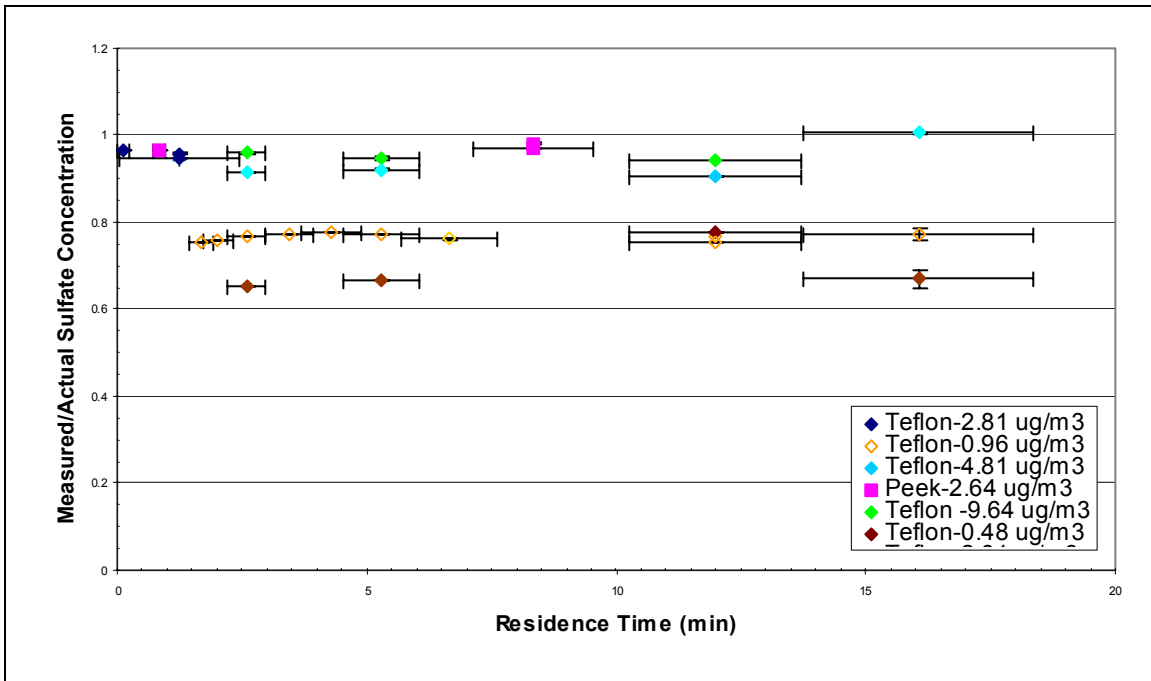
Figure 6. Residence time experiments run with Teflon and PEEK tubing. The legend indicates the concentrations of the sulfate solution injected into the ICs.

The research concluded that the Teflon tubing carrying the liquid sample from the PILS to the IC effectively stripped away a fraction of the ammonium. The loss rate is a function of the liquid sample residence time in the tubing. As the liquid flow rate is increased, the tubing has less of an effect. Conversely, the alternative PEEK tubing showed no significant ammonium loss. The tubing experiments produced a constant ammonium loss dependent on the sample residence time. This verifies the 0.60 μg/m^3 experimental error assigned to the ammonium values.

Quality Assurance

The majority of the QA for the PMTACS-NY PILS-IC data was done the day after the data was recorded. All of the 15-minute chromatographs recorded were reviewed to confirm that the peaks were correctly identified with the corresponding species. The resulting study long-term series was further reviewed by checking any anomalous structure.

The IC calibration was checked three times during the 4-week study. The actual calibration was performed immediately prior to the beginning of the data collection. A solution of known concentrations for all species was injected directly into the IC and compared against the reported values. Each calibration check was within 5% of the correct value. Henceforth, calibration was only performed at the beginning of the study.

Throughout the campaign, particulate matter was simultaneously collected upon filters as part of the PILS unit. These filters were then added to a sample bottle filled with distilled

deionized water and sonicated for a minimum of 24 hours. The solution from the sample
bottle was then injected into the anion ion chromatograph. The sulfate concentration was
compared to the average sulfate concentration measured online by the PILS-IC over the
same sample period. Figure 7 illustrates the compared sulfate values. It is important to
note that the large differences between the filter and online measurements usually
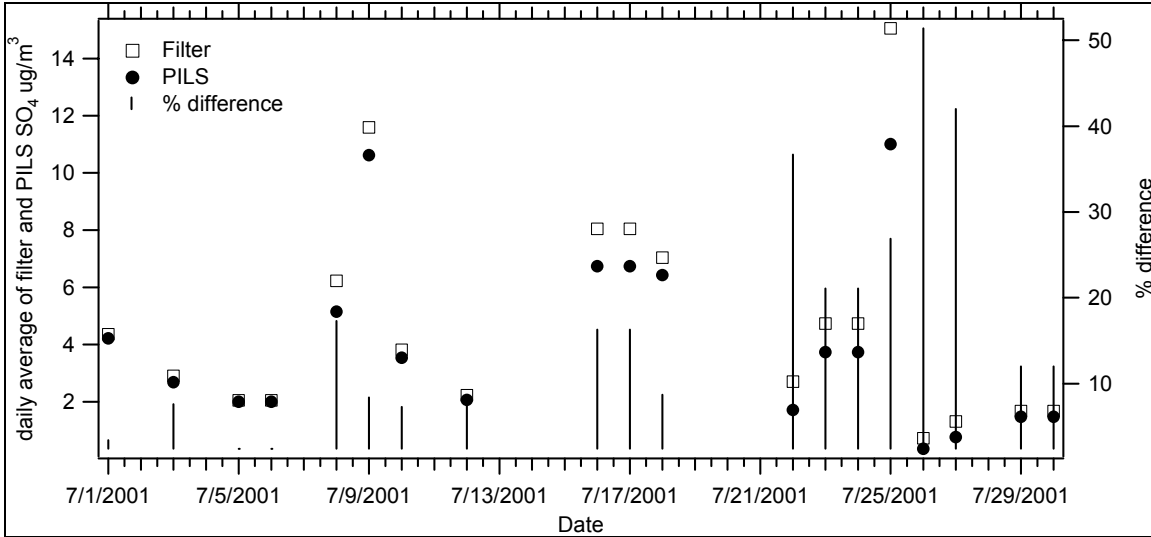coincide with low concentrations of sulfate.

Figure 7: Measured sulfate as reported by the internal filter check and the average of the
online PILS-IC measurements over the same time period.

Data completeness

The following table summarizes the PMTACS-NY PILS-IC data completeness:

Data Period: 7/1/2001 0:00 - 8/4/2001 0:00
Total possible hours: 816

Ions	Hours recorded	Data completeness
Cation	551	68%
Anion	611	75%

The next table summarizes the data loss causalities:

IC problems	45%
Operational errors	25%
PILS problems	20%
Daily operations	10%

Flagging

All data has been flagged and turned into the NARSTO template for review. Unlike most
instruments, the PILS-IC has irregularly spaced periods of downtime. The IC software
does not activate upon specified timeslots, so sampling periods were not started or

stopped at regular intervals. When an irregular period of down time occurred, this anomalous time period was marked as "*999*" in both the start and end points. Each corresponding ion data block was left blank and flagged with "M1." The utilized flags are as listed:

M1   Missing value because no value is available (PILS-IC was down)
M2   Missing value because invalidated by data originator
V0   Valid value
V1   Valid value but comprised wholly or partially of below detection limit data
V5   Valid value but qualified because of possible contamination (e.g., pollution source, laboratory contamination source)
V6   Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sample handling)