

Library Reference 3.6

PT Study 0094 Results

PT Sample	TP94-1	TP94-2	TP94-3	TP94-4	TP94-5	TP94-6	TP94-7	TP94-8	TP94-9	TP94-10
Lab Sample#	2906162	2906163	2906164	2906165	2906166	2906167	2906168	2906169	2906170	2906171
Result (mg/L)	0.094	0.014 ^{#WH}	0.366	0.060	0.233	0.006	0.005	0.696	0.024 ^{#WH}	0.162
Assigned Value (mg/L)	0.0910	0.0080	0.345	0.0550	0.225	0.0040	0.0015	0.696	0.0200	0.158
Hi Warning Limit	0.100	0.0125	0.371	0.0635	0.247	0.00718	0.0074	0.746	0.0234	0.174
Hi Acceptance Limit	0.105	0.0147	0.384	0.0677	0.258	0.00877	0.0104	0.771	0.0250	0.182
SD	0.00464	0.00224	0.0130	0.00424	0.0110	0.00159	0.00295	0.0251	0.00168	0.0079

Note: ^{#WH} within the high warning limit of between 2 and 3 standard deviations (SD) of the assigned value.
acceptance limits is greater than 3 standard deviations (SD) away from the assigned value.

Onondaga County
Department of
Water Environment Protection

Inter-Office Letter

Subject: AMP Proficiency Test Sample - Environment Canada
Study # 0094

To: Janaki Suryedevara
From: Mark Fowkes
Date: Thursday, October 08, 2009
CC: Jeff Noce, Joseph Mastriano

An investigation on the above noted PT samples was conducted to check for possible error(s) as to why the warning criteria was reached on two out of ten samples from study # 0094. To briefly review, our laboratory received two sets of samples at various concentration levels from Environmental Canada on June 2, 2009. One set of ten samples was for determining Total Phosphorous and the remaining set of ten samples was for determining Turbidity. The submitted results from **both sets were within the established acceptable limits**. However, out of the sample set for Phosphorous, two of the ten samples were within the warning limit. Normally, when a proficiency test result falls within the warning limit, the laboratory practice is to check for possible errors, even though the result is acceptable. Below are the results of that investigation, conclusions, and any remedial plan.

1. Review of digestions and analyses: (see attachments)

- a. PT samples (Study 0094) was received as a blind (unknown concentration levels) set and integrated into part of the regular analytical sample load. As part of our normal procedure, these samples were treated as a regular sample and digested along with the rest of the week's samples (see attachment).
- b. Samples were prepared on June 2, 2009 and phosphorous analysis was performed on June 3, 2009 using one of the laboratory's spectrophotometer following method reference Standard Methods 18th Edition, 4500-P E. All quality control solutions and results fell within the laboratory's acceptance criteria as outlined in the section's SOP Document No. Wet-9.
- c. The total phosphorous concentration on two samples exceeded the highest standard concentration of 0.300 mg/L. As per laboratory and NELAC protocol all samples must fall within the standard calibration range. Therefore, these two samples were manually diluted that same day and re-analyzed. The sample dilution performed for samples TP94-3 and TP94-8 was a 1:5 dilution.
- d. Review of all QA/QC batch analysis indicated compliance (see checklist below) for all quality control criteria.

Batch QC Checklist

1. Calibration Correlation Coefficient equal to or greater than 0.955: **Yes**
2. Initial Calibration Verification (secondary source standard) within acceptance criteria: **Yes**
3. Continuous Blank below MRL: **Yes**
4. Laboratory Reagent Blank below MRL: **Yes**
5. Laboratory Fortified Blank below MRL: **Yes**
6. Continuous Calibration Verification(s) with acceptance limits: **Yes**
7. Laboratory Fortified Sample(s) within acceptance criteria: **Yes**
8. Duplicate Difference(s) within acceptance criteria: **Yes**

2. Review Of Method(s):

- a. A review was conducted of analytical SOP Doc. No. "Wet-9", which details the general procedures for TP determinations of total phosphorous using spectroscopy. The review with analyst indicates that all proceeds were conducted properly.
- b. A review was conducted of analytical SOP Doc. No. "Wet-9", which also details the preparation procedures for treatment of samples before analysis of total phosphorous. The review with the technicians indicates that all procedures were conducted properly.

3. Discussion:

- a. Total phosphorous is routinely performed using EPA Method 365.2 on the laboratory's spectrophotometer instrument. The laboratory has been using this approved EPA method for over twenty years. Additionally, the laboratory has successfully achieved acceptable NYS certification PT results for this method when determining total phosphorous.
- b. The samples were integrated into the laboratory's normal workload and analyzed by the same methods as our routine ambient water samples. They were taken through a preliminary digestion using sulfuric acid and ammonium persulfate. All samples were heated and taken down to a volume of approximately 5-10 mL. The samples were cooled and pH was adjusted using 1N NaOH drop wise to just below the phenolphthalein endpoint (sample pH is taken to the endpoint and then back down using one drop of 1M H₂SO₄ acid. All samples are then brought back to 50 mL solution volume.
- c. All phosphorous PT samples prepared on June 2, 2009 were within the acceptance criteria established by Environment Canada. Two of the ten PT samples were within the warning limits of between 2 and 3 standard deviation of the mean and were flagged "WH" for warning high.
- d. The phosphorous PT samples were evaluated for possible bias using a standard "Z-Score". If a laboratory is concluded to show bias, the results are flagged accordingly. The evaluation report did not find any bias for either the phosphorous or turbidity samples.
- e. A performance rating was also provided for both phosphorous and turbidity. The turbidity received a "good" rating since all ten samples did not recent any flags. The phosphorous results received a "satisfactory" rating. The "satisfactory" scored is given when 2 up to 5 results have been flagged. In this case they were flagged for 2 samples receiving flags of "WH".

4. Conclusions:

All samples met the acceptance criteria established by Environmental Canada. Two phosphorous samples showing flags of “WH” indicating that the laboratory results were within the warning limits on the high side. This means that the results were between two and three standard deviation above the assigned value. The statistical data from Environmental Canada indicated that there is no systemic or laboratory bias for phosphorous. All batch quality control solutions setup during the analysis of PT samples (Study 0094) were acceptable and performed according to the stated procedures. Since all analytical requirements were met, and all results fell within acceptable limits, I do not recommend any further action.

5. Remedial Plan:

No further investigation of the method is recommended.