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1. Overview

Disinfection by chlorination using chlorine gas or sodium hypochlorite solution in water treatment systems and protection from contamination by maintaining a chlorine residual throughout the distribution of water to customers' taps, are of prime importance in order to ensure the safety of water supplies and are basic essentials of water systems. Chlorination is also widely used as an effective method of removing iron, manganese and ammonium nitrogen from raw water.

In chlorination processes, on-line residual chlorine analyzers are effectively used for water quality monitoring and economical chlorine dosing. In recent years in particular, reducing the formation of chlorination by products and reducing a chlorine residual in tap water for a better taste, have become important themes as pollution of rivers and lakes, which are used as source water, has been worsening. Therefore, higher accuracy and reliability are required in measurement of residual chlorine.

This document describes Yokogawa's reagent-free type, free available chlorine analyzer, Model FC400G, which provides high accuracy and reliability. The analyzer employs the rotating electrode polarographic method that does not require reagents that are used for pretreatment of sample water. This allows easy maintenance. Typical applications for the FC400G include post-filtration processes at water systems and distribution systems. For other applications or for highly stable measurement, a residual chlorine analyzer that requires pretreatment of sample water with reagents (RC400G in Yokogawa's model) may be suitable.

2. Features

FC400G's features are outlined below. For details, refer to Chapter 5.

Microprocessor-based intelligent converter

- One-touch simple calibration.
- Self-diagnostic function automatically checks zero point, slope and response of the detector at calibration.
- Field configurable output ranges.
- Sensor characteristics in sample water can easily be obtained through plateau characteristic check.
- Enhanced display and contact output functions.
- Easy-to-use, interactive operation panel.

Field-proven, upgraded detector

- Improved rotating electrode and ceramic bead cleaning provide more effective, continuous automatic cleaning.
- Uses a reliable sliding contact.
- Cell construction is designed for ease of clean and for applicability to a wide range of flow rates.

3. What is Residual Chlorine

3.1 Definition of Residual Chlorine

Residual chlorine is defined by the Standard Methods for Examination of Water (2001), issued by Japan Water Works Association, and the Testing Methods for Industrial Water (Japan Industrial Standards, JIS K0101-1998), as follows:

Residual chlorine = free available chlorine + combined available chlorine; or

Residual chlorine = free residual chlorine + combined residual chlorine.

Sometimes free available chlorine is also called free chlorine, and residual chlorine is also called total chlorine.

3.2 Free Available Chlorine

When chlorine gas (Cl_2) is added to water, it reacts to form hypochlorous acid (HClO) and hydrochloric acid (HCl) and the reaction reaches equilibrium, as shown in chemical equation (3.1). If the pH of the solution is 4 or higher, the reaction shifts to the right with predominant production of HClO .



HClO dissociates in equilibrium to hydrogen ion (H^+) and hypochlorite ion (ClO^-), as shown in equation (3.3). The equilibrium constant is dependent on the temperature and pH of the solution.

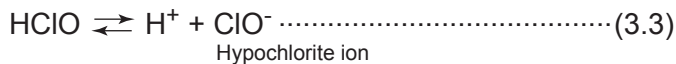


Figure 3.1 shows the relationship between HClO and ClO^- to pH. At pH 5 or less, only HClO exists. Chlorine water has strong bactericidal properties on the acid side and weak bactericidal properties on the alkaline side. Therefore, HClO is considered to be effective as a disinfectant. Free available chlorine, in general, refers to chlorine that is present in forms of Cl_2 , HClO , ClO^- , etc. in water.

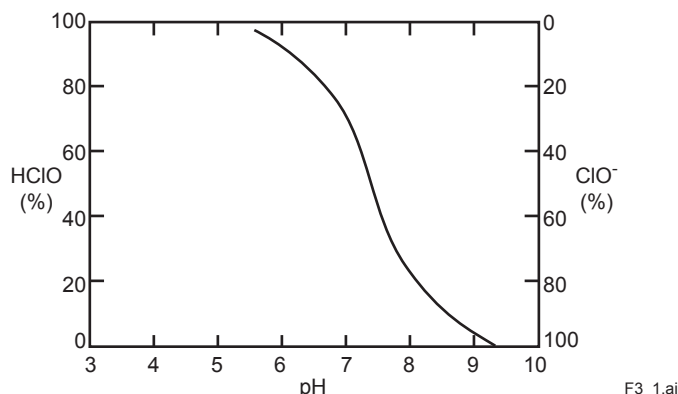
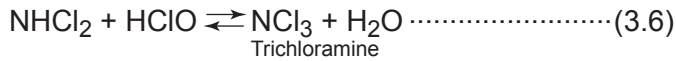
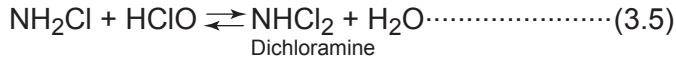


Figure 3.1 Dissociation of Hypochlorous Acid (HClO) vs. pH (20 °C)

3.3 Combined Available Chlorine

If water contains ammonia nitrogen, such as ammonium ion (NH_4^+) caused by contamination of river or other source water, chloramines are generated by reactions shown in equations (3.4), (3.5) and (3.6).



Chloramines are one of combined available chlorine and exist in different forms: monochloramine (NH_2Cl); dichloramine (NHCl_2) and trichloramine (NCl_3). The predominant form is dependent on pH. At pH 8.2 or higher, only NH_2Cl exists, where the pH is between 5.0 and 8.0, NH_2Cl and NHCl_2 coexist, and at pH 4.4 or lower, only NCl_3 exists. The relationship between chloramine forms and pH is shown in Figure 3.2.

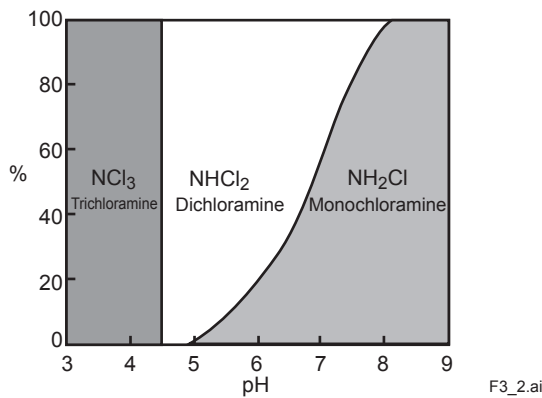


Figure 3.2 Chloramine Forms Depending on pH

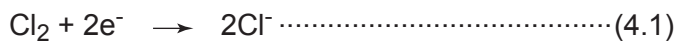
Chloramines are far less effective as disinfectants than free available chlorine. To kill bacteria completely in a certain period of time, combined available chlorine is required about 25 times more than free available chlorine in terms of quantity. It is also said that when combined available chlorine and free available chlorine have the same concentration, disinfection with combined available chlorine will take 100 times longer than the one with free available chlorine.

