

COS's Fundamental Technologies and Product Development

Kazunori Sasaki, Riichiro Suzuki, Koji Uchimura

Abstract

COS Co., Ltd. is a group of experts in liquid measurement within the HORIBA group. This article first reviews the founding of COS and its history up to the present, and then introduces COS's fundamental technologies and product lines, showing as examples the automatic total nitrogen and phosphorus meter that is being jointly developed with HORIBA through technology transfer, the organic pollutant monitor that has a long-established reputation of reliability, and COS's proprietary technologies such as the effluent treatment monitoring system for agricultural communes, and the semiconductor process monitor. This article also introduces COS's ongoing efforts for excellent products through recent developments, such as the GC-96RW, a two-channel simultaneous resistivity converter, and the SLIA-300, a high-sensitivity silica monitor.

1 History of COS

COS was founded in 1975 with the aim of entering the consumer market of analytical and measuring instruments. The company first developed and sold unique products intended for home consumers such as the "Green Box" (containers for tank farming). Following a far-reaching structural reform in 1983, COS decided to specialize in quality control of industrial and domestic wastewater. This was a very challenging field with diverse sample properties, severe measurement conditions, and rather limited market size. COS solved such challenges one by one with HORIBA's superb measurement technology and agile marketing, and has now earned an excellent reputation as a manufacturer of reliable measuring instruments for the agricultural, forestry, fishery, and food processing fields. In the latter half of the 1980s, it launched process monitors such as chemical solution monitors and resistivity meters, leading the liquid measurement field in the HORIBA group.

From 1985, COS developed a nationwide service network that primarily offered maintenance for HORIBA products; this business grew into another mainstay of COS. When HORIBA Techno Service Co., Ltd. was founded in 2000, COS transferred its service business to the new company, and started taking new steps as a team of experts in liquid measurement within the HORIBA group.

2 Fundamental Technologies and Product Lines

COS manufactures and sells a wide variety of water quality measuring instruments for customers working in agricultural commune effluent, semiconductor manufacturing, and preserving the environment. Based on their measurement principles, these instruments are divided broadly into two types: applications of optical measurement technology, and applications of electrochemical measurement technology.

2.1 Applications of Optical Measurement Technology

Applications of optical measurement technology perform measurement by making use of the phenomena of light absorption, refraction, scattering, and coloring. COS offers a wide variety of liquid measuring instruments that perform measurements in wavelength ranges from ultraviolet to infrared. Fig.1 shows the relationship between the coverage of COS products and wavelengths of light.

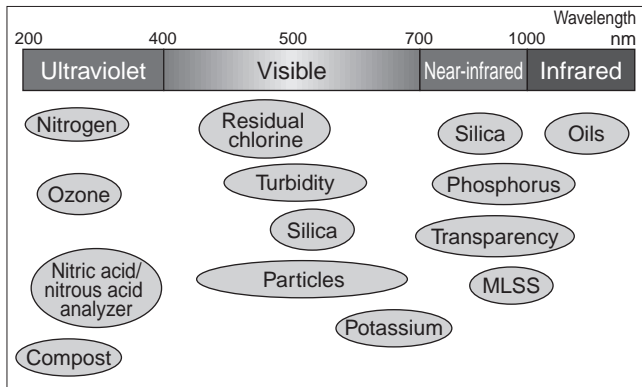


Fig.1 COS Products Based on Optical Measurement Technology

(1) Automatic Total Nitrogen/Phosphorus Meter

A typical example of products that use absorption spectrometry is the PN-100 (Fig.2), an automatic total nitrogen and total phosphorus meter. In the Japanese areas adjacent to closed waters such as the Inland Sea, Tokyo Bay, and Ise Bay, corporations that discharge 400 tons or more of wastewater per day are required by the Fifth Water-Quality Total Pollutant Load Control Regulations to install total nitrogen and total phosphorus meters in order to stem eutrophication. The PN-100 measures total nitrogen and total phosphorus by oxidizing and decomposing samples with an oxidizer under ultraviolet irradiation, and analyzing produced nitric acid or orthophosphoric acid by means of absorption spectrometry. It uses ultraviolet light of 220 nm for nitric acid measurement, and near-infrared light of 880 nm for phosphoric acid measurement. Fig.3 shows the measurement flow of the PN-100.



Fig.2 PN-100 (Total Nitrogen/Phosphorus Meter)

The biggest advantages of the PN-100 are excellent running cost and easy maintenance, as it uses ultraviolet oxidization and decomposition, and requires a smaller amount of reagents compared to other autoclave-type analyzers.

