Measurement and Control of Trihalomethane

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1. Introduction

The carcinogenic trihalomethane has been the target of regulation for the past 16 years since a notice was issued by the Ministry of Health and Welfare, and for 4 and a half years in an appended article to the water quality standard prescribed by the Waterworks Law.

However, a survey by the Ministry of Health and Welfare reports that water utilities in which the trihalomethane concentration in drinking water exceeds 70% of a standard value have not decreased but increased in number and that the concentration has already exceeded the standard value in some utilities. This threatens the safety of drinking water, its most important quality.

Concentration of the population in urban areas (near rivers) and large quantities of consumption (waste) in the present age have created an adverse environment for the raw water used in water supplies. This paper outlines the current status of the mechanism that produces trihalomethane and the measures for reduction. A new analyzer for trihalomethane and a monitoring and reduction system capable of automated and rapid instrumentation are described.

2. Environmental Changes and Water Quality Regulation

2.1 Mechanisms that produce trihalomethane and environmental changes

The expansion and concentration of population and industry has caused rapid increases in water demand and at the same time, a shortage of water has exerted an enormous adverse influence on the society.

A conventional waterworks and sewerage system usually has a water purification plant in a river upstream, and a wastewater treatment plant that processes drainage in the vicinity of the river mouth to discharge the processed water to the sea. This type of water purification system is known as "monocycled". On the other hand, new systems have two or more water purification plants and wastewater treatment plants existing together in one river. This type of water purification system is known as "recycled". Refer to Fig. 1. In many recent cases, the situation has forced the waterworks and sewerage system to switch from the monocycled type over to the recycled one.

Sufficient self-purification of the river water cannot be expected from Japan's water environment, because the distance from the head to the mouth of a river is as short as several hundreds of km. To use the river water repeatedly, it is inevitably necessary to biodegrade the BOD (biochemical oxygen demand) components and decompose the ammonia of the industrial and domestic wastewater in the wastewater treatment plant. However, at present, the expansion of sewerage still lags behind that of waterworks.

The trihalomethane problem was first reported by Dr. Rook of the Rotterdam water service. The Rotterdam water service has an intake point downstream in the Rhine, where water has been used repeatedly for many years. Dr. Rook detected chloroform (a kind of trihalomethane) in the water of the Rhine in 1972 and pointed out that the cause was chlorination in the river water.

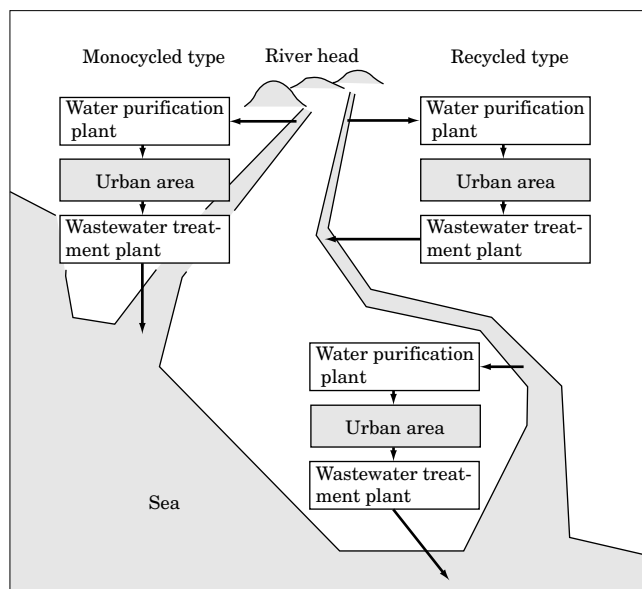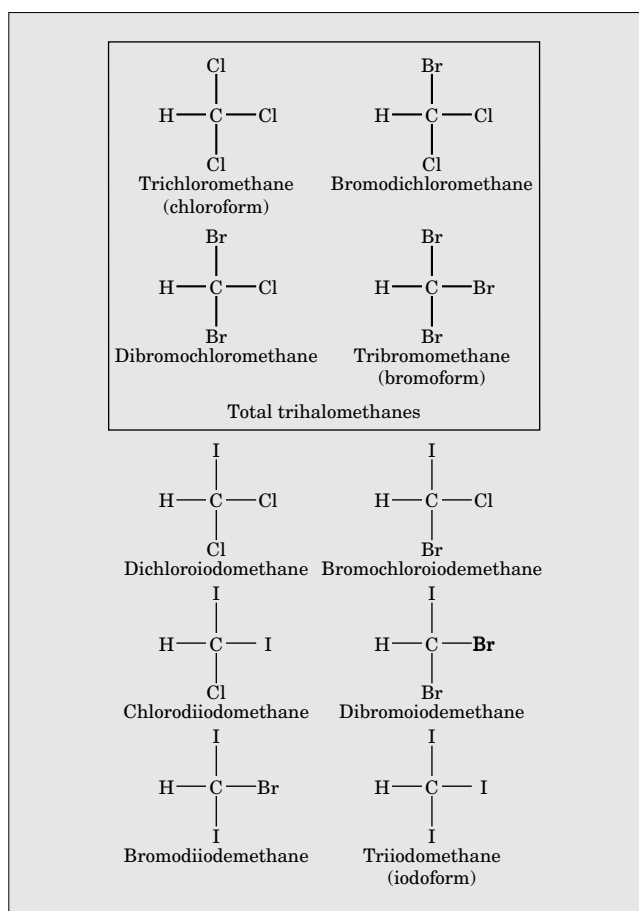Fig.1 Monocycled type and recycled type waterworks and sewerage

