PMTACS-NY 2001
Data and QA Summary Report for R&P 5400 Carbon Particulate Monitor
May 2002

Overview of Instrument Operation and Data Generation:

- Ambient air stream passes through a 16.7 LPM URG cyclone, then into the instrument where it is diverted to one of two identical collectors, Collector A or Collector B.
- During collection cycle the 16.7 LPM (nominal) sample air flows though a specially designed stainless steel impaction type collector. The collector is toroidal, with a series of precision drilled holes acting as impactor jets, and a flat stainless steel plate acting as collector for particles. The manufacturer's design parameters specify a 50% collection efficiency for particles of size 140 nm or 0.14 μm (i.e., D_{50} = 0.14 μm).
- Flow control is achieved by the pressure drop across the collector. This means there is no active flow control and no flow controller. Flow is measured by a mass flow meter and converted to volumetric flow using values for average seasonal temperature and pressure entered by the user. Pressure at the collection plates is about 22" Hg, or about 0.73 atm.
- The collector temperature is held constant at 50°C.
- After the collection period (one hour for this campaign), valves switch the sample flow and collection to the other collector, and the previously collected sample is analyzed. Thus, during normal operation, one collector is collecting sample, and the other is undergoing analysis.
- During the analysis cycle the collector, afterburner, CO_2 sensor, and a circulating pump are isolated as a closed analysis loop.
- The complete analysis phase consists of about 24 steps for this configuration of the instrument. It is beyond the scope of this report to detail all these steps, but instead a condensed description of the analysis sequence will be attempted.
- After analysis begins, the loop is purged with filtered ambient air, the afterburner is heated to 750°C, and the loop is purged again.
- The CO_2 sensor then measures the amount of CO_2 in the analysis loop before performing the stepwise oxidation of the material collected in the collector(M0).
- The collector is heated to 275°C and held for 8 minutes and the amount of CO_2 in the loop is measured(M3).
- The collector is heated to 750°C and held for 4 minutes and the amount of CO_2 in the loop is measured(MF).
- The collector and afterburner are cooled and purged. Filtered purge air is "collected " for 90 s to form the basis of the instrument's residual measurements and computations.
- The afterburner is heated to 750°C and the loop is purged again.
- The CO_2 sensor then measures the amount of CO_2 in the analysis loop before performing the stepwise oxidation to compute residuals($M0_{res}$).
- The collector is heated to 275°C and held for 8 minutes and the amount of CO_2 in the loop is measured($M3_{res}$).

- The collector is heated to 750°C and held for 4 minutes and the amount of CO_2 in the loop is measured(MF_{res}).
- The collector and afterburner are cooled and purged.
- Data collection and computations are done by the instrument's electronics and computer. At the end of each analysis cycle about 40 parameters are stored in memory. This data can be displayed on the front panel, or downloaded to a computer. For this campaign the data was downloaded to a computer using the RPCOMM software provided by the manufacturer. (The instrument can store at least three months of hourly cycle data – or more than 2000 cycles.)

Data Reduction:

- Instrument data records include about 40 fields, as noted above. Key parameters include the instrument status codes and the computed carbon mass concentrations in micrograms per cubic meter for the intermediate (275°C) and final (750°C) oxidation steps (referred to as "burns").
- Ambient background CO_2 concentrations, purge and residual concentrations are also included in the data record, but these parameters are not needed under normal circumstances.
- The recorded data is insufficient to rigorously check the instrument's computation of mass concentrations from the CO_2 sensor's measurements because the pressure in the sample loop during analysis varies, and this information is not stored. However, assuming the CO_2 amounts measured are correct, and using the collection volumes, one can check the calculation of mass concentrations.
- Based on instrument status codes and operator notes, the data records are assigned a flag. (NARSTO flags are used – see below.)
- A zero offset correction is subtracted from each MC3 and MCF value to obtain the final data with fields denoted as "275 Burn" and "TC".

