# Feature Article

## Environmentally-Friendly Automated Total Nitrogen/ Total Phosphorus Analyzer TPNA-300

Susumu Yamauchi

For the purpose of global environment conservation, the Japan's Fifth Water Quality Total Pollutant Load Control Regulation has made it mandatory to measure the water pollution loads (multiplying concentration by drainage volume) of total nitrogen and total phosphorus in wastewater from business premises. In response to this regulation, HORIBA developed the Automated Total Nitrogen/Total Phosphorus Analyzer that has helped effect a great reduction in environmental loads. We have improved our conventional ultraviolet radiation oxidative dissolution method further, and through reducing the quantity of measurement samples, we achieved the reduction of costs in management and maintenance for materials such as reaction reagents (a reduction of up to 10 %). In addition, HORIBA has incorporated a lot of its unique technologies adopting a dissolution/ measurement cell integrated architecture. This concept has gained the support of many users, and 1000 or more units are currently working in their fields playing their part in water pollution monitoring.

### Introduction

HORIBA Environment Group has sold the TPNA-200 as an instrument to automatically and continuously measure the concentration of total nitrogen and total phosphorus in wastewater, which has adopted the ultraviolet radiation oxidative dissolution method. Our new TPNA-300 introduced in this article has significantly reduced reagents, pure water, power consumption, wastewater after measurement, and installation area compared to conventional products so it is more environmentally-friendly. Many of these units have already been used in factory effluent and sewage treatment plants to play a part in global environment conservation through automatic measurement of total nitrogen and total phosphorus. This article introduces the product features of the TPNA-300 focusing on its technologically improved points for environmental-friendliness.

Table 1 List of Methods of Automated Total Nitrogen/Total Phosphorus Analyzers

| | 120 °C Decomposition Method | Ultraviolet radiation oxidative dissolution Method | Flow Injection Method | Catalytic Pyrolysis Method |
|---|---|---|---|---|
| Measured Elements | TP, TN | TP, TN | TP, TN | TN only |
| Temperature during Decomposition | 120 °C | 55 to 95 °C | Approx. 160 °C | 700 to 800 °C |
| Pressure during Decomposition | 2 atm | 1 atm | 10 atm | (Combustion) |
| TP Measurement Principle | Molybdenum blue method | Molybdenum blue method | Molybdenum blue method, Coulometric method | - |
| TN Measurement Principle | Ultraviolet absorption method | Ultraviolet absorption method | Ultraviolet absorption method | Chemiluminescence method |
| Measurement time | 60 minutes | 30 to 60 minutes | 10 to 20 minutes | 5 to 15 minutes |
| Reagent | Necessary | Necessary | Necessary | Unnecessary |
| Main consumables | Pressure-resistant container, heater | UV lamp, reaction tube | Pump tube, heater | Catalyst, reaction tube, combustion furnace |

## Overview of the Fifth Water Quality Total Pollutant Load Control Regulation

In order to reduce water pollution and improve water quality in closed water areas, the Japan's Fifth Water Quality Total Pollutant Load Control Regulation came into force in April 2004. In addition to the conventional regulation on COD (Chemical Oxygen Demand) in wastewater, regulations on the amount of water pollution loads of total nitrogen (TN) and total phosphorus (TP) were incorporated into the Fifth Water Quality Total Pollutant Load Control Regulation. Business premises that produce wastewater above a certain amount are required to perform continuous measurements by means of Automated Total Nitrogen/Total Phosphorus Analyzers. The Fifth Water Quality Total Pollutant Load Control Regulation determines values for individual business premises according to the loads calculated by multiplying the concentration of total nitrogen, total phosphorus, and COD by wastewater volume.

For automatic analyzers complying with the Fifth Water Quality Total Pollutant Load Control Regulation, there is no specification for measurement principles and methods. A measurement principle and method that satisfy the tests on performance criteria and management criteria determined by the Ministry of the Environment can be used as an official method. Table 1 lists the principles and methods for the automatic analyzers currently on the market.

