**On-line Heated UV/Persulfate or Ozone Digestion and Analysis of Total Phosphorus**

1. General Discussion

*a. Principle:* The Total phosphorus (TP) concentration can be measured using two different methods. Both methods use advanced photochemical oxidation, heat, sulfuric acid, and UV/irradiation. The difference between method (A) and (B) is the oxidizer used ozone and persulfate, respectively (Figure 1).
Both methods lead to complete oxidation of the phosphorus in the sample, exhibit comparable results, and as a result an accurate representation of the TP level in the sample.
To ensure complete oxidation of the dissolved and particulate phosphates, the oxidation is performed at near boiling water temperature. Sulfuric acid ammonium molybdate is used in both methods, where it reacts with the phosphate ions converting them to Phosphomolybdate complex. The phosphomolybdate is then reduced, using ascorbic acid, to molybdenum blue. The intensity of the blue color is detected at 880 nm and is proportional to the phosphate concentration present in the sample.

*b. Minimum detectable concentration:*
Approximately 10 µg P/L.

2. Apparatus

An online/offline automated instrument consisting of,

- *a.* Automated p*retreatment filtration system* (optional), filters water samples containing suspended particles for preparation of the sample for digestion and analysis.
- *b. Multi function injection system*, with two 8-port valves, that allows sample preparation for digestion and analysis (Figure 2). As a result, saves time and money, eliminates sample preparation error, and reduces reagent consumption because not continuous.
- *c. Oxidation reactor vessel* consisting of a heated (90 $^{o}$C, Method A; 95$^{o}$C, Method B) UV irradiated chamber, which ensures complete oxidation of phosphorus.
- *d. Absorbance detector* with the capability of measuring the absorbance of light at 880 nm. The detector is thermally stabilized at ~50$^{o}$C, to prevent any drifting.

3. Reagents

Use purified water to prepare all standards and solutions, and for dilution.

- *a. Sodium hydroxide, 5 M:* Dissolve 32 g NaOH in 160 mL purified water.
- *b. Sulfuric acid:* Dilute 62.5 mL concentrated $H_2SO_4$ to 250 mL with purified water.

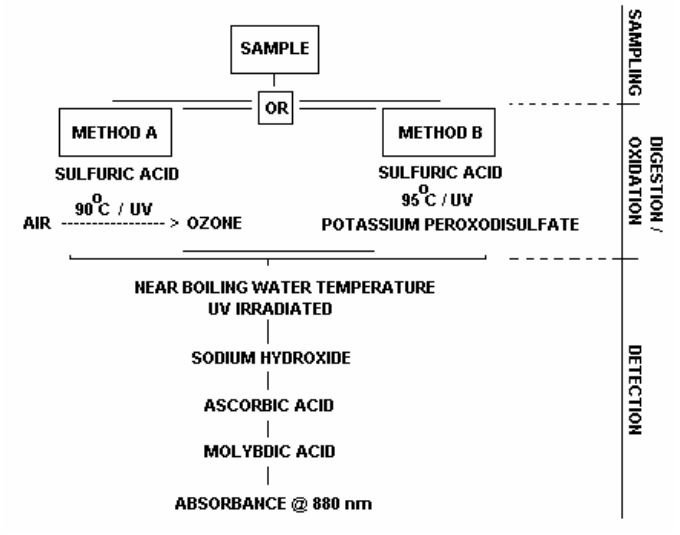


**Figure 1. Outline of Methods Used for Analysis of TP**

- *c. L(+)-ascorbic acid:* Dissolve 1.44 g ascorbic acid in 60 mL purified water.
- *d. Molybdic acid:* Dissolve 1.08 g Ammonium molybdate tetrahydrate, 99%, and 0.0432 g Potassium antimonyl tartrate trihydrate, 99%, in 90 mL purified water.
- *e. Standard phosphate solution:* Dissolve 4.394 g Potassium dihydrogenphosphate (heated for 1 hour at 105-110$^{o}$C and cooled in a desiccator) in 1L of purified water.