Period of Operation and Operations Log:

- Instrument was set up and began running on June 28, 2001 in an outdoor enclosure.
- Reported data begins with cycle 9, beginning at 00:00 on June 29, 2001.
- July 7,2001 – audits and checks (see below).
- July 18, 2001 – filter blank test 15:00-17:59.
- July 20, 2001 – vacuum blank test 10:00-13:59.
- July 23, 2001 – afterburner on loop B fails at 4:00; not replaced until July 27 at 14:00. All 275 Burn data on loop B flagged for this period.
- July 31, 2001 – audits and checks (see below).
- August 6, 2001 – instrument off at 12:00. Last valid data point at 10:00.

Data Flagging:

The following flags are used for the data generated by this instrument during this campaign:

- V0 Valid Value
- M2 Missing Value because invalidated by data originator (i.e., zero checks, calibrations, malfunctions and instrument maintenance.)

Summary Statistics:

There were 923 hours starting at 00:00 on June 29 and ending at 11:00 on August 6. This is the total used for completeness statistics of the hourly data. Daily or 24 hour averages were considered valid if 75% of hours (18 or more) were valid values. Days from June 29 to August 5 are considered (37 days).

	Hour averages		24 hour averages	
	275 Burn	TC	275 Burn	TC
Number of valid values	835 (90.5%)	881 (95.4%)	32 (86.5%)	36 (97.3%)
Number of missing values	88 (9.5%)	42 (4.6%)	5 (13.5%)	1 (2.7%)

Data Summary:

Summary of concentrations measured during period of operation (all data in $\mu g/m^3$):

	Hour averaged data	Hour averaged data
	275 Burn	TC
Minimum	0.559	0.698
25^{th} percentile	1.191	1.664
Median	1.516	2.357
75^{th} percentile	1.889	3.242
Maximum	2.963	9.348
Mean	1.545	2.576

Quality Assurance Experiments:

- On July 7, a number of checks and audits were performed. First a manual CO_2 audit was done. The expected values for the zero, low CO_2 , and high CO_2 were 0, 1501, and 3987, respectively; and the measured values were –25, 1405, and 4028. A calibration of the LICOR sensor was then done, followed by a leak check and flow audit. The instrument passed the leak check and flow audit (16.66 LPM indicated while the BIOS calibrator measured 16.89). Another manual audit was done, this time with measured values of 3, 1445, and 4064. The percent errors for the low CO_2 points were –6.8% before and –3.7% after. The percent errors for the high CO_2 points were +1.0% before and +1.9% after.

- A second and final set of audits and checks were done on July 31. Both A and B channels passed leak checks. Manual audits of the CO_2 sensor were done twice. As before, the expected values were 0, 1501, and 3987 for zero, low CO_2 , and high CO_2 . Measured values for the first audit were –21, 1398, and 3995; and those for the second audit were +41, 1408, and 4000. The percent errors for the low CO_2 points were –6.9% and –6.2%. The percent errors for the high CO_2 points were +0.0% and +0.0%.
- Blank tests were attempted on July 18 and July 20. On July 18, a Zeflour filter was placed in a metal housing and placed upstream of the 5400 inlet. Three 5400 cycles ran sampling filtered air and mass concentrations measured. The average reported value for MC3 was about 2.6 $\mu g/m^3$ and for MCF was nearly 5 $\mu g/m^3$. These values are higher than most of the ambient data, and could not reasonably be "zero offsets". On July 20, a cap was placed on the inlet and "vacuum blanks" were attempted. In this case one cannot look at reported mass concentrations (because the sample volume is almost zero), but instead at the increase in carbon measured during the thermal oxidation cycles. Fro these vacuum blanks with sample volumes of 2 liters or less (compared with 940-1000 liters), the carbon difference signal was within 5% of those from the Zeflour filter blanks.
- Zero offset corrections were determined from comparisons with TEOM and speciation filter data since the attempts to generate "blanks" using filters or zero sample flow were unsuccessful. Estimates of the zero offset were obtained by considering very low PM periods as measured by the TEOM. Three periods were chosen: July 2, July 26-27, and July 29. Average TEOM MC's for these periods were between 1 and 2 $\mu g/m^3$. From speciation filter measurements, and from AMS measurements during the same periods, we expect total carbon to generally contribute at most 65% of the mass, and organic carbon to contribute at most 50% of the mass. If one uses these numbers, the estimated zero offset corrections used in this data set are 0.32 $\mu g/m^3$ for the 275 Burn, and 0.48 $\mu g/m^3$ for total carbon.

