

# Product Introduction

## Automatic Total Nitrogen/Phosphorus Monitor TPNA-500 – Reduction of maintenance time result from improvements of reagent formulas and a gauging method –

Akio ISHII

Tadashi KAWANO

Automatic Total Nitrogen/Phosphorus Monitor TPNA-300 is widely accepted by the market because of its high reliability and low environmental load. TPNA-500 inherits its advantage and is enhanced its maintainability. Main improvement points are two; one is an extension of reagents exchange term and another is a gauge method less detection error due to line stain. In a case of waste water measurement of foods plant, maintenance time could be reduced to less than 1/6 compared with TPNA-300. This reduction of maintenance time will contribute to lowering of Life Cycle Costs<sup>\*1</sup>.

\*1: Life Cycle Cost: Total operating costs from purchase to disposal.

### Introduction

The Earth, also known as “water planet,” is believed to have abundant water, which amounts to 1.35 billion km<sup>3</sup>. However, more than 99% of the water is brine, and a major portion of freshwater forms glaciers and groundwater. Therefore, the amount of water that is readily available for humans, such as river water and lake water, is reportedly no more than 100,000 km<sup>3</sup>, accounting for only 0.01%<sup>[1]</sup>. With an aim to utilize the limited water resources in a safe, efficient and sustainable manner, measurements have been conducted chiefly in advanced countries to ensure appropriate water quality management. Also, in view of the glowing population and environmental pollution in developing countries, as well as global climate change, water management is estimated to be more and more important.

Japan embarked on full-scale efforts in the period of postwar industrial recovery when water pollution issues came up to the surface. Former two laws concerning water quality were established in 1958, which was followed by the Basic Law for Environmental Pollution Control enacted in 1967. After that, the total emission control scheme for water quality management was established in 1978 to respond to the pollution of closed water areas such as inland seas and lakes<sup>[2]</sup>.

The scheme has come to the 6th stage. In the 5th total

emission control enacted in 2004, the water pollution load of total nitrogen (TN) and total phosphorus (TP) was newly regulated, in addition to the chemical oxygen demand (COD).

Prior to the 5th total emission control, the Horiba Group released in 2002 an automatic total nitrogen/phosphorus monitoring system TPNA-300. In comparison with previous products, the TPNA-300 required a minimal amount of sample and much less test reagents (a tenth of those required by former products). The product was adopted in various industrial plants and sewerage treatment plants for its environmental friendliness, and has played a role in conservation of regional environments<sup>[3]</sup>.

In 2013, the TPNA-500 was released as a successor to the TPNA-300. The new system is based on highly reliable technologies accumulated in the past while realizing further reduced maintenance load (Figure 1). The running cost of conventional systems was high when compared to the product cost because those systems would require various maintenance tasks including frequent replacement of test reagents, treatment of waste liquids, and cleaning of piping and measuring tubes. The TPNA-500 has achieved a reduction of the total cost required during the period from purchase to disposal of the product (Life cycle cost: LCC) by cutting the time and efforts required for maintenance. Here we introduce the

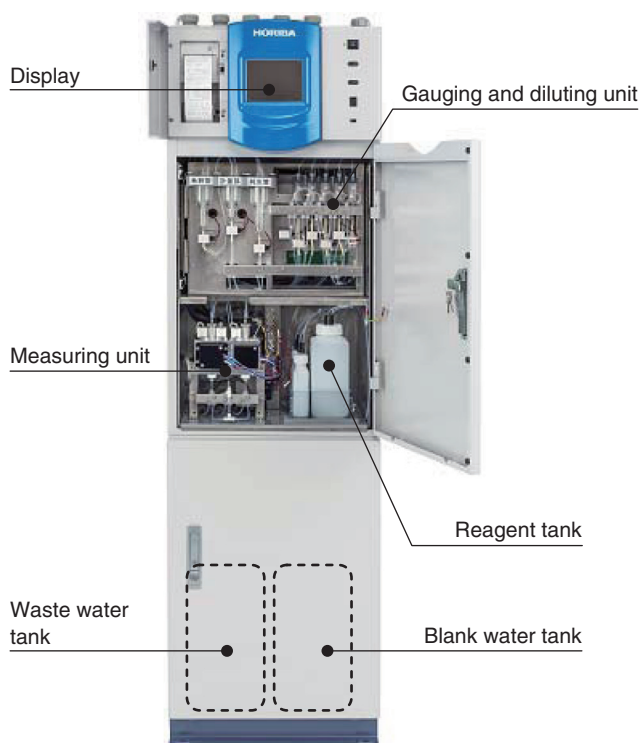


Figure 1 Outlook of TPNA-500

technical improvements and LCC reduction realized in the TPNA-500, while comparing the model with the TPNA-300.

