

## Measurement of Total Nitrogen/Total Phosphorus in Wastewater by TNPC-4110 Plus

As a measure to improve eutrophication of closed bodies of water, total pollutant load control regulations were implemented in Japan from 1979 to reduce the total load of organic contaminants discharged into such waters to a standard value or less. Beginning with the 5<sup>th</sup> Total Pollutant Load Control regulations, total nitrogen and total phosphorus were added and designated to the object items. Many places of business which are subject to those regulations measure these substances with automatic measuring devices. In a recent model change, Shimadzu improved the performance and functions of its TNPC-4110 series online total nitrogen/phosphorus analyzer, which had been used since the 5<sup>th</sup> Total Pollutant Load Control regulations were implemented, and now offers the new model as the TNPC-4110 Plus series.

In the improved model, the thermal decomposition/chemiluminescence method was adopted for measurement of total nitrogen. This method provides the same high oxidative decomposition capacity and enables detection with minimal interference as the previous model, and samples containing contaminants or sea water can be measured with virtually no interference effects. The reagent and measurement sequence were also improved in this series, and in total phosphorus measurement, the influence of contaminants was minimized as far as possible, enabling highly accurate measurement.

This article introduces an example of measurement of samples containing seawater and minerals with the TNPC-4110 Plus.

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### ■ Total Nitrogen (TN) Analysis Method

The thermal decomposition/chemiluminescence method is used in measurement of total nitrogen (TN) in the TNPC-4110 Plus. This method enables measurement unaffected by metal ions and bromide ions, which are interference components in ultraviolet (UV) spectrophotometry. Therefore, measurement unaffected by coexistent substances is possible, even when the sample is contaminated with seawater.

The sample used in this experiment was prepared by adding a nitrogen compound to a solution of diluted seawater (dilution rate: 2x) to obtain a concentration of 0.5 mgN/L (i.e., nitrogen concentration: 0.5 mg/L), and measurements were carried out by the summation method (manual analysis), ultraviolet spectrophotometry (manual analysis), and thermal decomposition/chemiluminescence method.

**Table 1 Total Nitrogen Measurement Conditions with TNPC-4110 Plus**

Analyzer	: TNPC-4110 Plus total nitrogen/phosphorus analyzer
Measured item	: Total nitrogen (TN)
Measurement method	: Thermal decomposition/chemiluminescence
Calibration	: 2-point calibration using 0-2 mgN/L potassium nitrate aqueous solution (full scale (FS): 2 mgN/L)
Sample	: Liquid prepared by adding potassium nitrate to natural diluted seawater (dilution rate 2x) to a concentration of 0.5 mgN/L

### ■ Total Nitrogen (TN) Analysis Results

Table 2 shows the measurement results for each method. The column on the right shows the difference between the UV spectrophotometry/TNPC-4110 Plus results and the value measured by the summation method as a standard, calculated as the full scale ratio (%FS). UV spectrophotometry gave a large value, showing the interference effect of components contained in the seawater. On the other hand, the result by the TNPC-4110 Plus measurement was approximately the same as that by the summation method, demonstrating that measurement unaffected by seawater components is possible.

**Table 2 Total Nitrogen Measurement Results**

Analysis method	Measurement principle	Measurement results (mgN/L)	Difference from summation method (%FS)
Manual analysis	Summation	0.59	—
Manual analysis	UV spectrophotometry	0.84	+12.5%
TNPC-4110 Plus	Thermal decomposition/chemiluminescence	0.54	-2.5%

### ■ Total Phosphorus (TP) Analysis Method

Total phosphorus (TP) measurement by the TNPC-4110 Plus is based on molybdenum blue spectrophotometry, but uses an improved reagent and measurement sequence. Because abnormal coloring during spectrophotometric measurement due to metal ions or other contaminants in the sample is slight, accurate measurement is possible regardless of the sample properties.

The sample for TP analysis was prepared by adding a phosphorus compound to groundwater containing silica to obtain a concentration of 0.5 mgP/L (phosphorus concentration: 0.5 mg/L), and measurements were conducted by potassium peroxydisulfate decomposition-molybdenum blue spectrophotometry (manual analysis), the conventional TNPC-4110 instrument, and the improved TNPC-4110 Plus.



**Table 3 Total Phosphorus Measurement Conditions with TNPC-4110 Plus**

Analyzer	: TNPC-4110 Plus total nitrogen/phosphorus analyzer
Measured item	: Total phosphorus (TP)
Measurement method	: Ultraviolet oxidative decomposition – molybdenum blue spectrophotometry
Calibration	: 2-point calibration using 0-1 mgP/L potassium dihydrogen phosphate (FS: 1 mgP/L)
Samples	: ① Liquid prepared by adding potassium dihydrogen phosphate to groundwater containing potassium silicate with a silica concentration of 50 mgSi/L to obtain a potassium dihydrogen phosphate concentration of 0.5 mgP/L ② Liquid prepared by adding potassium dihydrogen phosphate to groundwater containing potassium silicate with a silica concentration of 30 mgSi/L to obtain a potassium dihydrogen phosphate concentration of 0.5 mgP/L

### ■ Total Phosphorus (TP) Analysis Results

Table 4 shows the results of the measurements by each method. Using the values measured by the potassium peroxydisulfate decomposition-molybdenum blue spectrophotometry (manual analysis) as a standard, the column below the measured values shows the difference between the measured results by that method and by the conventional TNPC-4110/improved TNPC-4110 Plus, calculated as %FS of the analyzers. With the conventional TNPC-4110, the value was large, and the interference effect of contaminant components was apparent. However, the measured values obtained with the improved TNPC-4110 Plus were substantially the same as the manual analysis values, showing that measurement unaffected by contaminants is possible.

**Table 4 Total Phosphorus Measurement Results**

Analysis method	FS error between measurement result (mgP/L) and manual analysis	
	Sample ①	Sample ②
<b>Manual analysis</b> Molybdenum blue spectrophotometry	0.5069 (--)	0.5013 (--)
<b>Conventional TNPC-4110</b> Molybdenum blue spectrophotometry (conventional analyzer)	0.6575 (+15.1%)	0.5970 (+9.6%)
<b>TNPC-4110 Plus</b> Molybdenum blue spectrophotometry (improved analyzer)	0.5114 (+0.45%)	0.5025 (+0.12%)

### ■ Conclusion

This experiment demonstrated that the TNPC-4110 Plus is resistant to the effects of contaminants in samples and can make more accurate measurements of both total nitrogen and total phosphorus than the conventional techniques.



**TNPC-4110 Plus Online Total Nitrogen/  
Total Phosphorus Analyzer**