<u>Comparisons with Filter Data</u>

- Comparison data is available from the EPA Speciation sampler (R&P 2300) at PS219. The sampler collected 24 hour samples every third day during the intensive. One of the filters collected (a quartz substrate) was analyzed for OC (organic carbon), EC (elemental carbon), and TC (total carbon) using the thermal-optical transmittance (TOT) method specified in NIOSH 5040.
- Filter data is shown both with and without an average blank correction determined from approximately 60 filter blanks from the five New York sites using the R&P 2300.
- Figures 1-6 show the comparisons of the 5400 data and the Speciation filter data for carbon. The 5400 measures much lower total carbon than the filters as seen in Figures 1 and 2. If the three very low (and potentially incorrect) filter measurements are rejected, the difference is about 70% (i.e., filters measure 70% more total carbon than the 5400). For the selected data, the correlation is high (.967), and the blank corrected data has an intercept (-0.173) that is fairly close to zero. [NOTE: The standard deviation on the blank correction for total carbon is 0.26 $\mu g/m^3$ – out of a total blank of 1.10 $\mu g/m^3$.]

- Agreement is even worse for organic and elemental fractions, as seen in Figures 3-6. Part of this may be due to the different collection temperatures; and oxidation temperature profiles of the analysis methods.
- There are errors in the organic and elemental fractions which partially compensate for each other, but as noted above, even the total carbon values do not agree between the methods.
- As currently operated, it appears that the methods are not comparable. There is good correlation in some cases, but quantitative results are so different that one or both of the methods is clearly in error.

Problems or Issues with the Instrument and/or Data:

- The lack of an experimental procedure to determine the zero offsets for the instrument is troubling – see discussion above.
- The poor comparison with filter data, even when the data is selected to remove data that seems to be outliers, is also troubling.
- It would be very useful for the manufacturer to provide to the user community a detailed description of the low level data collection, transfer, and computation routines for this instrument.