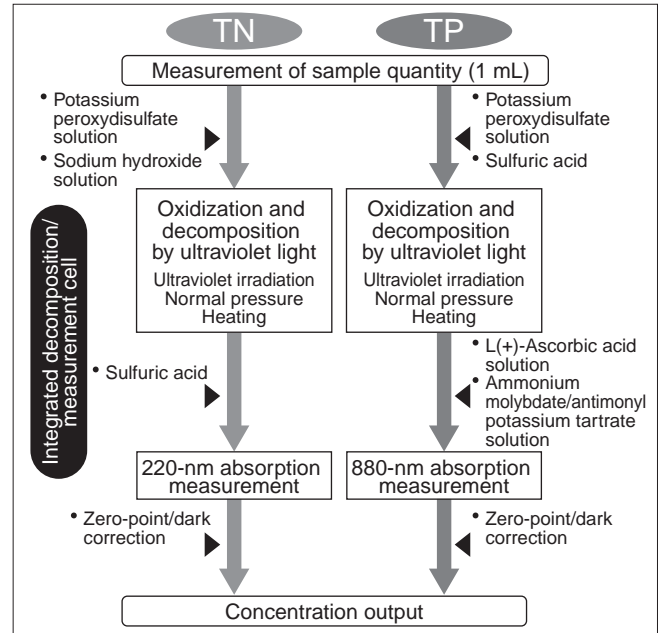


Fig.3 PN-100 Measurement Flow

(2) Organic Pollutant Monitor

Another example of unique environment measuring instruments born of the optical measurement technology is the CW-100/1000 UV (Fig.4), which is an organic pollutant monitor. It measures organic pollutants using the principles that the pollutants absorb ultraviolet light (around 254 nm) and that their absorption has a strong correlation with chemical oxygen demand (COD) obtained by manual analysis. As this ultraviolet absorption method requires no reagent, it offers the advantage that it can save manpower and minimize running cost. Further, with its proprietary rotary cell length modulation method, the CW-100/1000 UV is able to measure even highly polluted samples stably with high accuracy over a long period of time.



Fig.4 CW-100/1000 UV Organic Pollutant Monitor

2.2 Applications of Electrochemical Measurement Technology

The roots of HORIBA, Ltd., which marked the 50 th anniversary of its founding in January 2003, are pH meters. COS, which is the core of the liquid measurement field of the HORIBA group, has built its electrochemical measurement technology as another mainstay on the foundation provided by HORIBA's leadership in pH meters.

Fig.5 shows COS products based on electrochemical measurement technology. In this figure, products are divided into potentiometric sensors that mainly use glass electrodes, voltammetric sensors such as polarographic or galvanic cell sensors, and electrical conductivity sensors based on their detection principles.

| Potentiometry | Voltammetry | Electrical conductivity |
|---------------|-------------------|-------------------------|
| pH | Dissolved oxygen | Conductivity |
| ORP | Hydrazine | Resistivity |
| Sodium | Metal ion | Ammonia |
| Fluoride | Residual chlorine | TMAH |
| | | Fluorine |
| | | IPA purity |

Fig.5 COS Products Based on Electrochemical Measurement Technology

(1) Effluent Treatment Monitoring System for Agricultural Communes

Since its foundation, COS has had a strong relationship with the primary industries, i.e. agriculture, forestry, and fishery, and has created various measuring instruments for these fields. Above all, the effluent treatment monitoring system for agricultural communes is a grand sum of HORIBA's excellent sensing technology and the engineering technology COS has developed. As a recent trend, small-scale effluent treatment plants are built for flush toilets in individual regions so as to create a better environment where people can lead a comfortable life even in agricultural or fishing villages that are presently not covered by sewage disposal plants.

Our monitoring system places water quality monitors such as a sludge concentration (MLSS) meter and a dissolved oxygen (DO) meter in various places within the treatment process, helping assure proper operation of the effluent treatment system.

Fig.6 shows the agricultural commune effluent treatment process and measuring instruments by the intermittent inflow and intermittent aeration method, and Fig.7 a monitoring system using an intelligent printer.