## Technological improvements and features for environmental friendliness

Due to their measurement principles, automated total nitrogen/total phosphorus analyzers use reagents for decomposition and measurement, which has imposed a heavy user-maintenance burden. Under the concept of environmentally-friendly instruments, HORIBA developed the TPNA-300 and succeeded in reducing costs in management and maintenance by large amounts compared to conventional products. This achievement includes the following important factors to breaking down the conventional wisdom of the reagent-based automatic water quality analyzer : (1) The sample quantity for measurement has been reduced to 1 mL down to a tenth or less of the conventional amount, and (2) The analysis unit has been miniaturized by integrating the decomposition and measurement cells.

The Features of the TPNA-300 are as follows.

(1) Miniaturized ultraviolet radiation oxidative dissolution section: one tenth of our conventional product

The reduction of the sample quantity and development of a new dissolution bath allows oxidative dissolution of the sample by means of a 4 W class small-sized low-pressure mercury lamp.

(2) Reduced reagent consumption: one fifteenth of our conventional product.

The amount of reagent consumption has been reduced up to one fifteenth by reducing the sample amount and developing a new reagent mass measurement method that uses comparatively minute quantities. As a result, a maintenance interval of one month and a significant reduction of the annual running cost have been achieved. An optical non-contact level sensor that does not have any moving parts has been adopted for the new measurement method. Figure 1 shows the block diagram of the sampling flow.

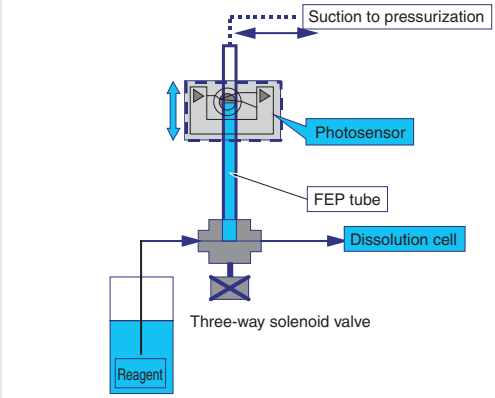


Figure 1 Block Diagram of the Minute Sample Reagent Sampling Flow

(3) Reduced wastewater quantity through measurement: one fifth of our conventional product

The amount of wastewater through measurement has been reduced down to approx. 15 L per month and a maintenance interval of one month has been achieved. 100% zero emissions have been realized by collecting all washing water in the measurement cell to the wastewater tank. Also, incorporation of the wastewater collection tank into the equipment has allowed the enhancement of safety and reduction of the equipment footprint.

(4) Reduced pure water consumption: One tenth of our conventional product

The consumption of pure water used for diluting the sample, or washing the measurement cell or flow has been reduced, and the life of the ion exchange resin has been prolonged. In addition, the equipment has been miniaturized by incorporating the water purifying unit.

(5) Miniaturized analysis unit: One tenth of our conventional product's analysis unit

Significant miniaturization of the analysis unit has been achieved by reducing the sample and reagent quantities and developing a new integrated architecture for the dissolution and measurement cells. Figure 2 shows the analysis unit.

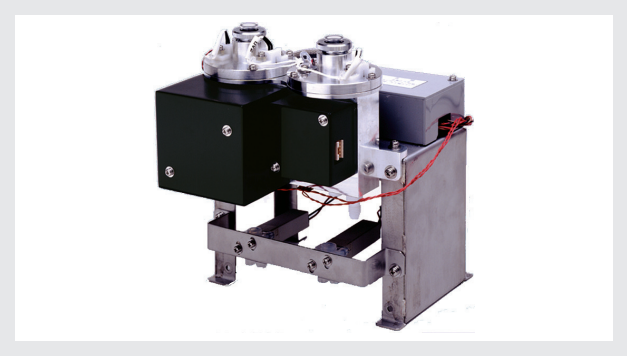

Figure 2 Small-sized Analysis Unit of the TPNA-300 in which the Dissolution and Measurement Cells have been Integrated

(6) Reduced power consumption: Half of our conventional product

Power consumption of the heater was significantly reduced by low temperature breakdown under 1 atm using the ultraviolet radiation oxidative dissolution method and miniaturization of the dissolution bath.