4. Procedure

*a. Calibration curve:* According to the manual provided with the instrument, prepare and set the standards. The calibration curve is created automatically by the instrument using the appropriate standards.
*b. Sample preparation, digestion, and analysis overview:*

***Method A:*** *Using Ozone for oxidation*

- The sample is pulled automatically into a syringe where it is mixed with the appropriate reagents by the multifunction injection system.
- The sample is mixed with sulfuric acid, heated, sparged with ozone, and UV irradiated at 90$^{o}$C, as a result the phosphorus in the treated sample is oxidized to phosphate ions.
- The treated sample is then mixed with sodium hydroxide (pH control, pH~0.4)
- Molybdic acid solution is added to the sample, where the phosphate ions form phosphomolybdate complex

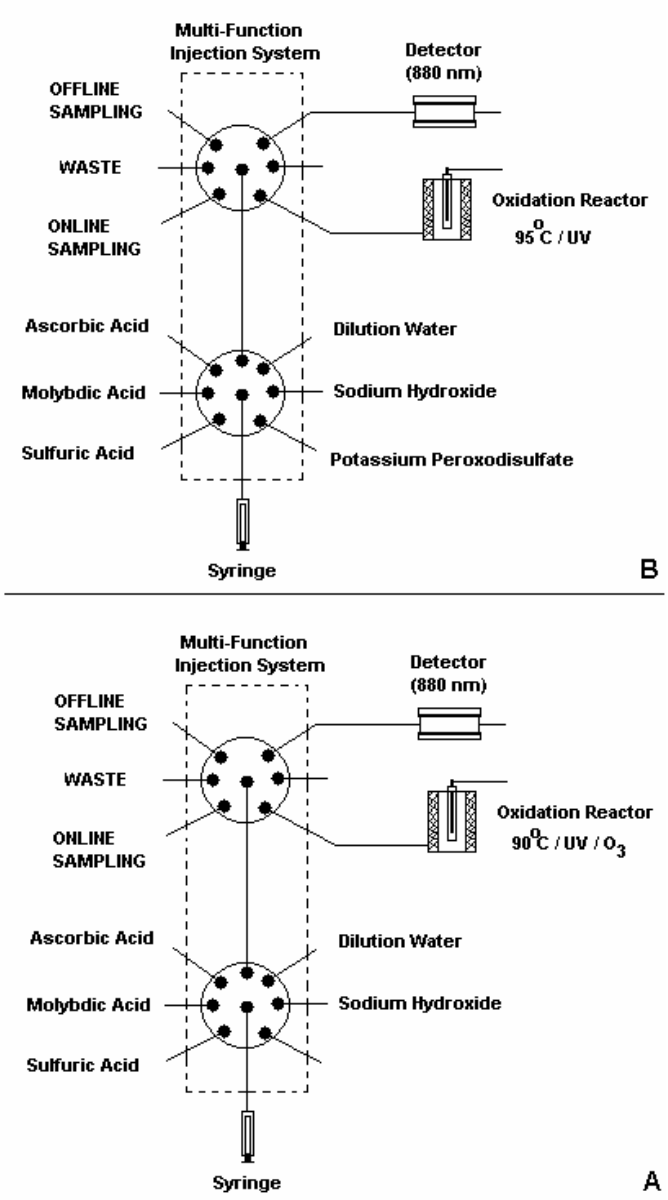


**Figure 2. Multifunction Injection System for TP Analysis. (A) Using ozone for oxidation, (B) Using Persulfate for oxidation**

- Ascorbic acid is then added to the sample where the phosphomolybdate complex is reduced, and yields an intense blue color

***Method B:*** *Using Persulfate for oxidation*
- The sample is pulled automatically into a syringe where it is mixed with the appropriate reagents by the multifunction injection system.
- The sample is mixed with potassium peroxodisulfate and sulfuric acid, heated, and UV irradiated at 95°C, as a result the phosphorus in the treated sample is oxidized to phosphate ions.
- For pH (~0.4) control, the treated sample is mixed with sodium hydroxide
- Molybdic acid solution is added to the sample, where the phosphate ions form phosphomolybdate complex
- Ascorbic acid is then added to the sample where the phosphomolybdate complex is reduced, and yields an intense blue color