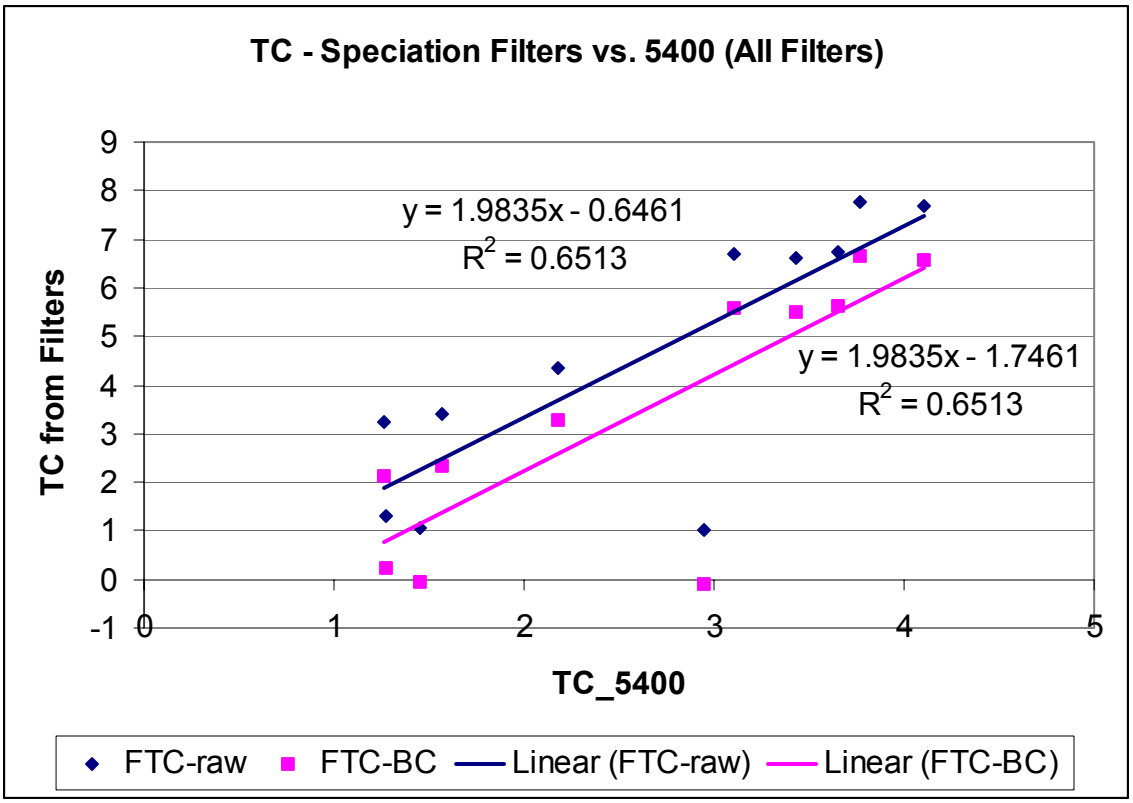

Figure 1. Total Carbon scatter plot – all data.

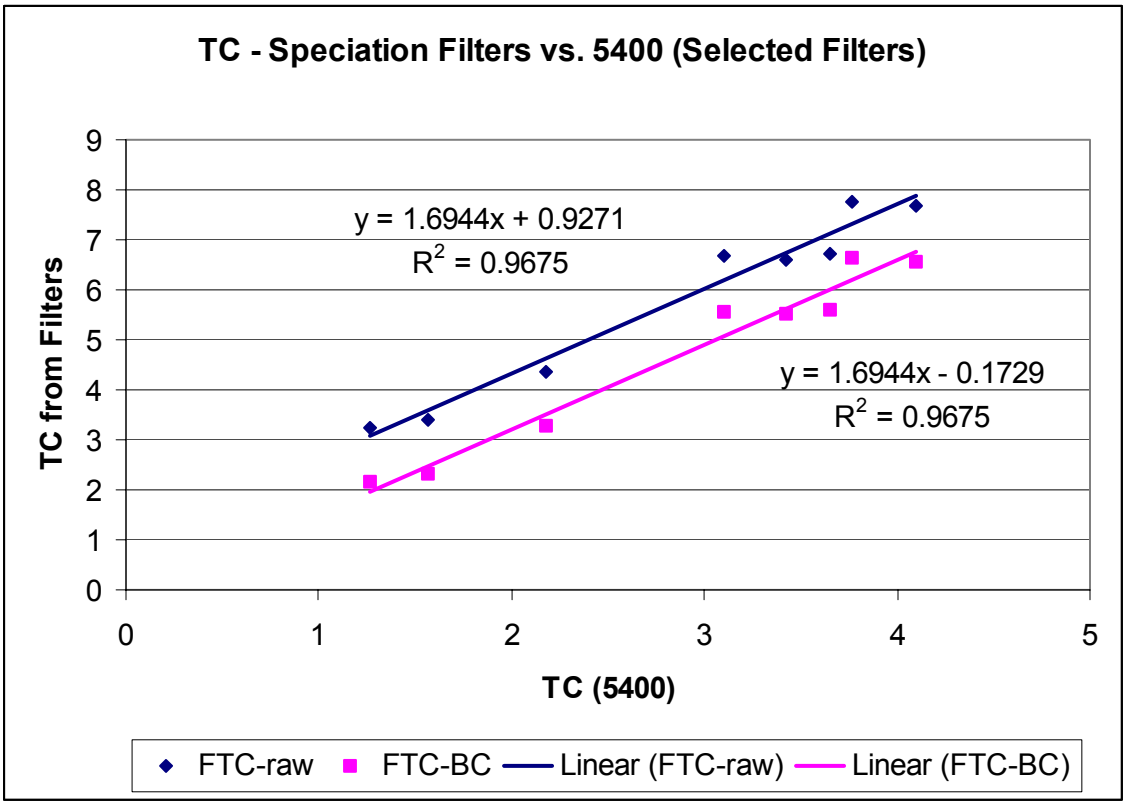

Figure 2. Total Carbon scatter plot – selected filters only.