4. Measurement Principle

The FC400G Free Available Chlorine Analyzer employs the polarographic method and uses a rotating gold electrode as the indicator electrode and a silver/silver chloride electrode as the counter electrode.

4.1 Electrode Reaction

When a DC voltage is applied between the indicator electrode and the counter electrode that are immersed in a sample solution, the following reactions take place at each electrode surface, which causes a current to flow. A reduction reaction takes place at the indicator electrode, as shown in equation (4.1), and an oxidation reaction takes place at the counter electrode, as shown in equation (4.2).



4.2 Polarographic Method Using a Rotating Electrode

When a DC voltage is applied between an indicator electrode and a counter electrode that are immersed in a sample solution and the voltage is swept in the negative direction, as shown in Figure 4.1, chlorine (Cl_2), an electrochemically reducible substance, is reduced at the surface of the indicator electrode. By this reduction reaction, a current-voltage characteristic (called a polarogram or plateau characteristic) is obtained, as shown in Figure 4.2. The concentration of chlorine in the solution adjacent to the indicator electrode can be illustrated as shown in Figure 4.3.

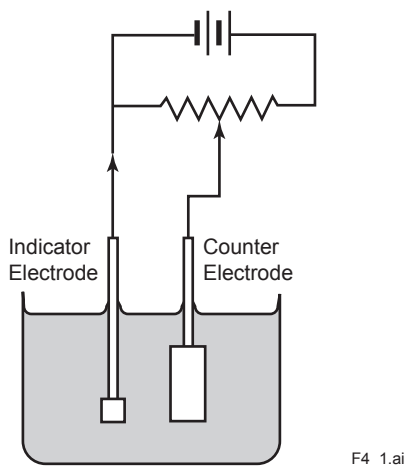


Figure 4.1 Basic Polarography Diagram

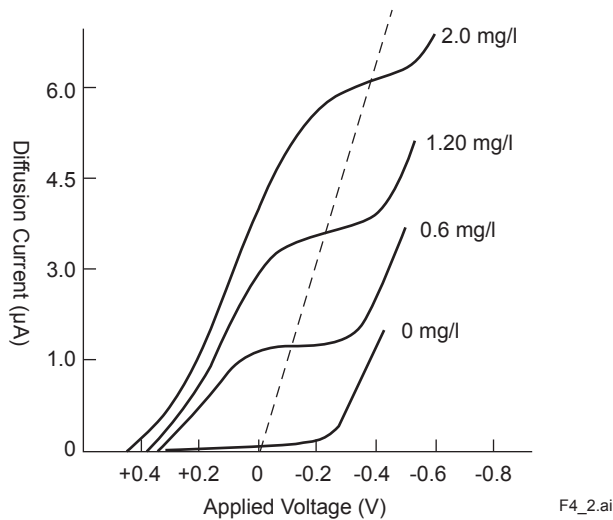


Figure 4.2 Current-Voltage Diagram at Different Chlorine Concentration

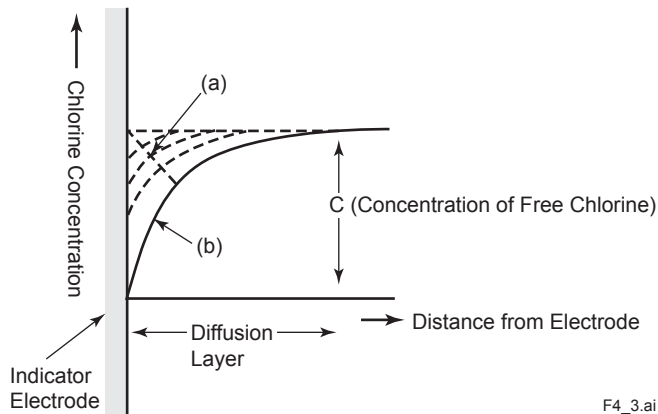


Figure 4.3 Diffusion Layer and Chlorine Concentration Adjacent to Indicator Electrode

When the applied voltage is low, the reduction reaction at the surface of the indicator electrode is not achieved thoroughly, resulting in remaining, unreacted chlorine at the electrode surface (Figure 4.3 (a)). As the applied voltage is increased, the rate of reaction increases and finally all the chlorine is reduced, i.e. no chlorine remains unreacted (Figure 4.3 (b)). Until this point, the reduction reaction depends on the applied voltage. That is, the rate of reaction is limited by the applied voltage.

When the applied voltage is large, no chlorine remains unreacted at the electrode surface (Figure 4.3 (b)), and thus the reaction is independent of the applied voltage. The rate of reaction is limited by the rate of supply of reactant, i.e., chlorine. This is called the diffusion-limited reaction and the current that flows as the reaction takes place is called the diffusion current.

The FC400G measures chlorine concentration under the condition that this diffusion-limited reaction takes place.

What is important for the chlorine measurement in this diffusion-limited process is that the diffusion coefficient (the physical property determined by temperature) and the thickness of diffusion layer should be kept constant so as to obtain a stable ratio of chlorine concentration and diffusion current. For that purpose the FC400G compensates the diffusion coefficient for temperature changes and rotates the indicator electrode continuously at a constant speed to keep a constant thickness of the diffusion layer.

The diffusion current in the plateau region is expressed in equation (4.3).

$$I_d = K \cdot n \cdot F \cdot C \cdot D^{2/3} \cdot v^{1/3} \dots\dots\dots(4.3)$$

Where:

I_d : Diffusion current (A)

K : Constant

n : The number of electrons involved

F : Faraday constant (96,500 C)

C : The concentration of the electroactive species (chlorine) (mol/l)

D : The diffusion coefficient (cm²/s)

v : The rotation number of indicator electrode (/s)

The FC400G is designed to have the following features:

- A fixed voltage in the plateau region, where a reduction reaction takes place stably, is applied and the diffusion current is measured. The plateau region shifts depending on the chlorine concentration. As the chlorine concentration increases, the diffusion current increases. Then, a voltage drop due to the solution resistance between electrodes, increases based on the Ohm's law. The FC400G automatically changes the applied voltage as well as the diffusion current to determine an appropriate voltage that is always in the plateau region and applies it between electrodes for measurement (see Figure 4.2). By this means, the diffusion current output that is linear to the chlorine concentration, can be obtained (see Figure 4.4).