Fig.2 Family of trihalomethanes

Table 1 Standard values of trihalomethanes

Item	Standard value (mg/L)
Total trihalomethanes	0.1 or less
Chloroform	0.06 or less
Dibromochloromethane	0.1 or less
Bromodichloromethane	0.03 or less
Bromoform	0.09 or less

Table 2 Number of water service utilities in excess of trihalomethane standard values

Term of survey	Number of utilities in excess of 70% of standard values	Number of utilities in excess of standard values	Number of utilities surveyed
1991 to 1993	94	——	——
1993	34	8	——
Jan. to Aug., 1994	79	4	1,469 (only including surface water utilities)

At that time, another paper was published concerning the high cancer death rate of the citizens of New Orleans, downstream of the Mississippi in the United States. The reported cause was drinking water.

Simultaneously, trihalomethane (especially high concentrations of chloroform) was detected in drinking water in a survey by the Environmental Protection Agency in the United States. Further, an animal experiment has disclosed the carcinogenicity of trihalomethane. Since these events, the worldwide concern for trihalomethane has risen.

Figure 2 shows the family of trihalomethanes. Chloroform, bromodichloromethane, dibromochloromethane and bromoform are types of trihalomethane. Their content rate is high in drinking water and is generically defined as the total trihalomethane content. These trihalomethanes are produced in the following processes.

At first, the above-mentioned BOD formation potentials biometabolize by self-purification of the river and the sewerage process, and produce biodegradable persistent organic matter, for example, humic acid or fulvic acid, etc. Then, this matter is disinfected by chlorine in the water purification plant and in the wastewater treatment plant. This process forms the trihalomethane.

In general, changes in the following water environment cause an increase in trihalomethane concentration.

(1) Prechlorination

If the river is short in length, ammonia is insufficiently nitrified by self-purification. In this case, prechlorination is performed in the water purification plant to oxidize ammonia with chlorine completely. Therefore, biodegradable persistent organic matter reacts with highly concentrated chlorine before it is removed by coagulation-sedimentation and produces trihalomethane.

(2) Concentrated biodegradable persistent organic matter

To use river water repeatedly to prevent shortages, the waterworks and sewerage systems of the recycled type have been expanding. Therefore, large amounts of biodegradable persistent organic matter that have leaked from wastewater treatment plants have become more concentrated in the downstream areas.

As mentioned above, the trihalomethane problem in our country is significant due to the fact that river distance is short in Japan.

2.2 Water quality regulations

The first regulation concerning trihalomethane in Japan assumed a control target value of the total trihalomethanes concentration to be "0.1 mg/L or less", based on the maximum permissible concentration level (0.1 mg/L) that the Environmental Protection Agency established in 1979. The maximum permissible concentration level is prescribed in the notice "Measures

Fig.3 Example of repetitive processes
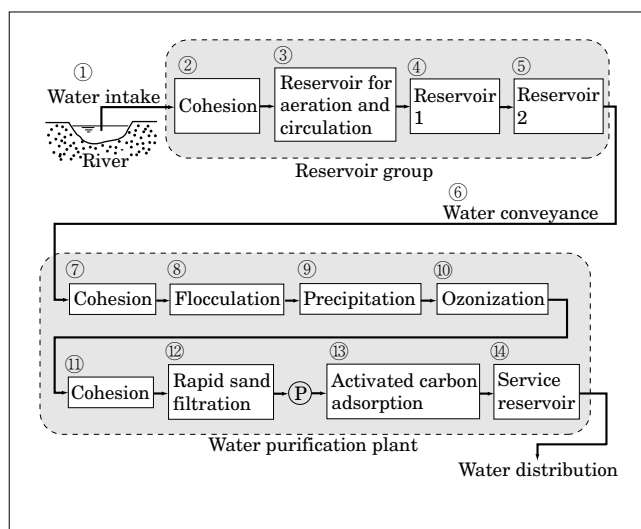
against trihalomethane in water service" issued by the manager of the Water Supply and Environmental Sanitation Department of the Ministry of Health and Welfare on March 25, 1981.