5. Calculations

The instrument calculates the final concentration of the TP within the sample automatically by referencing the calibration curve that was developed using the standard phosphate solution, and using the following equation,

$$C_{TP} = (A_{TP}-A_z).[C_s / (A_s-A_z)]$$

where,

$C_{TP}$ = Phosphorus concentration in sample
$C_s$ = Concentration of span calibration standard
$A_s$ = Absorbance of span calibration standard
$A_z$ = Absorbance of zero calibration standard
$A_{TP}$ = Absorbance of phosphorus in sample

6. Precision and Bias

*a.* TP was measured for several compounds using method A and method B, and the results were compared to the data acquired through the Japanese Industrial Standard (JIS) Method (Table 1).

*b.* The recovery of TP levels in wastewater samples acquired from different industries are displayed in Table 2. The reliability of the data is demonstrated by comparing the results, to the data acquired by analyzing for the TP in the samples, using the JIS method.

7. References

Shimadzu On-line Total Nitrogen/Total Phosphorus Analyzer, TNPC-4110(C) Instruction Manual. Shimadzu Corporation: Analytical and Measuring Instruments Division: Kyoto, Japan.

Shimadzu On-line Total Nitrogen/Total Phosphorus Analyzer, TNP-4110 Instruction Manual. Shimadzu Corporation: Analytical and Measuring Instruments Division: Kyoto, Japan.

**TABLE 1. Recoveries of Total Phosphorus Containing Compounds**

| Compound | TP (mg/L) | Method A (TNPC-4110)* | | Method B (TNP-4110)** | | JIS *** Method |
|---|---|---|---|---|---|---|
| | | Recovery (%) | RSD (%) | Recovery (%) | RSD (%) | Recovery (%) |
| **Disodium Phenyl Phosphate** | 1 | 98.0 | 0.379 | 99.7 | 0.033 | 100 |
| **Benzyltriphenylphosphonium Chloride** | 1 | 99.7 | 0.314 | 101 | 0.713 | 102 |
| **ATP (Adenosine Triphosphate)** | 1 | 99.4 | 0.728 | 97.6 | 0.611 | 100 |

* n = 3
** n = 2
*** JIS (Japanese Industrial Standard) method is based on “Methods 46.3 Total phosphorus and 46.3.1 decomposition with Potassium Peroxodisulfate analysis in JIS K-0102 Testing Methods for Industrial Wastewater”, RSD (3-10 %)

**TABLE 2. Total Phosphorus Measurement within Waste Water Samples from Different Industries**

| Type of Industry | Method A (TNPC-4110)* | | Method B (TNP-4110)* | | JIS method** |
|---|---|---|---|---|---|
| | TP (mg/L) | RSD (%) | TP (mg/L) | RSD (%) | TP (mg/L) |
| **Food A** | 0.243 | 0.824 | 0.246 | 2.71 | 0.235 |
| **Food B** | 2.11 | 0.667 | 2.10 | 1.03 | 2.11 |
| **Food C** | 8.07 | 0.869 | 8.16 | 2.06 | 8.12 |
| **Chemical A** | 1.08 | 1.05 | 1.03 | 2.10 | 1.10 |
| **Chemical B** | 1.10 | 0.833 | 1.06 | 0.269 | 1.11 |
| **Chemical C** | 6.64 | 0.077 | 6.83 | 0.669 | 6.67 |
| **Electrical** | 0.68 | 0.360 | 0.64 | 0.230 | 0.68 |
| **Brewing** | 1.05 | 0.838 | 1.02 | 2.08 | 1.05 |
| **Sewage Treatment** | 0.694 | 0.504 | 0.682 | 0.198 | 0.705 |
| **Pharmaceutical** | 0.487 | 0.349 | 0.453 | 0.185 | 0.478 |

* n = 3
** JIS (Japanese Industrial Standard) method is based on “Methods 46.3 Total phosphorus and 46.3.1 decomposition with Potassium Peroxodisulfate analysis in JIS K-0102 Testing Methods for Industrial Wastewater”, RSD (3-10 %)