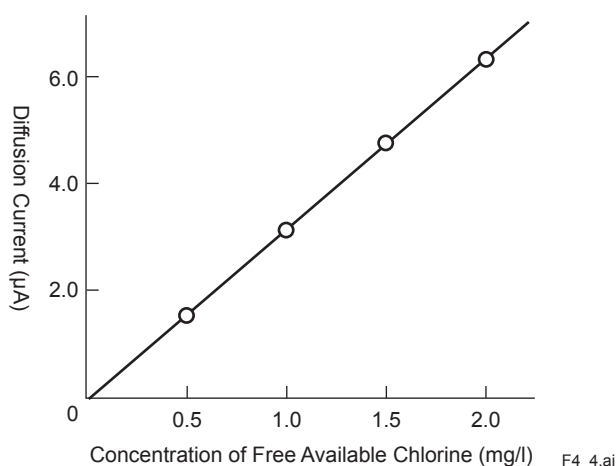


Figure 4.4 Working Curve of Diffusion Current vs. Chlorine Concentration

- The diffusion coefficient varies with solution temperature. The FC400G measures the solution temperature and compensates the diffusion coefficient for temperature changes.
- In order to allow a stable diffusion layer, the FC400G rotates the indicator electrode at a speed of 600 rpm (for power supply frequency of 50 Hz).

5. Configuration

The FC400G Regent-Free Type Free Available Chlorine Analyzer consists of a detector, which contains a measuring cell and electrode assembly, and a converter. For easy installation, a dedicated sampling system, ST401G, is available.

5.1 External View

An external view of the analyzer is shown in Figure 5.1.

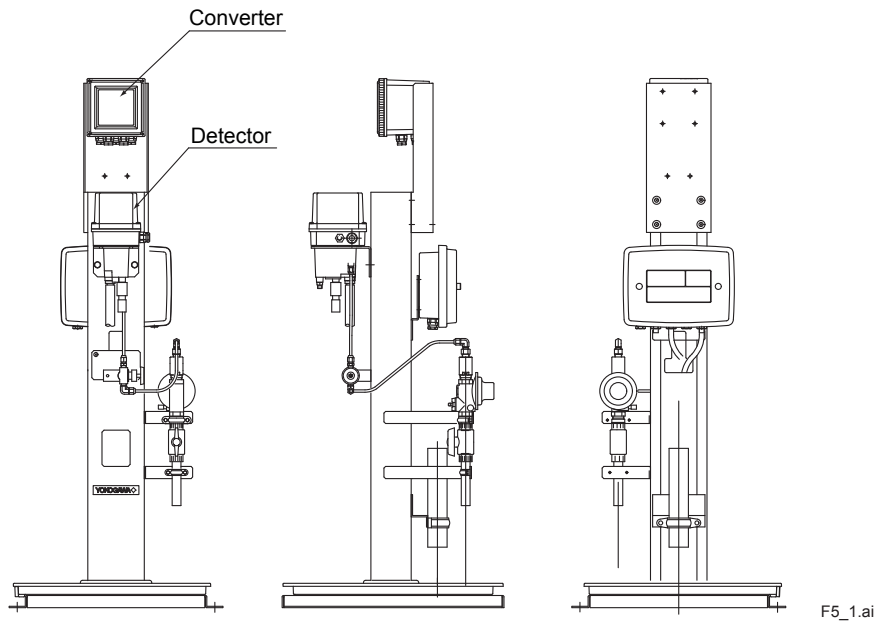


Figure 5.1 Analyzer and Sampling System

5.2 Detector

An external view of the detector is shown in Figure 5.2 and the schematic diagram of the measuring cell and electrode assembly in Figure 5.3.

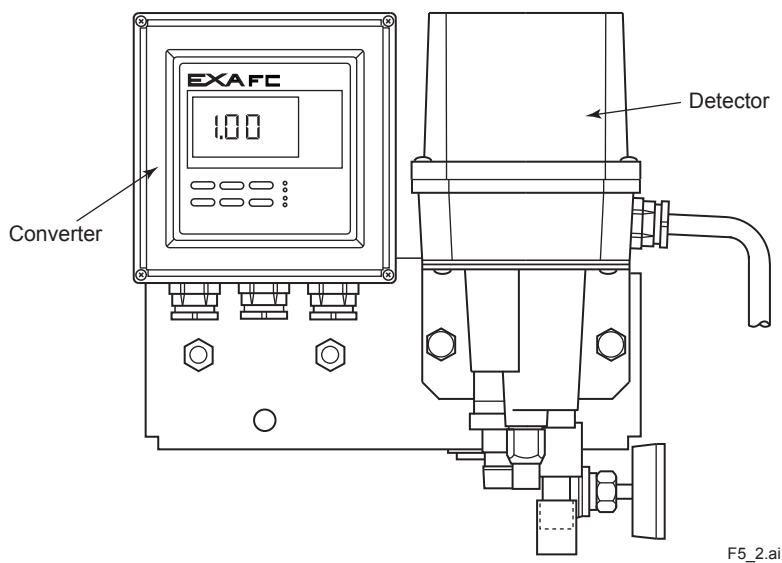


Figure 5.2 Detector and Converter

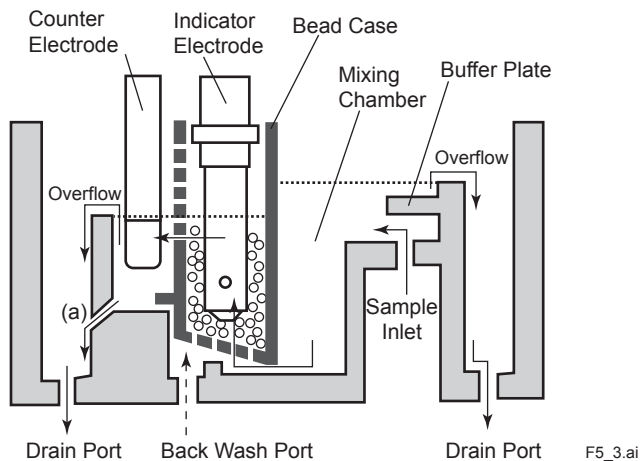


Figure 5.3 Schematic Diagram of Measuring Cell and Electrodes

Sample water flows through the mixing chamber, bead case, indicator electrode, counter electrode and overflow weir, and flows out from the drain port. The overflow weir and the buffer plate near the sample inlet allows an almost constant sample water flow rate in the range of 0.1 to 2.5 mL/min at the indicator electrode.

A small hole, (a) in Figure 5.3, is placed for draining the standing water from the cell when the flow of sample water stops. This prevent the counter electrode from being exposed to stagnant water, thereby protecting the electrode against silver plating.

