On-line Heated UV/Persulfate Digestion or Catalytic Combustion Oxidation and Analysis of Total Nitrogen

1. General Discussion

a. Principle: The Total Nitrogen (TN) concentration can be measured using two different methods (Figure 1),

Heated UV/Persulfate (HUP) Method, involves ultraviolet radiation, heated (70 ^{o}C) digestion, and the oxidation of nitrite, nitrate, ammonia, and organic nitrogen into nitrate. The nitrate concentration is determined by measuring the absorbance at 220 nm.

Catalytic Combustion (CC) Method, involves the decomposition of nitrates, nitrites, ammonia, and organic nitrogen compounds into nitrogen monoxide (NO) at 720 ^{o}C. The carrier gas containing the NO is cooled and dehumidified using the electronic dehumidifier, and passed to the Chemiluminescence detector. Within the chemiluminscence, ozone is generated which interacts with the NO, generating excited nitrogen dioxide (NO_2*). A silicon diode is used to detect the light emitted from the excited molecules, which result in a signal that is proportional to the concentration of TN

b. Interference:

HUP Method: Bromine and heavy metals such as Fe, Mn, or Cr, may cause some interference if present. In seawater there is no interference if the bromine is less than 2 to 3 %, above that, the sample may be diluted to reduce the effect of interference. In addition, metals in seawater will cause no interferences if less than 1 mg/L.

CC Method: No interference from metals or bromine in seawater, as the method uses chemiluminescence for detection.

c. Minimum detectable concentration: Approximately 50 µg N/L, for both methods.

2. Apparatus

***HUP Method*:**
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, which allow 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.

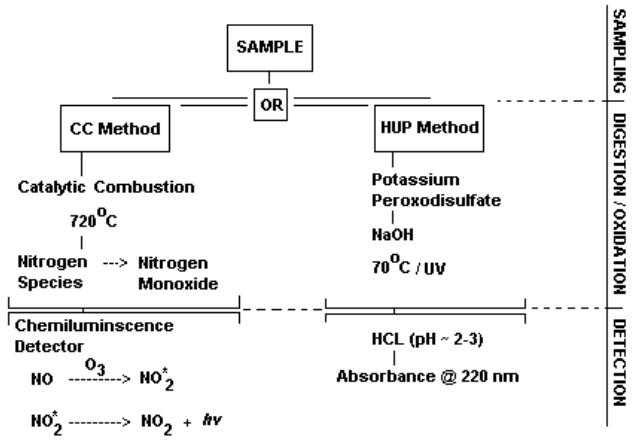

Figure 1. Outline of Methods Used for Analysis of TN

c. *Oxidation reactor vessel* consisting of a heated UV irradiated chamber
d. *Thermally heated absorbance detector* with capability of measuring the absorbance of light at 220 nm

***CC Method*:**
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 analysis (Figure 2). As a result, saves time and money, eliminates sample preparation error, and reduces reagent consumption because not continuous.
c. *Combustion chamber*, that encloses the combustion tube containing the platinum catalyst that is heated at 720 ^{o}C, where the catalytic oxidation occurs
d. *Chemiluminescence detector*, allows detection of the nitrogen species, as a result of the interaction with the generated ozone

3. Reagents

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

***HUP Method*:**

a. Sodium hydroxide, 5 M: Dissolve 60 g NaOH in 300 mL purified water.