## Features of TPNA-500

### Principle and method of measurement

There is no specification concerning the measurement principle and method for automatic TN/TP measurement systems compliant with the total emission control. If a system satisfies the test criteria on performance and management defined by the Ministry of the Environment,

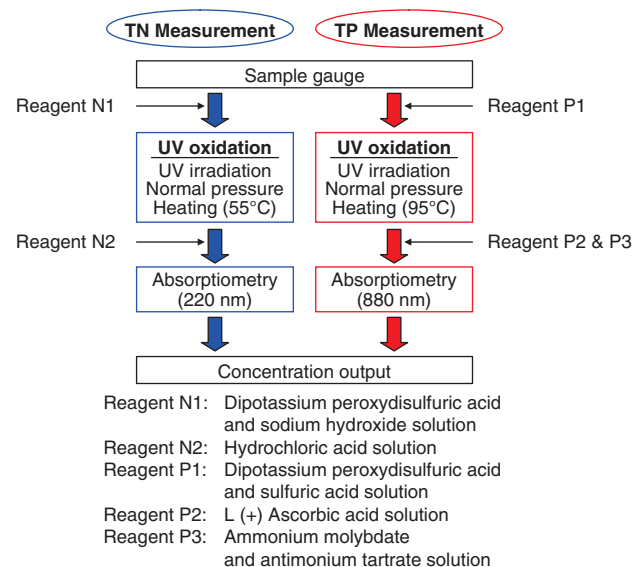


Figure 2 Measurement flow of TPNA-500

Table 1 Principles and methods of TN and TP commercial monitors

Items	Decomposition with 120°C	UV Oxidation	Flow Injection	Contact Thermal Decomposition
Measurement items	Total Phosphorus Total Nitrogen	Total Phosphorus Total Nitrogen	Total Phosphorus Total Nitrogen	Total Nitrogen
Degradation temperature	120°C	55°C ~95°C	approx. 160°C	700°C ~800°C
Degradation pressure	2 atoms.	Normal pressure	20 atoms.	
Measurement method	Total Phosphorus	Molybdenum blue	Molybdenum blue	Molybdenum blue – coulometry
	Total Nitrogen	UV absorbance	UV absorbance	UV absorbance Chemiluminescence
Measurement time	60 min.	30 min. ~60 min.	10 min. ~20 min.	5 min. ~15 min.
Reagents	Need	Need	Need	Not need
Representative Consumables	pressure tight case heater	UV lamp Reaction cell	Pump tube, heater	Catalyst Reaction cell Combustion furnace

it is deemed to be used in accordance with an official method. The principles and measurement methods of commercially available automatic TN/TP monitoring systems are shown in Table 1. Like previous products, the TPNA-500 uses the ultraviolet oxidative decomposition method. The measurement flow of the UV oxidative decomposition method is shown in Figure 2. The UV oxidative decomposition method enables reactions under a normal pressure and at a lower temperature (100°C or below) in comparison with other methods, and thus is advantageous in terms of downsizing of instrument parts and elongation of service life. We opted to continuously use this measurement method while using our technologies accumulated in the past.

### Maintainability

In recent years, measuring instruments are required not only to accurately measure the object but also to reduce the maintenance load<sup>[4]</sup>. The automatic COD monitoring system CODA-500, released by the Horiba Group in 2011, successfully realized the reduction of reagent consumption to a tenth of that of previous measurement systems, without sacrificing measurement accuracy. In parallel with the achievement, we have made approaches to halving running costs by reducing the consumption of tap water and electricity, as well as the amount of wastewater, in order to ultimately reduce the LCC of our products.

On the basis of the same policy, we have developed the TPNA-500 with reduced LCC, which was achieved by improving maintainability. Below are listed the essential points in addressing technological development to improve maintainability. Of these items, here we describe

the details of “Lengthening of replacement cycle of reagent by improving its composition” and “Method for measuring liquid without false detection due to contamination on the wall of the gauging tube and piping.”