The bead case is easily detachable. With its wide opening, the measuring cell is easy to clean and maintain.

The FC400G uses a rotating electrode with ceramic bead cleaning, which has been improved from the field proven technique of rotating electrode with glass bead cleaning, for automatic electrode cleaning. This more efficient, continuous cleaning system has extended maintenance intervals. The ceramic beads are placed in the bead case and so cleaning and replacement are easy.

As the electrical contact to pick up the signal from the rotating electrode (indicator electrode), the FC400G uses a sliding contact of brushes and rotor. This improves the safety. The contact is made of a gold alloy that provides excellent resistance to wear and corrosion. With the rotating gold electrode rotating, the contact resistance is 500 Ω or less. If this resistance value increases, the effective applied voltage will decrease and then the sensitivity will decrease, causing errors.

5.3 Converter

An external view of the converter is shown in Figure 5.2. The converter's measuring circuit is housed, together with an operation panel and an external wiring terminal board, in a splashproof (rainproof) case. The microprocessor-based converter has many useful functions and features.

(1) Selectable display parameters

Chlorine concentration, sample water temperature, applied voltage, diffusion current, output signal (%), zero point, slope, error message, interactive menu, key prompt.

(2) Easy operation

- Three-level operating system:

Operation level: for daily inspection and maintenance, e.g., one-touch automatic calibration

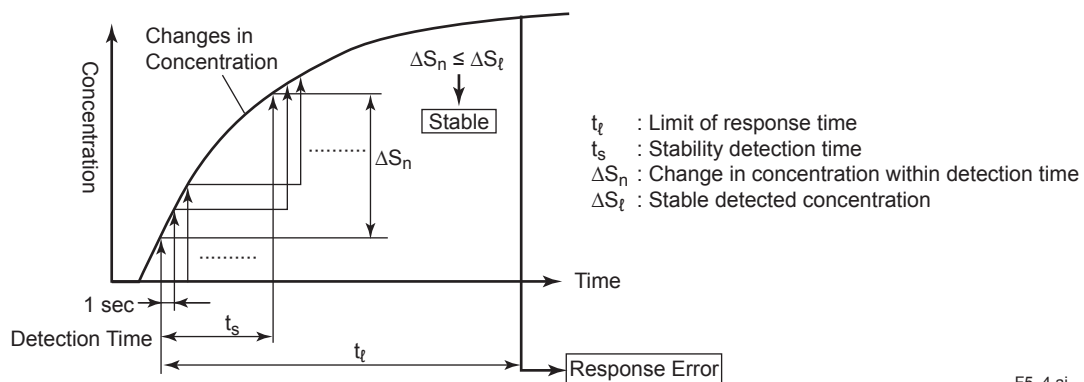
Setting level: for function selection and data setting, e.g., setting of output range

Service level: for function selection and data setting, e.g., setting of stability check parameter

- Interactive operation with key prompt indication
- Key operation without opening the case cover

(3) One-touch automatic calibration

After a calibration solution is introduced, the converter automatically determine whether the sensor output has stabilized or not. This prevents calibration errors and personal errors (see Figure 5.4).



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Figure 5.4 Stability and Response Checks at Calibration

(4) Automatic self-diagnostic function

At one-touch calibration, the converter automatically checks how much the zero point and slope (the ratio of the magnitude of diffusion current to chlorine concentration) of the sensor have deteriorated from the initial condition. The converter also checks the response by determining the time required for the output to stabilize (see Figure 5.4).

(5) Plateau characteristic check

As described in Chapter 6, a change in water quality may affect the plateau characteristic, thereby affecting the output characteristic. To correct this, the converter checks the plateau characteristic and accordingly it can reset the applied voltage to the one most appropriate for the sample water being analyzed (see Figure 5.5, Chapters 4 and 6).

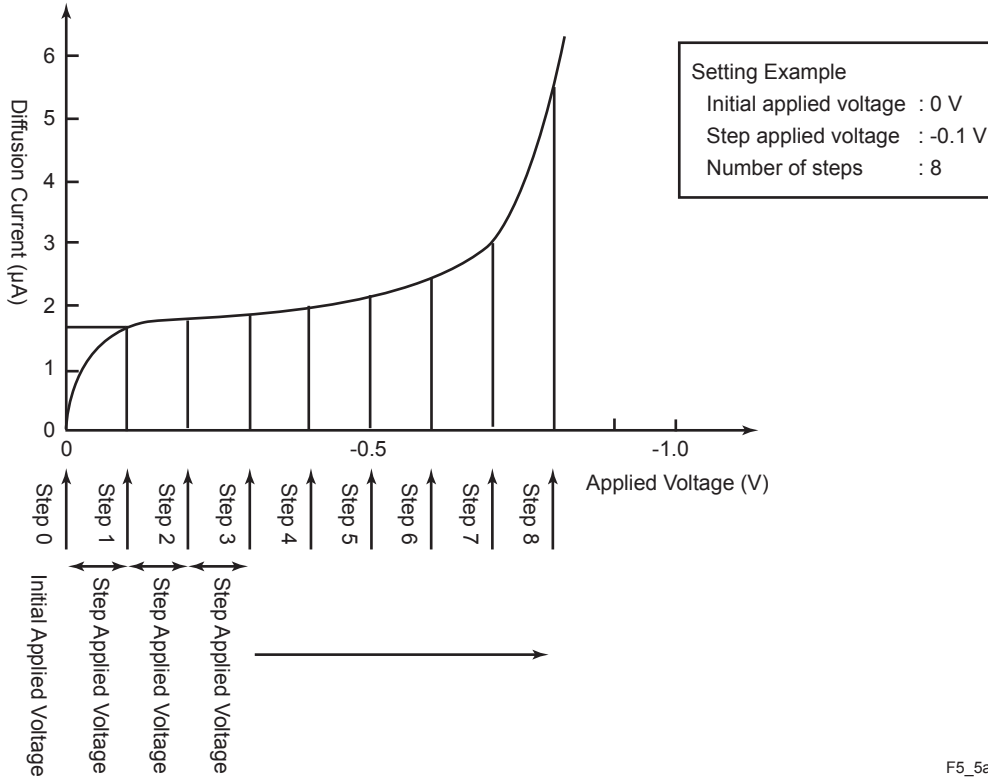


Figure 5.5 Measurement of Plateau Characteristic

(6) User configurable measuring range

(7) Improved accuracy of temperature compensation

A high precision platinum temperature sensor (Pt 1000 Ω) is incorporated in the counter electrode and a microprocessor is used for computation of temperature compensation.