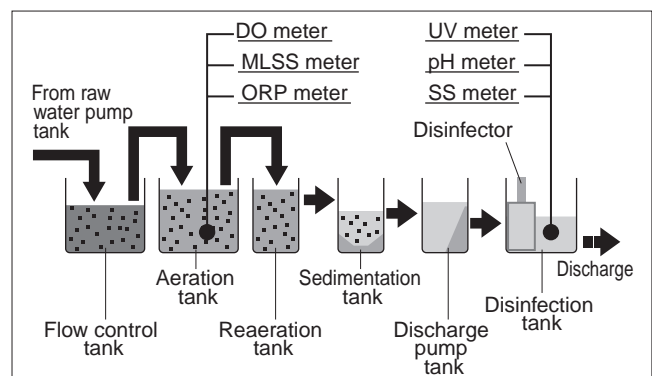


Fig.6 Agricultural Commune Effluent Treatment Process and Measuring Instruments

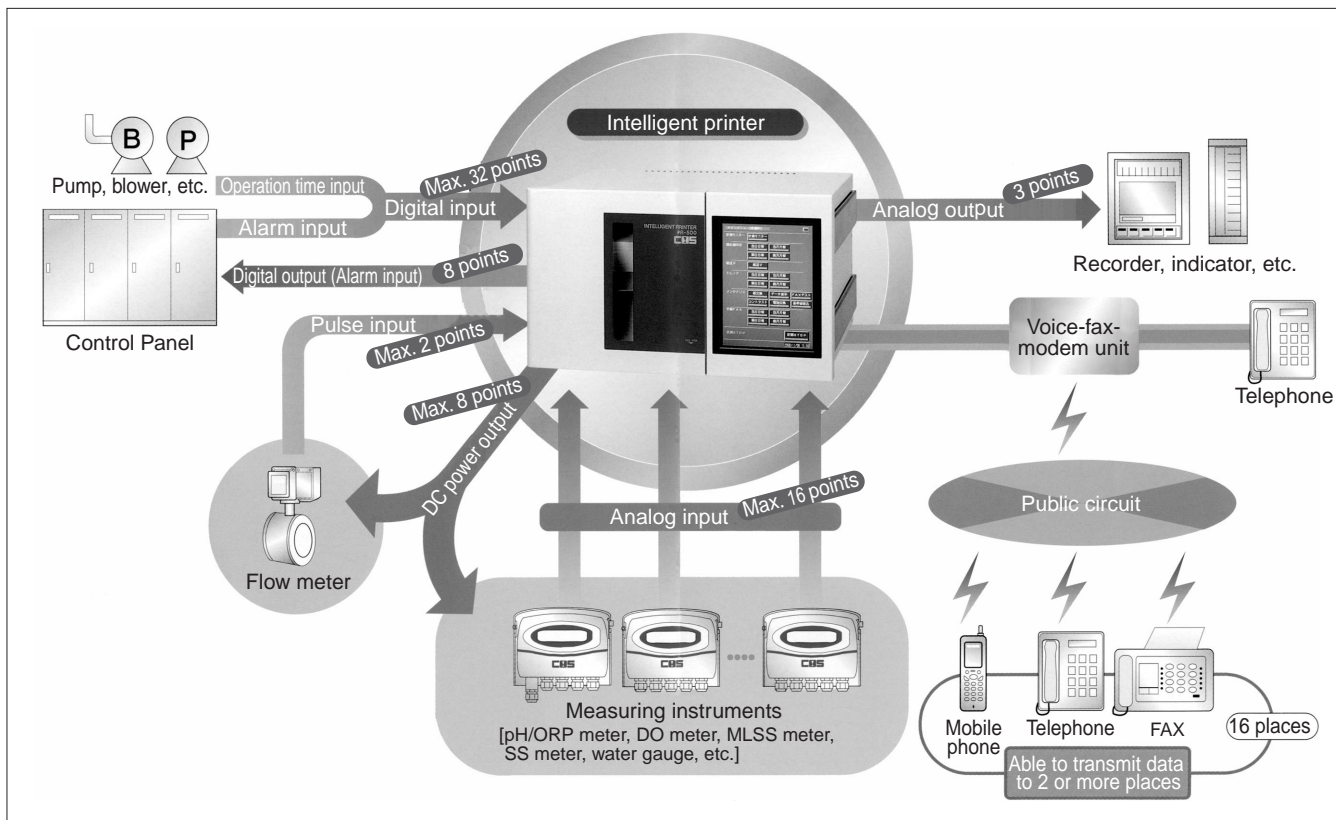


Fig.7 Agricultural Commune Effluent Treatment Monitoring System

(2) Semiconductor Process Monitor

Recently, COS is placing particular emphasis on the semiconductor process monitors based on the electrochemical measurement technology. Resistivity meters that measure utilizing the conductivity principle are widely used to monitor and control the quality of ultrapure water that is gaining more and more importance in semiconductor factories.