- Lengthening of replacement cycle of reagent by improving its composition
- Method for measuring liquid without false detection due to contamination on the wall of the gauging tube and piping
- Automatic cleaning of sample gauging tube and piping by means of chemical (optional)
- Automatic cleaning of reagent gauging pipe by means of chemical
- Streamlining of reagent replacement work by means of replacement sequence
- Reduction of pure water used for cleaning
- Reduction of waste liquid and lengthening of replacement cycle of waste liquid tank
- Improvement of operability by means of touch panel display
- Improvement of data usability by means of USB flash drive
- Maintenance from the front side
- Corrosion prevention for circuit boards by enhancing sealing performance

### Lengthening of replacement cycle of reagent by improving its composition

As shown in the measurement flow in Figure 2, measurement of total nitrogen/total phosphorus requires a variety of reagents. In particular, potassium peroxydisulfate is an important reagent used in the UV oxidative decomposition method. As a general-purpose reagent used in aqueous solution systems,

peroxydisulfuric acid ion has an outstanding oxidizability, with a standard redox potential of +1.96 V<sup>[5]</sup>. Conversely, it can be said that this is a very reactive oxidant. In an aqueous solution, the reagent reacts with the solvent water and degrades to peroxymonosulfuric acid ion and hydrogen peroxide<sup>[6]</sup>. As the decomposition reaction proceeds at normal temperatures and pressures, the concentration of peroxydisulfuric acid ion drops even during storage. Reduced concentration means reduced oxidizability, reduced efficiency in oxidative decomposition, and deterioration of measurement accuracy. To prevent this, users of conventional models were advised to use up the reagent within a month under normal temperatures.

In the course of the development of TPNA-500, we discovered that the decomposition of the reagent can be delayed with use of appropriate additive. During the study of optimal additive, we also found that there is a clear relationship between the decomposition reaction rate and the storage temperature. Potassium peroxydisulfate decomposes by reaction with the solvent water. Since an excess amount of water is present, the reaction rate constant can be obtained using Equation 1 on the assumption that the reagent degrades by a monomolecular reaction. In addition, we confirmed that this is obviously related to Arrhenius' equation shown in Equation 2 by conducting an experiment using different storage temperatures. (The data is omitted here.) In the experiment, the concentration was determined by redox titration in accordance with JIS K 8253<sup>[7]</sup>.

$$\frac{[P]}{[P]^0} = e^{-kt} \dots\dots\dots (1)$$

$$\ln k = \frac{-E}{RT} + \ln A \dots\dots\dots (2)$$

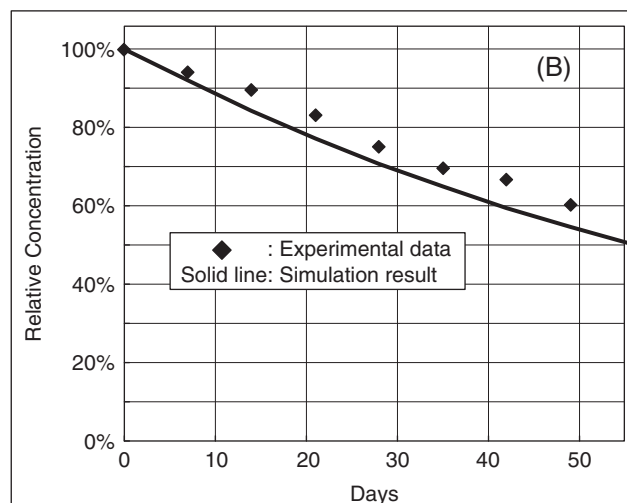
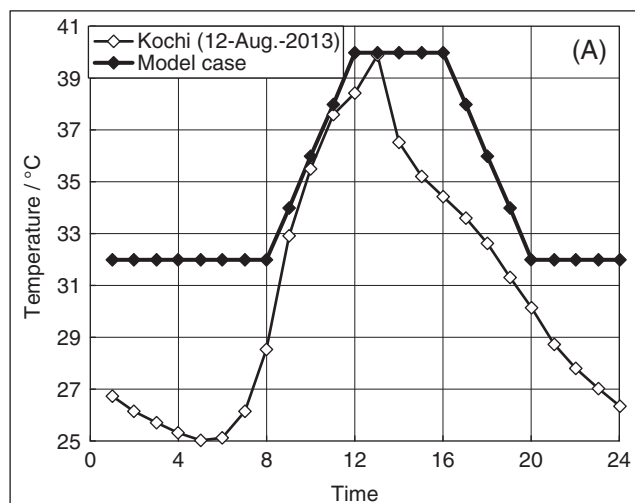