(8) Applied voltage compensation

As shown in Chapter 4, in the sensor’s electrochemical characteristic, the plateau region shifts along the voltage axis depending on the chlorine concentration. In order to achieve highly accurate measurement, the plateau region should be properly determined in the wide measuring range. The converter performs applied voltage compensation as shown in equation (5.1).

$$x = Ay + B \dots\dots\dots(5.1)$$

Where:

x : Applied voltage (V)

y : Diffusion current (µA)

A : Constant (coefficient: the ratio of applied voltage to diffusion current)

B : Constant (applied voltage when diffusion current is zero)

Applied voltage compensation is done by the microprocessor. As shown in Figure 5.6, by multiplying the difference (④ - ⑤) between the actual diffusion current, ④, and the diffusion current at the current applied voltage on the compensation equation, ⑤, by coefficient C and then adding the current applied voltage, ③, a new calculated applied voltage, ⑥, can be obtained. By

repeating this calculation, the intersection, D, of the compensation line and the plateau curve is obtained, from which a compensated applied voltage, ⑦, is obtained.

The factory default settings are: A = -0.02 V/ μ A; B = -0.1 V.

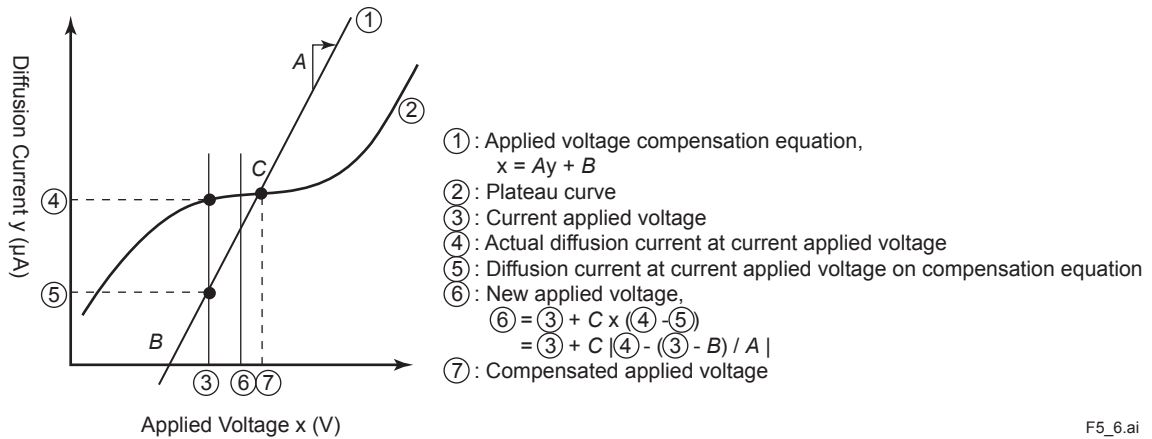


Figure 5.6 Applied Voltage Compensation

(9) Measuring circuit

Figure 5.7 shows the block diagram of measuring circuit. A voltage is applied between the indicator electrode and the counter electrode. The diffusion current (I_d) occurs between the electrodes in response to the concentration of free available chlorine in sample water in the measuring cell.

The diffusion current is converted to a voltage signal at the input circuit, then the voltage signal is converted to a digital quantity at the A/D converter, and then the digital signal is loaded into the CPU. The diffusion current varies with temperature of sample water. To compensate for this, the temperature is measured by the temperature sensor incorporated in the counter electrode. The temperature signal is converted to a voltage signal at the temperature circuit, then in the same manner as the diffusion current processing, the voltage signal is converted to a digital quantity at the A/D converter, and then the digital signal is loaded into the CPU. Computations of temperature compensation and of conversion to free available chlorine concentration are executed by the microprocessor in the CPU.

In actual measurement of free available chlorine concentration, the applied voltage is not constant. Since the line of the plateau characteristic (current-voltage characteristic) has a slope (see Figure 4.2), the applied voltage needs to be changed in response to the chlorine concentration. The chlorine concentration calculated at the CPU and the signal calculated using a preset applied voltage compensation parameters are transferred to the A/D converter and converted to a voltage signal at the voltage circuit, and then the voltage is applied between the electrodes. In actual measurement these actions are executed repeatedly and the applied voltage is controlled automatically by the CPU so that the optimum voltage is applied (see Figure 5.6).

The calculated concentration of free available chlorine is displayed on the LCD. At the same time it is converted to a signal of 4-20 mA DC or 1-5 V DC at the analog output circuit and the signal is released. The analog output circuit is electrically isolated from the input and CPU circuits by the insulation circuit.

Various settings and operations, such as analog output range setting and calibration, can be done easily through operation keys.

The other circuits incorporated are: the reset circuit to ensure proper operation of circuits around the CPU when power to the instrument is turned on and off, and the power supply circuit to supply power to each circuit.

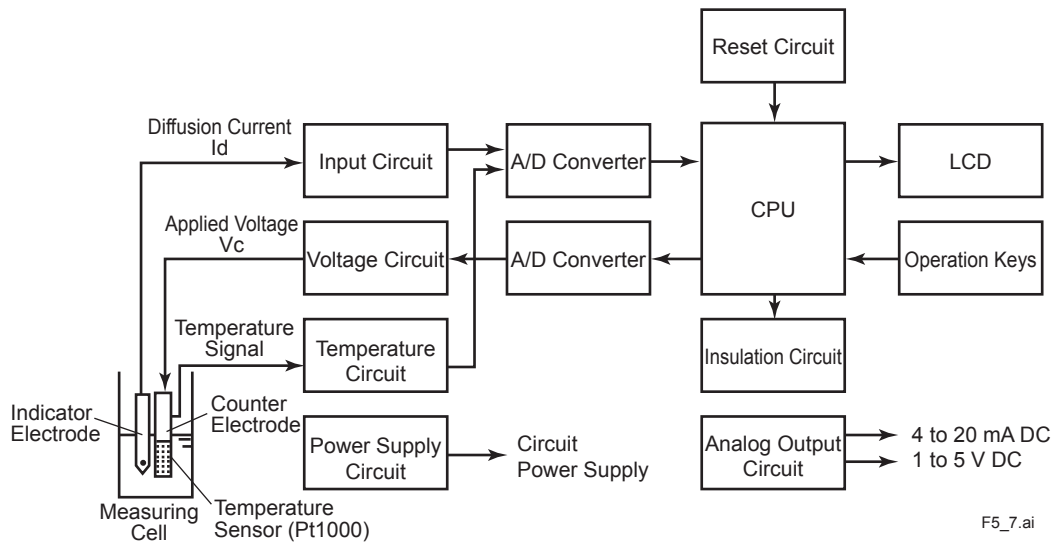


Figure 5.7 Block Diagram of Measuring Circuit

5.4 Sampling System

The external view of the dedicated sampling system is shown in Figure 5.1. The system incorporates a pressure reducing valve and a ball valve to allow the sample pressure of 100 to 750 kPa and the flow rate of 0.1 to 2.5 l/min.