In addition to them, COS is offering a wide range of wet process monitors including isopropyl alcohol purity monitors, ammonia concentration monitors, and carbon-sensor resistivity meters.

3 Technical Development for Excellent Products

One of COS's distinctive merits is agility in providing products and service that meet customers' needs. In addition, COS is making tireless efforts to develop and improve our technologies to provide products that continue to satisfy our customers. The following are two new products that illustrate our efforts.

3.1 GC-96RW Two-channel Simultaneous Resistivity Converter

Resistivity is a basic index used to check the purity of water. The newly developed GC-96RW (Fig.8) performs high-precision and stable resistivity measurement as a result of the ability to connect two sensors, and an improved temperature measurement accuracy.



Fig.8 GC-96RW (Two-channel Simultaneous Resistivity Converter)

(1) Improved Temperature Measurement Accuracy

To accurately measure resistivity of pure water, it is essential to accurately measure water temperature. For example, in the case of ultrapure water that has resistivity of approx. 18 MΩ · cm, resistivity becomes higher by 0.1 MΩ · cm if temperature rises by 0.1 °C. Therefore, strict temperature compensation is necessary. Water temperature is measured by the platinum resistance bulb embedded in the resistivity sensor, however, it had been necessary for customers to perform temperature calibration, as the characteristics of each platinum resistance bulb can vary. In the new product, ± 0.2 °C absolute temperature measurement accuracy and 0.01 °C temperature resolution have been achieved by the improvement of the method for determining instrument error in the platinum resistance bulb and the measurement circuit. The temperature compensation must be done taking the temperature coefficient of trace impurities in pure water into consideration. COS's resistivity meter performs temperature compensation using the temperature characteristics of pure water based on ASTM D 1125-91 regarding the conductivity testing method for water and on the assumption that most of the impurity is from sodium chloride. Through these, the GC-96RW achieved stable temperature compensation as Fig.9 shows.

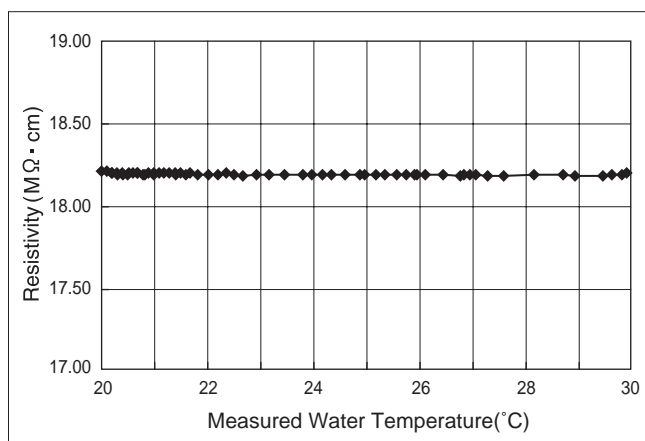


Fig.9 Temperature Compensation Characteristics of GC-96RW

(2) Improved Signal Cable

In resistivity measurement, it is necessary to take some countermeasures against disturbance by stray capacitance in signal cables and external noise, because the amount of electric current passing through the sensor

is small. It has been confirmed that the GC-96 RW is able to provide stable measurement even when the cable is elongated up to 30 m with a cell coefficient of 0.1 / cm, as it maintains the shields of sensor cable conductors at the same voltage (shield drive).

3.2 High-sensitivity Silica Monitor, SLIA-300

Purification of ultrapure water is the most important factor in the control of product yield in semiconductor factories, and impurities are eliminated by passing water through ion-exchange resin. As the resin deteriorates, silica ions are the first to detach. Continuous monitoring of silica concentration is vital to stabilize semiconductor processes. The high-sensitivity silica monitor SLIA-300 monitors a trace amount of silica ions in ultrapure water. COS developed a new long optical path cell based on optical fiber principles, realizing a minimum detectivity of 0.01 µg/L, ten times the sensitivity of conventional products.

(1) Double-pipe and Long Optical Path Measurement Cell

Silica concentration in pure water is measured by the colorimetric assay method using molybdenum blue. With this method it is possible to heighten sensitivity by elongating a measurement cell. However, when this is done the equipment becomes susceptible to external disturbances and becomes larger in size. COS applied optical fiber principles and developed a new long optical path cell (patent application no. 2001-295441) for the SLIA-300, achieving approximately ten times the conventional cell length and requiring about one third of the conventional sample amount.