## ISO14000 activities

For the developing of new products, HORIBA is working toward environmentally-friendly products according to the ISO14000 environmental management program. In the HORIBA system, the assessment criteria for an environmentally conscious design are established and the products that satisfy certain criteria are registered as environmentally conscious products.

The TPNA-300 satisfies these criteria and has been registered as such. Figure 3 shows the evaluation result on comparison between the new and conventional products.

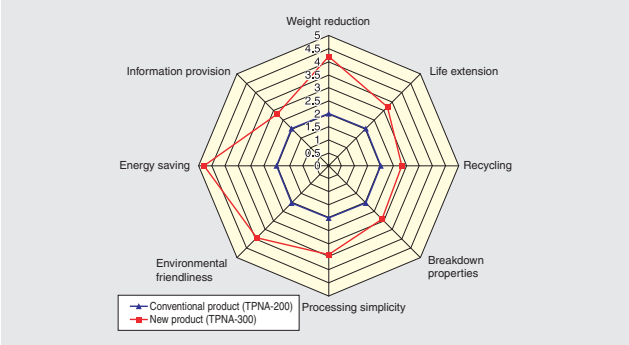


Figure 3 Evaluation Result for Environmentally Conscious Design

## Measurement principle

Figure 4 shows the measurement flow schematic. The TPNA-300 employs various technologies developed for the TPNA-200. In particular, the ultraviolet radiation oxidative dissolution method is used for a technique to decompose nitrogen compounds and phosphorus compounds in the sample. The dissolution conditions for the ultraviolet oxidation breakdown method are lower temperature (100 ºC or below) and lower pressure (1 atm) compared to other methods. Thus, this method has an advantage in that the components can be miniaturized and their life extended.

In addition to the reduction in sample quantity, the TPNA-300 has been successful in significantly miniaturizing the ultraviolet lamp by further improving the prior ultraviolet radiation oxidative dissolution method.

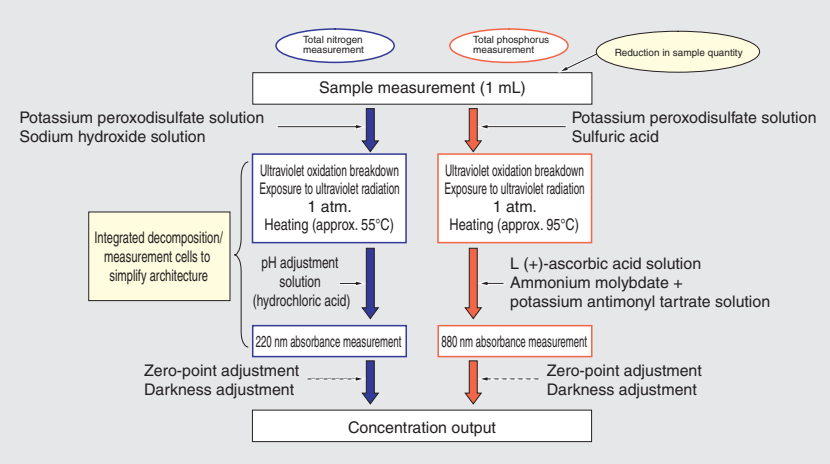


Figure 4 Measurement Flow Schematic for the TPNA-300, the Automated Total Nitrogen/ Total Phosphorus Analyzer

Figure 5 The TPNA-300 Automated Total Nitrogen/Total Phosphorus Analyzer

## Specifications

Table 2 shows the general specifications of the TPNA-300 and Figure 5 shows the appearance of the product.