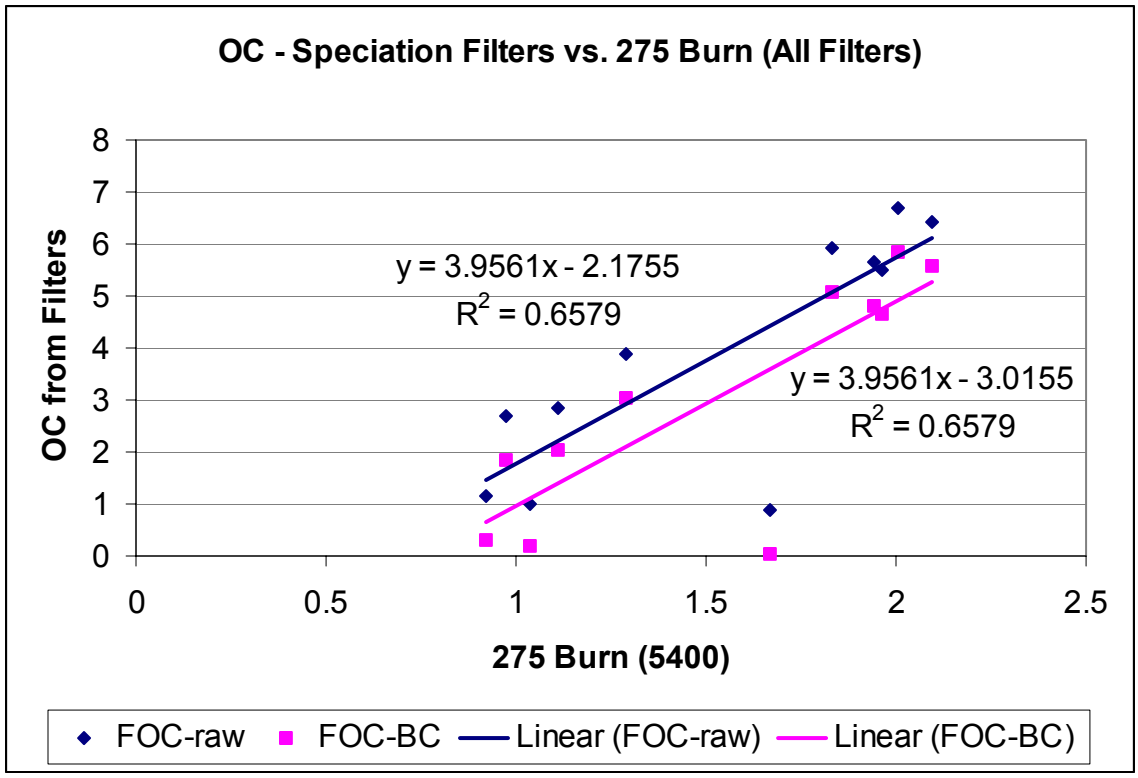

Figure 3.