6. Sample Conditions and Effects on Outputs

6.1 Effect of pH

As shown in equations (3.1), (3.2) and (3.3) in Chapter 3, free available chlorine is present in forms of HClO , ClO^- , etc. in water. How much chlorine dissociates is determined mainly by the pH of water. Depending on the dissociation condition the electrochemical activity varies, thereby affecting the output characteristic of the FC400G. That is, the output characteristic of the FC400G is affected by the pH of sample water (see Figures 6.1 and 6.2). However, as Figure 6.2 shows, when the pH variation is within one (e.g., the pH changes within the range of pH 6.5 to 7.5), it is considered that the measurement can be made without practical problems.

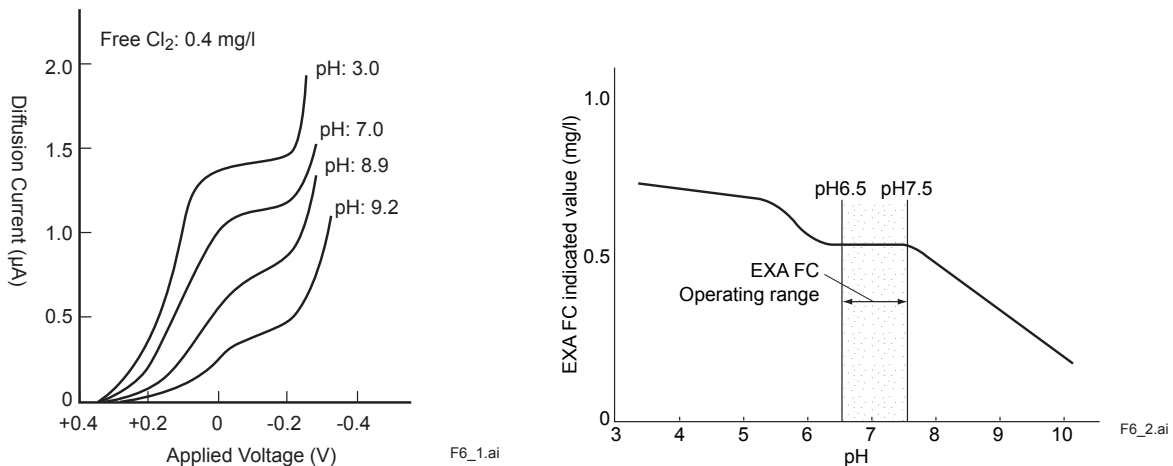


Figure 6.1 Plateau Characteristic at Different pH

Figure 6.2 Sensitivity of Diffusion Current at Different pH

6.2 Effect of Conductivity

As the conductivity of sample water changes, the plateau region shifts along the voltage axis (see Figure 6.3). As long as the shift does not cause the applied voltage to deviate from the plateau region, changes in conductivity of sample water hardly affect the output characteristic of the FC400G. If the shift is large enough to cause the applied voltage to deviate from the plateau region, the output characteristic of the FC400G is greatly affected by changes in conductivity of sample water. When the conductivity falls within the range of 100 to 300 $\mu\text{S}/\text{cm}$, the measurement can be made almost without errors (see Figure 6.4).

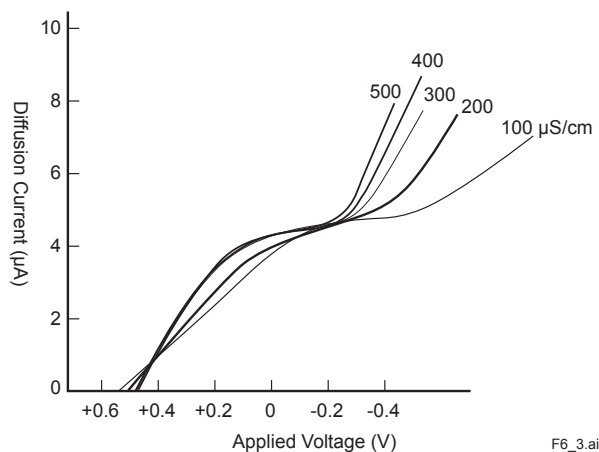


Figure 6.3 Plateau Characteristic at Different Conductivity

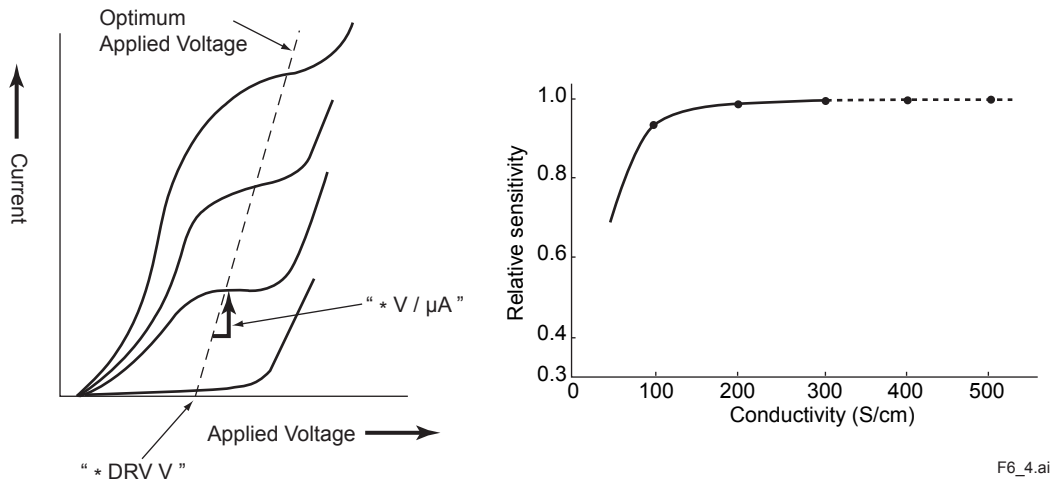


Figure 6.4 Sensitivity of Diffusion Current at Different Conductivity

[Reference]

When the conductivity exceeds 300 $\mu\text{S}/\text{cm}$, the plateau characteristic remains unchanged and shows almost the same as the one obtained when the conductivity is 300 $\mu\text{S}/\text{cm}$. Then, the slope of the applied voltage compensation line approaches zero (the optimum applied voltage is almost constant). This eliminates the need for applied voltage compensation. When only the sample conductivity is outside the specifications (exceeds 300 $\mu\text{S}/\text{cm}$) and the conductivity remains constant, the measurement is possible by setting the slope of the applied voltage compensation parameter ($*V/\mu\text{A}$) to zero (0). Note that in this case, approximately, the repeatability becomes 4% and the linearity $\pm 8\%$.