In response to a variety of samples and a wide range of user demands, the analyzer incorporates the following:

- Delivery supply of the ready-mixed reagent
- Calculation of pollution loads of total nitrogen and total phosphorus
- Calculation of the loads of three elements: total nitrogen, total phosphorus, and COD (UV)
- Personal computer software for automatic data processing and form preparation (Optional)
- Automatic dilution function for wide measurement ranges
- Sample pretreatment equipment according to various sample properties
- Unique seawater compensation function for seawater-mixed samples
- Support for inspections on performance and control criteria of the Ministry of the Environment
- Sample element investigation and issuance of the JIS

Table 2 General Specifications of TPNA-300 Automated Total Nitrogen/Total Phosphorus Analyzer

| | |
|---|---|
| Measurement principle | Total nitrogen: Alkaline potassium peroxodisulfate solution/ultraviolet radiation oxidative dissolution - Ultraviolet absorption method<br>Total phosphorus: Potassium peroxodisulfate/ultraviolet radiation oxidative dissolution Molybdenum blue absorption method |
| Measurement range | (Standard range)<br>Total nitrogen: 0 to 2 mg/L<br>Total phosphorus: 0 to 0.5 mg/L<br>(Single-stage dilution range)<br>Total nitrogen: 0 to 5/10/20/50 mg/L<br>Total phosphorous: 0 to 1/2/5/10 mg/L<br>(Two-stage dilution range)<br>Total nitrogen: 0 to 100/200/500/1000 mg/L<br>Total phosphorus: 0 to 20/50/100/250 mg/L |
| Number of measurement ranges | One range (standard)<br>Two ranges (optional) |
| Number of measurement points | One point (standard), two points (optional) |
| Measurement time | 60 minutes |
| Repeatability | Within ±3% of the full scale (standard range/single-stage dilution range)<br>Within ±5% of the full scale (two-stage dilution range) |
| Sample water conditions | Temperature: 2 to 40°C<br>Flow rate: 0.5 to 5 L/min (Flow rate for the overflow bath) |
| Blank water conditions | Amount used: 70 L/month (single-stage dilution specification)<br>(Note that the amount of pure water consumption increases or decreases according to the measurement range.)<br>Properties: Nitrogen and phosphorus compounds must not be contained.<br>(Continuous supply is permitted by the water purifying apparatus as an option.) |
| Power | 100 V AC ± 10V AC, 50/60 Hz |
| Mass | Approx. 80 kg |
| Dimensions | 460 (W) x 425 (D) x 1600 (H) mm |

(Japanese Standards Association) manual analysis and measurement certification by HORIBA Analysis Center

## Performance

The automated total nitrogen/total phosphorus analyzer (used under the Fifth Water Quality Total Pollutant Load Control Regulation) is required to satisfy the performance and control criteria specified by the Ministry of the Environment, and to show a high correlation with the JIS manual analysis method.

It has been demonstrated that the ultraviolet radiation oxidative dissolution method of the TPNA-300 has a high correlation with the JIS manual analysis in various wastewater samples. Table 3 and Table 4 show the collection rates using standard substances. Figure 6 and Figure 7 show the correlation data with the JIS manual analysis using various actual wastewater samples.

Table 3 Total Nitrogen Collection Rate Comparison using TN Standard Substances

| Standard sample (total nitrogen) | Collection rate (%) | |
|---|---|---|
| | Ultraviolet oxidation breakdown method | JIS manual analysis method |
| Ammonium sulfate | 99.4 | 97.7 |
| Thiocyanogen | 99.5 | 97.2 |
| Sodium nitrite | 101.5 | 93.2 |
| Hydroxylammonium chloride | 97.6 | 88.6 |
| Urea | 101.0 | 93.9 |
| p-nitrophenol | 102.8 | 102.9 |
| Sulfanilamide | 92.5 | 98.1 |
| L-glutamic acid | 100.8 | 101.9 |