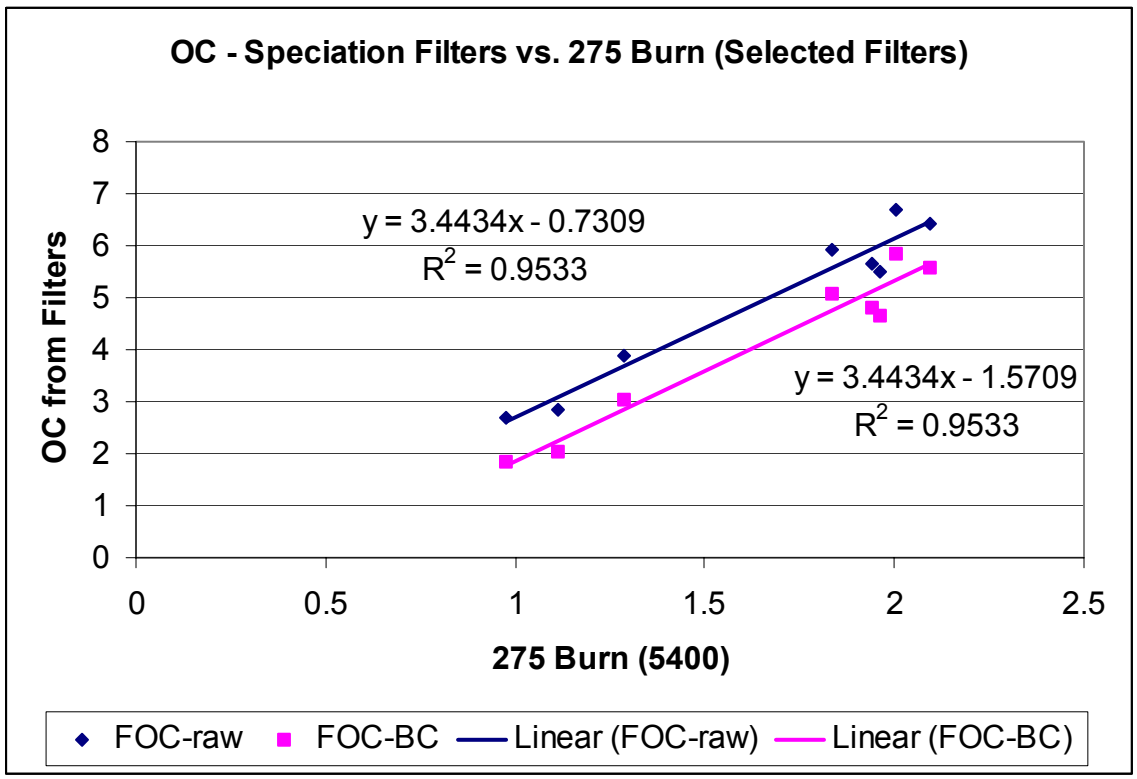

Figure 4.