Figure 3 Simulation and experimental results of degradation of peroxydisulfuric acid ion ((A) is a model case of temperature. (B) is results of a simulation (solid line) and an experiment (◆))

Here,  $[P]$  in Equation 1 denotes the concentration at a certain point of time,  $[P]^0$  the initial concentration,  $k$  the reaction rate constant, and  $t$  the time elapsed. In Equation 2,  $E$  denotes the activation energy,  $R$  the gas constant,  $T$  the absolute temperature, and  $A$  the frequency factor. A rough indication of replacement frequency can be obtained for each storage temperature by determining the respective parameters by experiment and then solving Equations 1 and Equations 2. For instance, if the reagent is to be stored at 35°C, the replacement cycle is calculated to be 34 days for the reagent of a conventional composition, which means replacement should take place once a month. On the other hand, the replacement cycle for the reagent with additive is calculated to be 60 days, an extension to two months. On the basis of the discussion so far, it is possible to estimate the replacement cycle even if the temperature changes during storage.

As an example, using a model case of daytime air temperature change indicated by symbols  $\blacklozenge$  in Figure 3A, we compared the actual change in concentration of the reagent, which was experimentally exposed to the temperature change in a continuous manner, with calculated values derived from the equations shown above. Incidentally, the symbols  $\diamond$  in Figure 3A show the daytime air temperature change observed in Ekawasaki, Kochi Prefecture on October 12, when the highest temperature in 2013 was recorded. The values in the model case were set to be higher than the actual temperature trend on that day, and such temperature

change as the model case is unlikely to persist in practice. The results are shown in Figure 3B. The figure indicates that the experimental data values ( $\blacklozenge$ ) and the simulation results (solid line) follow a similar trend, proving the possibility of rough prediction of the replacement cycle. As described above, the lowering of reagent concentration can be predicted by assuming temperature change, which allows optimization of the reagent replacement cycle. (Patent pending)

### Method for measuring liquid without false detection due to contamination on the wall of the gauging tube and piping

As shown in the measurement flow in Figure 2, the sample and several reagents need to be gauged in measurement. The liquid level detection method using an optical sensor has been conventionally employed. However, the method requires frequent cleaning under some sample conditions, in order to prevent false detection by the sensor due to contaminants derived from the sample. To minimize the impact of contamination, the TPNA-500 has adopted a time-controlled gauging method instead of liquid level detection using a sensor.

Figure 4 shows the scheme of the time-controlled gauging method. In this method, the measured quantity is defined by the positional relationship between a glass tube for measuring the sample and the piping for measurement. First, a negative pressure is created in the measuring tube to aspirate more than 1 mL of the sample from the sample