*Sample concentration: Measured by 2 mg/L, n=3
*JIS manual analysis method: JIS K0102-1993 "45.2 Total nitrogen - Ultraviolet absorption method"
*Ultraviolet radiation oxidative dissolution method: Measured by the Automated Total Nitrogen/Total Phosphorus Analyzer

Table 4 Total Phosphorus Collection Rate Comparison using TP Standard Substances

| Standard sample (total phosphorus) | Collection rate (%) | |
|---|---|---|
| | Ultraviolet oxidation breakdown method | JIS manual analysis method |
| Sodium phosphinate | 100.0 | 101.0 |
| Disodium hydrogenphosphate | 99.4 | 99.8 |
| Disodium phenylphosphate | 100.0 | 102.0 |
| Disodium β-glycerophosphate | 105.0 | 98.9 |
| Benzyl triphenylphosphonium chloride | 97.6 | 101.0 |
| 5´-AMP | 96.8 | 94.3 |
| Sodium pyrophosphate | 96.6 | 99.1 |
| Sodium tripolyphosphate | 95.0 | 101.0 |
| 5´-AMP·Na2 | 98.5 | 101.0 |

*Sample concentration: Measured by 0.5 mg/L, n=3
*JIS manual analysis method: JIS K0102-1993 "45.3.1 Total phosphorus - Potassium peroxydisulfate decomposition method"
*Ultraviolet radiation oxidative dissolution method: Measured by the Automated Total Nitrogen/Total Phosphorus Analyzer

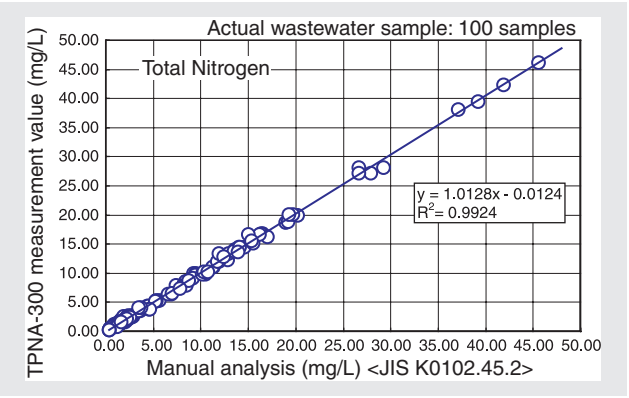


Figure 6 Correlation of Total Nitrogen Analysis using Actual Wastewater Samples

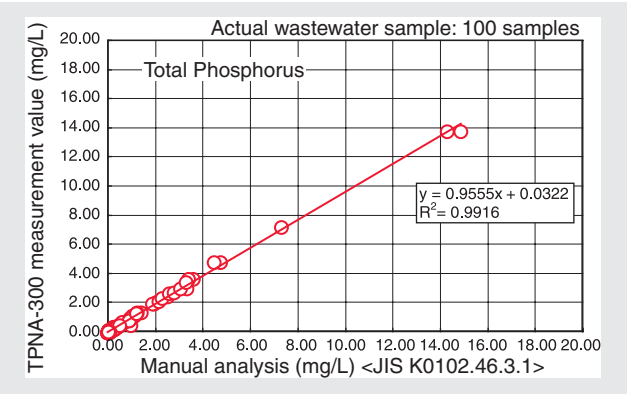


Figure 7 Correlation of Total Phosphorous Analysis using Actual Wastewater Samples