6.3 Effect of Flow Rate

Since the FC400G uses the polarographic method using a rotating electrode (at a speed of 600 rpm), the output characteristic is hardly affected by changes in flow rate of sample water (see Figure 6.5). The upper range limit (2.5 l/min) of the sample flow rate in the standard specifications is determined by the mechanical structure of the measuring cell and the lower range limit (0.1 l/min) by the minimum flow rate required to fill up the measuring cell.

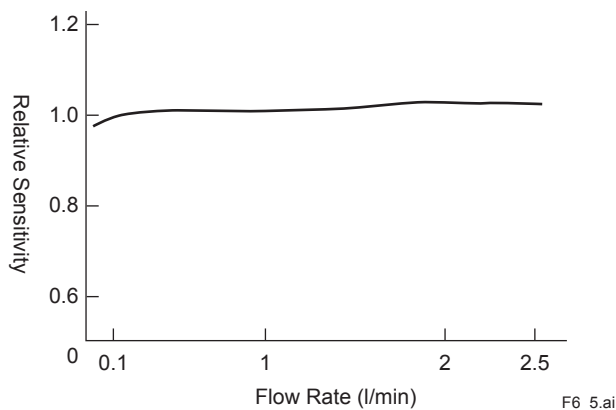


Figure 6.5 Sensitivity of Diffusion Current at Different Flow Rate

6.4 Effect of Temperature

The diffusion current in the plateau region is expressed by equation (4.3) in Chapter 4.

$$I_d = K \cdot n \cdot F \cdot C \cdot D^{2/3} \cdot v^{1/3} \dots\dots\dots(4.3)$$

As the sample temperature changes, the diffusion coefficient, D , in equation (4.3) changes, thereby changing the diffusion current, I_d .

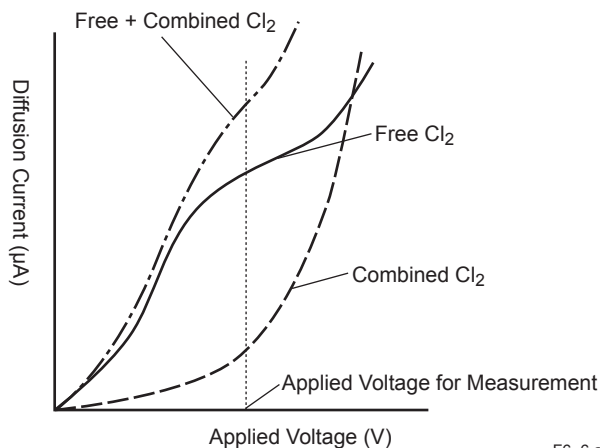
The FC400G accurately measures the water temperature with its temperature sensor (Pt 1000 Ω) and compensates the diffusion coefficient for temperature changes through accurate computing by the microprocessor. This allows the analyzer to provide the characteristic that is hardly affected by changes in temperature of sample water.

6.5 Effect of Combined Chlorine

The FC400G was originally developed for measuring free available chlorine. Figure 6.6 shows the current-voltage characteristic (plateau characteristic) measured when free available chlorine and combined available chlorine (monochloramine, dichloramine), individually and together, are supplied to the FC400G electrode system.

When combined available chlorine is present in sample water, the diffusion current that flows in response to the combined available chlorine is superimposed on the one that flows in response to the free available chlorine. That is, the output includes the amount of combined available chlorine in addition to the one of free available chlorine.

When the presence of combined available chlorine in sample water is anticipated, it is recommended that Yokogawa's residual chlorine analyzer, Model RC400G, be used. The RC400G can reduce the effect of the concentration of combined available chlorine on output to approximately 5% of the concentration of combined available chlorine.



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Figure 6.6 Plateau Characteristic at Different Chlorine Forms

7. Precautions for Calibration and Operation

7.1 Precautions for Calibration

Calibration is required to accurately measure free available chlorine concentrations using the FC400G. It is performed for the zero and span point.

Calibration is performed at start-up or when operation restarts after the FC400G is stopped for a long time. Also, calibration should be performed periodically (monthly) during operation. This is for the purpose of correcting the diffusion current value that decreases relative to a certain residual chlorine concentration as the electrode surface is contaminated and so on.

(1) Running-in for Calibration

Calibration should be performed in a stable condition while the electrode surface of the indicator electrode (rotating gold electrode) is not contaminated. Therefore, calibration should be performed after running-in for approximately one hour until the indicator electrode reading is stabilized after polishing the electrode surface of the indicator electrode.

(2) Zero Point Calibration

There are two methods of calibrating the zero point: the open input circuit and chlorine-free-water-based measuring methods. In the former, the electrode is exposed to the air so that no current flows between the indicator electrode (rotating gold electrode) and counter electrode. The latter uses chlorine-free water (e.g., water filtered through activated charcoal). Auto zero calibration is performed using the chlorine-free-water-based measurement method with the activated charcoal filter. Generally, zero point calibration is performed using the simple open input circuit method. However, to measure low free chloride concentrations, the chlorine-free-water-based measuring method should be used for zero point calibration.

(3) Span Point Calibration

When both the zero and span point are calibrated, first the zero point and then the span point should be calibrated. There are two span calibration methods. One is a sampling method in which the value obtained by sampling and laboratory analysis results is entered into the FC400G to perform span calibration. The other is a reference solution method that uses a calibration reference solution whose free available chlorine concentration is approximately 80% of the measurable range.

The reference solution method is suitable for performing more accurate calibration when only low concentrations are measured. In general cases, the sampling method is good enough.

7.2 Precautions for Operation

(1) Electrode maintenance

The FC400G has a highly effective automatic cleaning system. This is achieved by constantly rotating the indicator electrode in the measuring cell filled with ceramic beads. In long term operation, however, the surface of the indicator electrode may be stained, thereby reducing the electrode sensitivity. In such a case the indicator electrode needs to be polished at appropriate intervals (every 1 to 3 months) depending on the degree of deposits on its surface.

The surface of the indicator electrode should be polished with gauze on which supplied, alumina abrasive powder is put.

Immediately after polishing, the electrode is electrochemically unstable and does not provide stable characteristics. Before using it for measurement, the electrode should be put in measurement mode and left for a certain time (conditioning) until it stabilizes. Normally it takes 30 to 60 minutes, but it may need more depending on the polishing method.