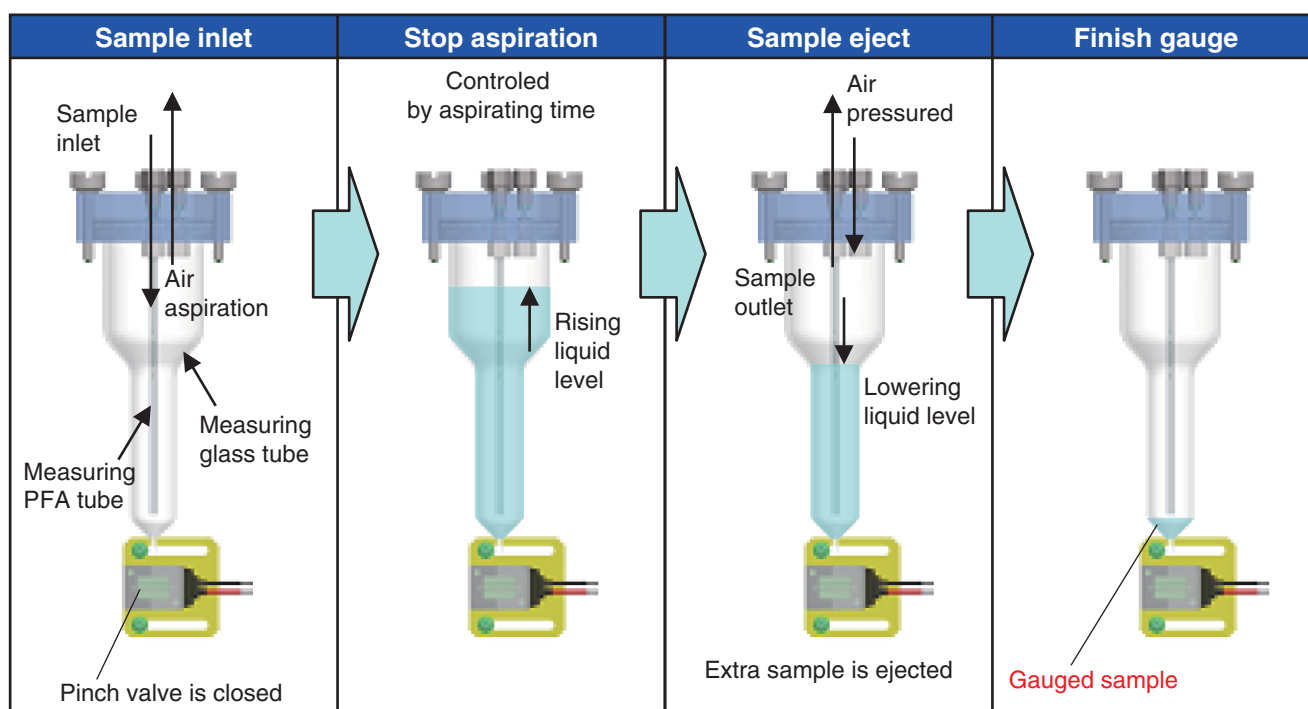


Figure 4 Sample gauge method of TPNA-500

overflow tank (OF tank). At this stage, it is not necessary to accurately aspire the desired amount. So, the mechanism is controlled only on the basis of aspiration time without using a level sensor. Next, a positive pressure is created in the measuring tube to discharge the

sample back to the OF tank except for the amount required. As shown in Figure 3, the required amount is defined by the space set up by the sample measuring tube and measurement piping. To further mitigate the impact of contamination, we reduced the number of solenoid valves and realized a clog-resistant design. In addition, reverse cleaning of the OF tank prevents the clogging of the mesh filter. If contaminant adhesion is conspicuous despite all these devices, chemical cleaning can be performed (provided as option) to comprehensively mitigate the impact of stains in the pipes. (Patent pending)

Table 2 Degradation efficiency of standard substances

Standard substance of TP	Degradation efficiency	
	TPNA-500	Manual measurement
Potassium dihydrogenphosphate	100.4%	100.0%
Sodium diphosphate decahydrate	98.7%	100.8%
Sodium phosphinate	101.8%	103.8%
Disodium hydrogenphosphonate	99.8%	99.2%
Disodium phenyl phosphate	101.9%	101.8%
Disodium β-Glycerophosphate	97.6%	98.8%
Benzyltriphenylphosphonium chloride	95.7%	99.8%
Sodium tripolyphosphate	99.5%	98.6%
5'-AMP	93.4%	94.2%
5'-ATPNa2	94.8%	96.2%

Sample concentration is 0.5 mg/L (n=3).  
Manual measurement is according to JIS K 0102-45.3.1.

Standard substance of TN	Degradation efficiency	
	TPNA-500	Manual measurement
Potassium nitrate	98.5%	100.0%
Ammonium sulfate	95.7%	94.8%
Sodium thiocyanate	94.9%	97.7%
Sodium nitrite	99.3%	94.1%
Hydroxylammonium chloride	95.5%	95.5%
Urea	95.9%	97.5%
4-Nitrophenol	98.6%	94.8%
Sulfonamide	88.3%	84.4%

Sample concentration is 2 mg/L (n=3).  
Manual measurement is according to JIS K 0102-45.2.