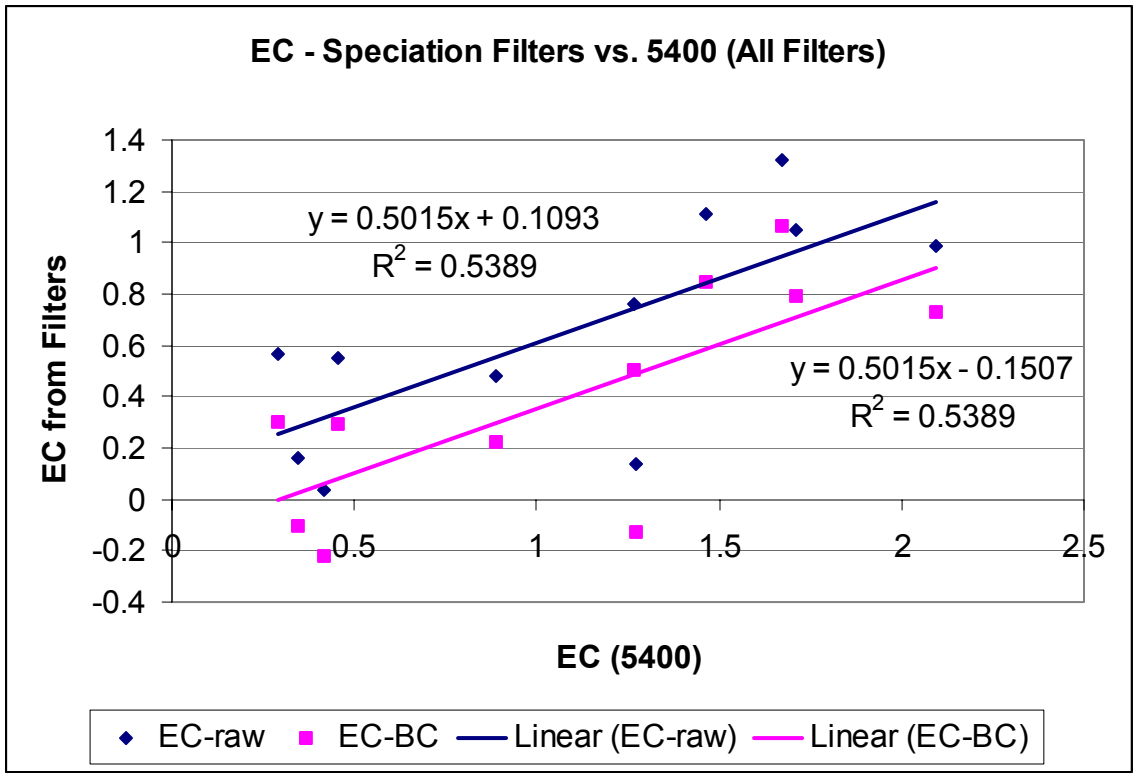

Figure 5.

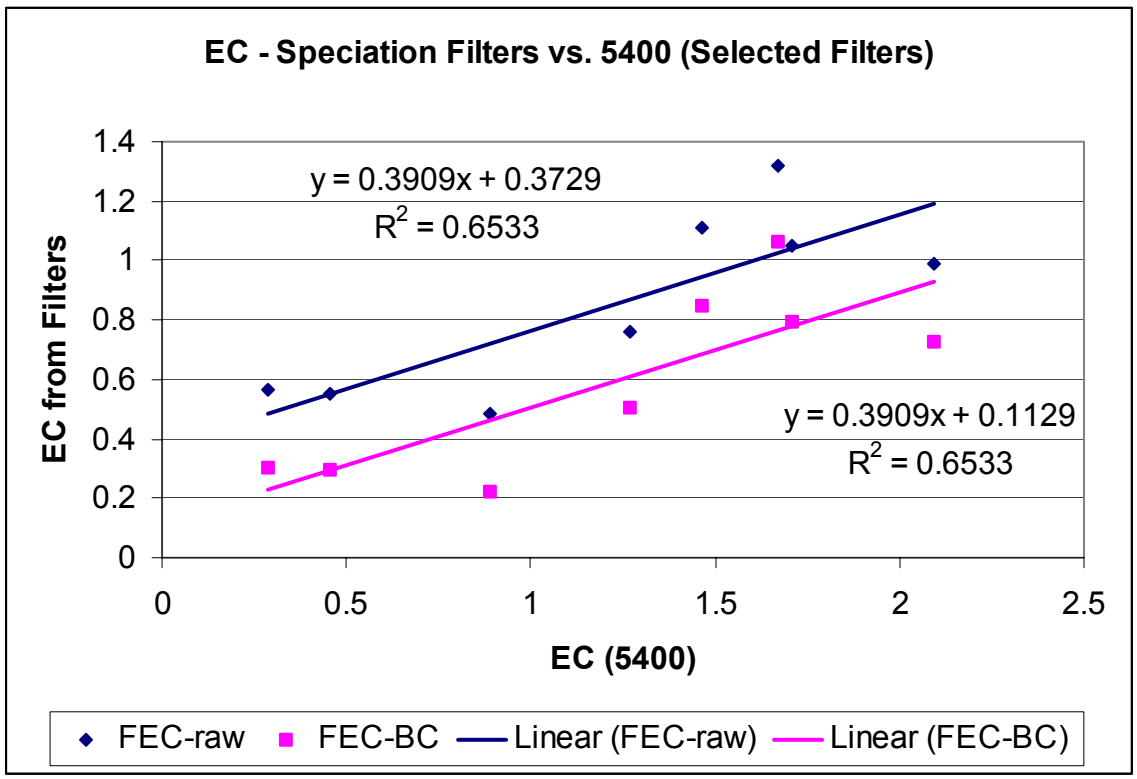

Figure 6.