As Fig.10 shows, the new measurement cell is of a double-pipe structure having a fluorocarbon resin tube, which is superior in light transmittance and chemical resistance, inside a stainless steel pipe. Samples are passed through the inside of the fluorocarbon resin tube, and changes in light intensity are measured in the longitudinal direction of the pipe. Light that enters from one side of the pipe reaches the opposite side reflecting back and forth in the pipe because of the difference in refractive indexes between the fluorocarbon resin tube and ambient air. (The mechanism of light transmission is easier to

understand when you imagine the relationship between the core and the cladding in an optical fiber.) Thanks to this flexible double-pipe measurement cell, it has become possible to mount a 1-meter long cell in a compact container.

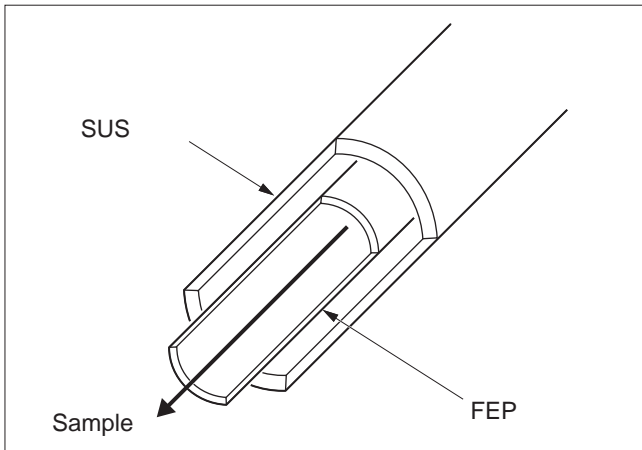


Fig.10 Double-pipe and Long Optical Path Measurement Cell

(2) Reduction in Sample and Coloring Reagent Consumption

The above-mentioned cell structure has made it possible to substantially reduce the amount of samples and coloring reagents required. Conventionally, when equipment has a 100-mm measurement cell (highest sensitivity), cell capacity is approx. 70 ml, and approx. 400 ml of sample is required including the amount used for cleaning. Although the SLIA-300 has a 1-meter cell, its capacity is approx. 7 ml and requires only about 60 ml of sample in total. As a result, the amount of coloring reagent used is also reduced by about one fourth.

(3) Result of Actual Mounting

While the double-pipe long optical path measurement cell has the aforementioned merits, it is susceptible to interference from ambient light and changes in temperature. The interference from stray light was overcome by creating a light-blocking structure for the measurement cell. Effects of changes in temperature are controlled by strict temperature control on the measurement system. Fig.11 shows the result of a continuous test conducted on the SLIA-300 mounted in an ultrapure water supply line. As shown in the figure, it satisfactorily monitored the low-level zone around 0.2 µg/L.

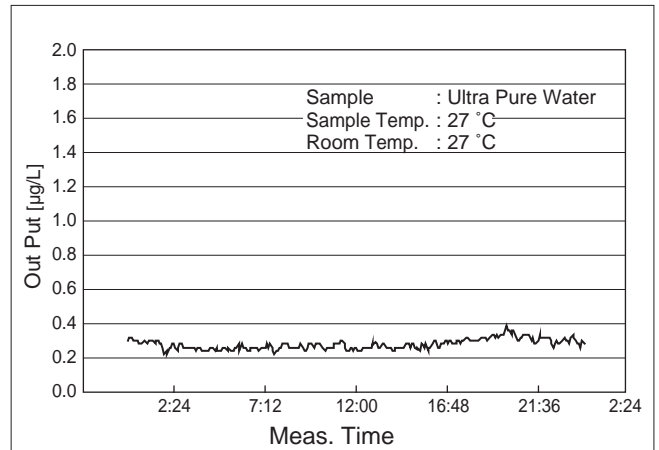


Fig.11 Result of Continuous Test on SLIA-300

4 Conclusion

For COS, which sees itself as specialists in water quality measurement, there is a strong desire to supply unique and high-quality products that can become the de facto standard in the industry. Our future aim is to broaden the range of expertise to in-line process measurement in food and drug plants, and global-level environment measurement like ocean monitoring, making full use of accumulated know-how in the fields of effluent treatment and semiconductor processes. To achieve this aim, we are committed to creating positive alliances with organizations inside and outside the company and providing the best solutions for customers.



Kazunori Sasaki

COS Co., Ltd.
Managing Director



Riichiro Suzuki

COS Co., Ltd.
Design Dept.
Manager



Koji Uchimura

COS Co., Ltd.
Design Dept.
Manager