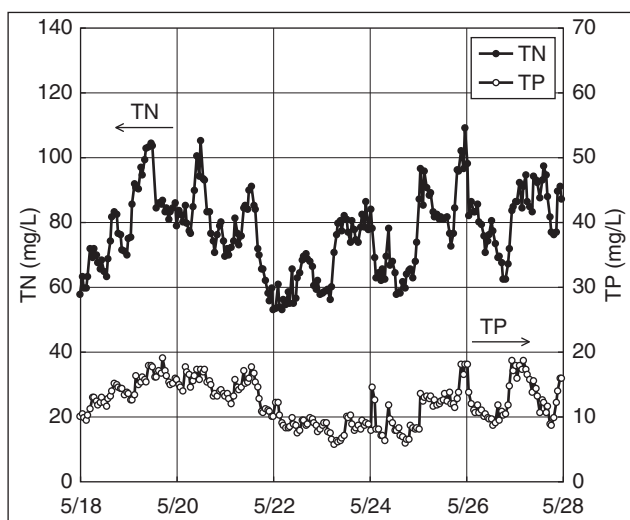


Figure 5 Continuous measurement of industrial waste water

## Performance and Measurement Example

### Correlation with manual analysis

An automatic TN/TP measurement systems used in the total emission control scheme for water quality management is required to comply with the criteria on performance and control defined by the Ministry of the Environment. Measurement results of the system must be correlated with those obtained by using a specified measurement method (JIS manual analysis method). From the past records, the UV oxidative decomposition method adopted by the TPNA-500 has been proven to correlate with the JIS manual analysis for a wide variety of wastewater samples<sup>[3]</sup>. As shown in Table 2, it has been also proven that the TPNA-500 boasts the collection rate equivalent to that of manual analysis for various standard substances.

### Measurement example

Figure 5 shows data on continuous measurement targeting industrial wastewater samples at a food processing plant.

A former model (TPNA-300) is installed at the site, allowing the comparison of maintainability. We compared the model with the TPNA-500 in terms of the maintenance tasks carried out in two months and the time spent for them (Table 3). As contaminants derived from the sample often sticks to the inside of the piping at the site, the former model requires pipe cleaning at least once a week. On the other hand, the piping of the TPNA-500 was

Table 3 Comparison of spent maintenance time for two months with TPNA-300 and TPNA-500

Maintenance items	TPNA-300	TPNA-500
Waste liquid disposal	20 min.	10 min.
Pipes Cleaning	360 min.	0 min.
OF tank cleaning	30 min.	30 min.
Reagents exchange	60 min.	30 min.
Total	470 min.	70 min.

cleaned only by the automatic cleaning function and did not require manual cleaning at all. As a result, it was confirmed that the new model can reduce the time required for maintenance by 400 minutes per two months, as far as the same site and period are concerned. When simply calculated, the maintenance time is expected to reduce by 2400 minutes in a year. Improved maintainability of the new model is valuable from the viewpoint of LCC, since this type of instruments are used for about 10 years.

## Conclusion

Recently the Horiba Group completed the development of the total nitrogen and phosphorus measurement system TPNA-500. The model inherits technologies including the highly reliable ultraviolet oxidative decomposition method from conventional models, while boasting its enhanced maintainability that helps the reduction of LCC. Water resources will grow more and more important. The Horiba Group intends to contribute to the conservation of the limited water resources through the development and supply of not only wastewater monitoring systems used to deal with the total emission control for water quality management, but also other various automatic water quality measurement systems.

## References

- [ 1 ] I. A. Shiklomanov, J. C. Rodda, *World Water Resources at the Beginning of the Twenty-First Century*, Cambridge University Press, 13 (2004)
- [ 2 ] *Processing and Utilization Encyclopedia of practical water*, edition 1, Industrial Research Center of Japan, Production Goods Work Station, 65 (2012)
- [ 3 ] Susumu YMAUCHI, *Readout (HORIBA Technical Reports)*, **31**, 56 (2005)
- [ 4 ] Katsunobu EHARA, *Readout (HORIBA Technical Reports Special issue)*, 26 (2013)
- [ 5 ] *Chemical Handbook Edition 4*, The Chemical Society of Japan, II -468 (1993)
- [ 6 ] *New Experimental Chemistry*, The Chemical Society of Japan, 8-338 (1976)
- [ 7 ] **Potassium peroxydisulfuric acid, JIS K 8253 (2006)**



**Akio ISHII**

Liquid and Water Quality R&D Dept.  
Application R&D Center  
Research & Development Division  
HORIBA, Ltd.



**Tadashi KAWANO**

R&D Dept.  
HORIBA Advanced Techno co., Ltd.