Calibration should be performed after the electrode has undergone conditioning and its characteristic has stabilized sufficiently.

(2) When sample water is not supplied

When sample water is not supplied, the measuring cell will be emptied. If measurement continues without water in the measuring cell, the indicator electrode will undergo stress from ceramic beads and be damaged.

When sample water is not supplied, stop the rotation of the indicator electrode by operating the keys on the converter.

8. Applications

The FC400G has been designed for use mainly at post-filtration processes at water treatment plants and distribution systems. For other applications or for highly stable measurement, a residual chlorine analyzer that requires pretreatment of sample water with reagents (RC400G in Yokogawa's model) may be suitable.

Table 8.1 lists differences in sample and operating conditions between the FC400G and the RC400G.

Table 8.1 Reagent-Free (FC400G) vs. Reagent (RC400G) Types Chlorine Analyzers: Sample and Operating Conditions

	Free Available Chlorine Analyzer Reagent-Free Type FC400G	Residual Chlorine Analyzer Reagent Type RC400G
Measurement	Free available chlorine	Free available chlorine, total chlorine
Sample pH	pH 6 to 8 (maximum variation: 1)	pH 3 to 9
Allowable suspended solids in sample	10 mg/l max.	500 mg/l max.
Sample conductivity	100 to 300 $\mu\text{S}/\text{cm}$ *	No limit
When sample contains combined chlorine	Not suitable	Suitable (combined chlorine insensitive version)
Where measurement accuracy is required	Suitable (but less suitable than RC400G)	Suitable
Application	Filtered water, treated water, distribution system, feed water, tap water	Each process at treatment plant: from reservoir to treated water, distribution system

* When sample conductivity exceeds 300 $\mu\text{S}/\text{cm}$, refer to Section 6.2.

9. Specifications and Characteristics

9.1 Standard Specifications

Measurement:	Free available chlorine in water supply and distribution system
Measuring range:	0 to 3 mg/l
Output signal:	4 to 20 mA DC (load resistance 550 Ω max.) or 1 to 5 V DC (output resistance 300 Ω max.)
Sample conditions:	
Temperature:	0 to 50 °C
pH:	6.5 to 7.5 (max variation: 1)
Conductivity:	100 to 300 μ S/cm
Flow rate:	0.1 to 2.5 l/min
Pressure:	1 to 150 kPa (100 to 750 kPa when dedicated sampling system, ST401G, is used)
SS (suspended solid):	10 mg/l or less

9.2 Characteristics (% display shows value relative to the upper limit of a range.)

Repeatability:	2%
Linearity:	\pm 5%
Drift:	
Zero drift:	\pm 1%/month max.
Span drift:	-10%/month max.
Response time:	Approx. 2 min (90% response)
Temperature compensation error:	\pm 3% or less (temperature compensation range: 0 to 40 °C)
Effect of ambient temperature:	\pm 0.5%/10 °C
Effect of power supply voltage changes:	\pm 0.5%/10% of rated voltage
Combined chlorine effects:	Approx. 30% of combined chlorine concentration

10. Correlation between On-line Analyzer and Laboratory Analysis Results

The Standard Methods for Examination of Water, issued by Japan Water Works Association, and the Testing Methods for Industrial Water (JIS K 0101), require that manual analyses of the colorimetry (DPD method) and titration (DPD, iodometric, and amperometric methods) be used as a quantitative analysis of residual chlorine. For evaluation of the water quality at water treatment plants, these manual analyses are used as standards.

For operation management at water treatment plants, however, an on-line residual chlorine analyzer is useful that has advantages including convenient measurement and continuous data collection. Continuous measurement, in particular, is essential for automatic control operation.

In actual operation management at water treatment plants, the correlation between on-line residual chlorine analyzer's outputs and laboratory analysis results should be checked. In evaluation of the correlation between the instrument's output data and laboratory analysis results, the following should be considered and understood.

10.1 Colorimetric Analysis

The DPD (diethyl-p-phenylenediamine) method is a colorimetric analysis. DPD is added to a sample and red or pink-red color is produced corresponding to the residual chlorine concentration. The concentration of free available chlorine is determined by comparing the intensity of the color produced to colorimetric standards. After this determination, by adding potassium iodide the residual chlorine can be determined. The repeatability is not good at 5 to 10% (coefficient of variation) and it is said that the reliable results are largely dependent on operator skill.

10.2 Titration Analysis

There are three titration procedures: DPD method, iodometry, and amperometric titration.

The DPD method: The DPD reacts with free available chlorine in a sample to produce a pink-red color and the sample is titrated with ferrous ammonium sulfate to determine the amount of free available chlorine.

Iodometry: Potassium iodide reacts with residual chlorine to liberate the iodine, which is titrated with sodium thiosulfate to determine the amount of residual chlorine.

Amperometric titration: Using phenylarsine oxide as a titrant, amperometric titration is conducted to determine the amount of residual chlorine. Free available chlorine, combined available chlorine, monochloramine and dichloramine can be separated and determined quantitatively by using potassium iodide and pH buffer solutions in combination. This method is not affected by coexisting ions and thus it is said to be the most reliable measuring method.

10.3 Correlation between FC400G Outputs and Laboratory Analysis Results

Although laboratory analysis results should be basic data for water quality analysis, it cannot be said that they do not have errors from the absolute values, as described in Sections 10.1 and 10.2. That is, when the correlation between the FC400G output and the laboratory analysis result is evaluated, the difference between them may not consist entirely of the FC400G's output error, but may include the measurement error of the laboratory analysis.

Prior to shipment from the factory, the FC400G is calibrated so that it reads the same values as the ones obtained by the manual laboratory analysis of the amperometric titration, the most reliable method, using a sodium hypochlorite solution as the standard solution. A manual analysis may be performed by the user with sufficient attention and meticulous care. Yokogawa thinks the accuracy of manual analysis as shown in Table 10.1.

Table 10.1 Accuracy of Laboratory Analysis

Laboratory Analysis	Accuracy
Colorimetric analysis: DPD method	±0.1 mg/l
Titration analysis: DPD method	±0.04 mg/l
Iodometry	±0.04 mg/l
Amperometric titration	±0.04 mg/l

Note: Accuracy involves the characteristics of the method (principle), such as repeatability and linearity, and the standards used for calibration (adjustment). The latter is the accuracy of colorimetric standards in the colorimetric analysis and is the accuracy of reagent factors and others in titration analysis. When an absorptiometer is used in the colorimetric method, the accuracy of calibration of the instrument is involved.

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