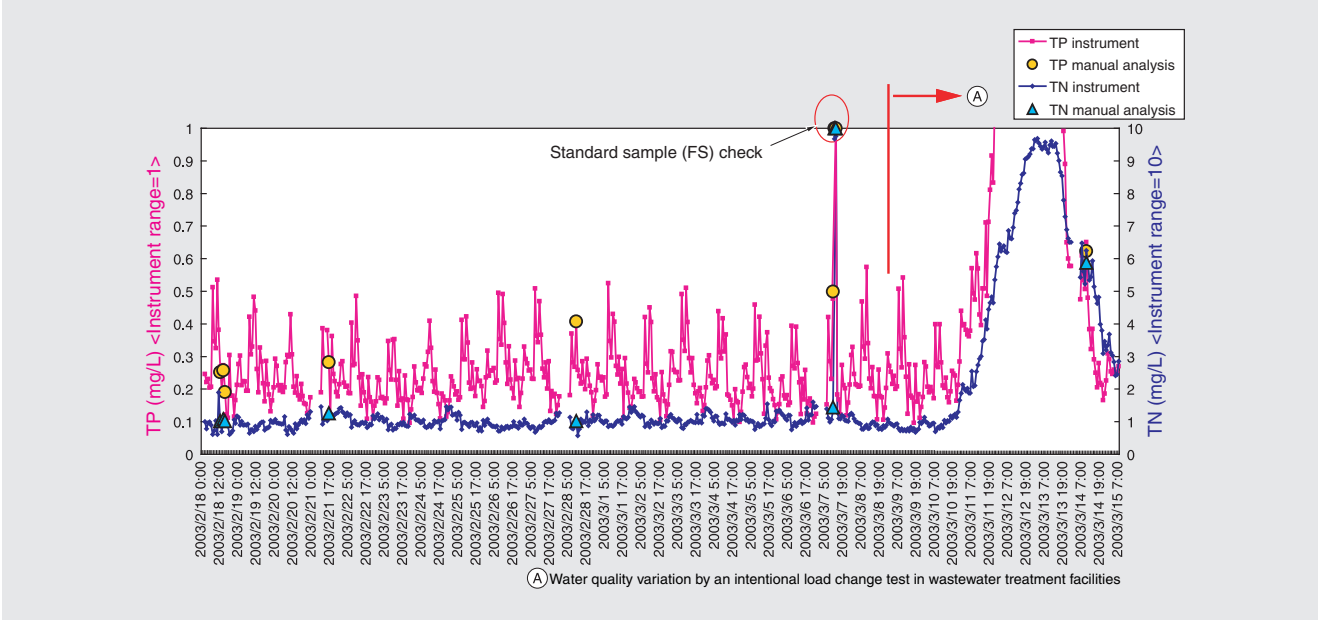


Figure 8 Example of Continuous Measurement Data using the Automated Total Nitrogen/Total Phosphorus Analyzer

As a matter of course, a high operating rate is required for automatic continuous measurement instruments used to satisfy legal regulations. Figure 8 shows an example of continuous measurement data in a sewage plant. Both periodic variations of drainage treatment and drastic water quality variation in an intentional load change test are well followed.

## Conclusion

HORIBA is developing and selling the Automated Total Nitrogen/Total Phosphorus Analyzers introduced in this article. HORIBA also markets wastewater monitoring equipment such as COD meters and UV meters for regulating water quality total pollutant, and other types of instruments for automatically and continuously analyzing a variety of water quality elements. Due to a necessity to comply with the JIS manual analysis method, automatic water quality monitoring instruments that require reagents and use chemical reaction principles are currently dominating the market. This places a significant maintenance burden on the users. The environmentally-friendly product introduced here is an improved product through extension of the conventional analysis technologies. These have indicated a move in the reagent-based automatic analyzer industry and have received support from a wide range of users. In recent years, emphasis of the global environment has again been on the importance of water resources. To further contribute to the reduction of water pollution, we would like to continue improvements and developments of more user-friendly and environmentally-friendly water quality monitoring equipment, while aiming for technical innovation toward non-reagent analysis.

Susumu Yamauchi
HORIBA Advanced Techno Co.,Ltd.
Engineering Dept.
Manager