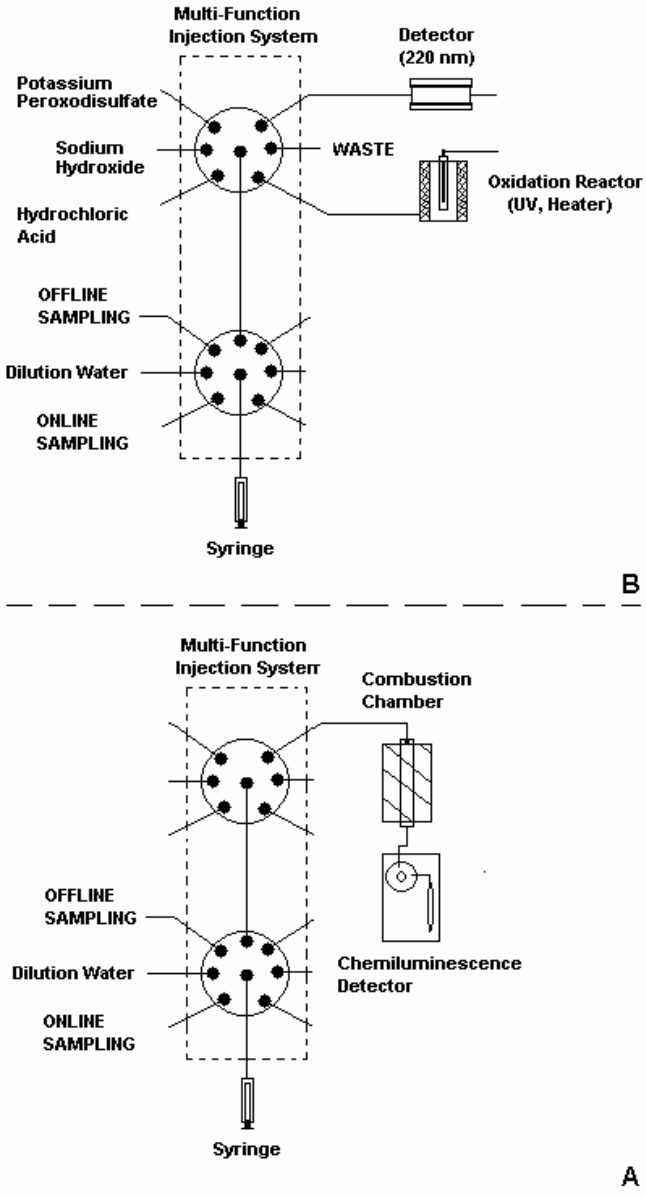

Figure 2. Multifunction Injection System for TN Analysis for the CC method (A) and HUP method (B)

b. *Persulfate (Potassium Peroxodisulfate):* In 1000 mL of purified water, dissolve 15 g of persulfate.

c. *Hydrochloric acid:* Add 15 mL of HCL (little by little and cautiously) to 240 mL of purified water, while agitating the flask.

d. *Standard nitrate solution:* Heat potassium nitrate (KNO_3) for approximately 3 hours at 100°C, and allow it to cool in a desiccator. Later dissolve 7.220 g of KNO_3 in 1L of purified water.

***CC Method*:**

a. *Standard nitrate solution:* Heat potassium nitrate (KNO_3) for approximately 3 hours at 100°C, and allow it to cool in a desiccator. Later dissolve 7.220 g of KNO_3 in 1L of purified water.
b. No other reagents are required for this method

4. Procedure

a. Calibration curve: Prepare and set the standards according to the manual provided with the instrument. A calibration curve is created automatically by the instrument using the prepared standards.

b. Sample preparation, digestion, and analysis overview:

HUP Method:

- 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 sodium hydroxide and potassium peroxodisulfate, sparged with ozone, and UV irradiated at 70°C, as a result, the nitrogen in the treated sample is oxidized to nitrate.
- The treated sample is then mixed with hydrochloric acid (pH control, pH~ 2-3)
- The nitrate concentration is detected by measuring the absorbance at 220 nm

CC Method:

- The sample is pulled automatically into a syringe where it is diluted or mixed with the appropriate reagents by the multifunction injection system.
- The sample is then passed through the combustion chamber and catalytically oxidized.
- The sample is then passed to the chemiluminscence detector where the concentration of TN is analyzed.

5. Calculations

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

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

where,

C_{TN} = Nitrogen 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_{TN} = Absorbance of Nitrogen in sample

6. Precision and Bias

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

b. The recovery of TN levels in wastewater samples acquired from different industries is displayed in Table 2. The reliability of the data is demonstrated by comparing the results, to the data acquired by analyzing for the TN 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 Nitrogen Containing Compounds

Compound	TN (mg/L)	HUP Method (TNP-4110)*		CC Method (TNPC-4110)**		JIS Method
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)
Ammonium Sulfate	2	97.3	1.50	102	3.44	101
L-gultamic Acid	2	101	0.452	102	0.636	96.3

* n = 2

** n = 3

*** JIS (Japanese Industrial Standard) method is based on "Methods 45.Total nitrogen and 45.2 UV Spectrophotometry Analysis in JIS K-0102 Testing Methods for Industrial Wastewater", RSD (3-10%)

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

Type of Industry	HUP Method (TNP-4110)*		CC Method (TNPC-4110)*		JIS Method**
	TN (mg/L)	RSD (%)	TN (mg/L)	RSD (%)	TN (mg/L)
Food A	0.74	3.78	0.81	1.09	0.77
Food B	16.0	0.975	16.1	5.38	15.2
Food C	22.8	5.48	22.6	0.867	22.1
Chemical A	11.3	3.91	11.7	1.68	10.8
Chemical B	9.96	2.17	11.5	1.08	10.6
Chemical C	29.1	0.538	26.7	1.53	27.7
Electrical	2.38	1.72	2.57	0.796	2.50
Brewing	9.91	1.62	10.1	1.44	10.0
Sewage Treatment	7.78	2.38	7.56	3.55	7.92
Pharmaceutical	0.862	3.99	0.891	0.594	0.960

* n = 3

** JIS (Japanese Industrial Standard) method is based on "Methods 45.Total nitrogen and 45.2 UV Spectrophotometry Analysis in JIS K-0102 Testing Methods for Industrial Wastewater", RSD (3-10%)