Thereafter, standard values for each trihalomethane were added as shown in Table 1, and enforced as of December, 1993, as the drinking water quality standard was revised by the Public Welfare Ministerial Ordinance No. 69 on December 21, 1992.

The number of the water utilities in excess of 70% of the standard value reached 79 utilities, and four utilities exceed the standard value, according to a survey by the Ministry of Health and Welfare concerning the quality of drinking water examined from January to August, 1994. These numbers greatly exceed previous values, even though various measures for reduction have been implemented since 1993. Refer to Table 2.

Those utilities in excess of 70% of the standard value might exceed the standard value if the water environment changes. Therefore, measures against trihalomethane are urgently required.

3. The Current Status of the Measures for Reducing Trihalomethane

3.1 Basic idea for reducing trihalomethane
A basic policy for reducing trihalomethane is presented as follows.
(1) Reduction of biodegradable persistent organic matter in the field water at intake
(2) Reduction of ammonia concentration before coming in contact with chlorine in the water purification plant
(3) Reduction of chlorine feeding volume in the water purification plant
(4) Removal of trihalomethane that is produced
(5) Monitoring and control of trihalomethane in the

water distribution network
The typical examples of the measures for reducing trihalomethane are described as follows.

3.2 Removal of organic matter by process repetition
In Amsterdam and Rotterdam, downstream areas of the Rhine, the repetition of the maximum possible treatment including the processes (1) to (3) mentioned above has been applied for long time to stabilize the water quality.

Fig. 3 shows the process flow of the Maas Bisbosch Klaringen systems in the Rotterdam water service.

The organic matter is sufficiently removed by a physicochemical process and biodegraded by cohesion at the water intake point and water storage for long time ((3) to (5)). Suspended matter in the field water, ammonia, biodegraded organic matter and trace toxicants are removed as shown in this figure. These treatments aim to effectively use processes (1) to (3) mentioned above.

The next stage of the treatments in the water purification plant follows as the coagulation-sedimentation processing ((7) to (8)), the decomposition of biodegradable persistent organic matter by ozonization, and the third cohesion. The final stage is the sand filtration and the feeding of the activated carbon.

A thorough removal of the organic matter is achieved in this way.

3.3 Reduction of chlorine feeding quantity
The chlorine is usually fed for the purpose of disinfection only filtration is completed. However, as a step to purify heavily-polluted field water, prechlorination is conducted before the coagulation-sedimentation and intermediate chlorination is performed during processing of the precipitation reservoir and the filtration reservoir. These treatments are performed for the following purposes. Refer to Fig. 8.
(1) To process germs
(2) To exterminate living organisms such as algae and bacteria
(3) To remove iron and manganese by oxidation
(4) To process ammonium nitrogen and organic matter
(5) To process offensive tastes and odors

Recently, the deterioration of the river water quality has forced many water purification plants to preprocess the field water with chlorine. Thus, the trihalomethane problem is more serious at present.

In recent years, there has been a change from prechlorination to intermediate chlorination. However, there is a limit to the removal of organic matter by coagulation-sedimentation. At high ambient temperatures or during a summer drought, when biodegradable persistent organic matter is heavily concentrated in the field water (the permanganic acid demand rises), the powdered activated carbon has to be fed before cohesion.

3.4 Advanced treatment using ozone and biological activated carbon

Currently, one of the most effective treatments as the measures for reducing trihalomethane is to use ozone and biological activated carbon.

Settled water is led to the ozone contact basin as shown in Fig. 8, and ozone oxidizes and decomposes the organic matter not removed by coagulation-sedimentation.

At the same time, the biodegradable persistent organic matter becomes biodegrading and is biodegraded by the latter treatment using biological activated carbon.

Moreover, ammonia that has not been nitrified is nitrified by the nitrifying bacteria being adsorbed on the surface of the activated carbon. This is also another effect of treatments using biological activated carbon.

Thus, this highly advanced treatment using ozone and biological activated carbon favorably reduces trihalomethane in the following respects.
(1) Reduces concentration of biodegradable persistent organic matter, the forerunner of trihalomethane formation
(2) Nitrification of the ammonia causes increased chlorine consumption

This treatment has begun to be introduced in water purification plants in large cities, for instance, in the Kanamachi Purification Plant of the Tokyo Waterworks Bureau and the Shibajima Water Purification Plant in Osaka city

4. Method of Measuring Trihalomethane

Gas chromatography, a simpler process, is able to analyze trihalomethane and other chlorinated organic compounds, that is, low-boiling-point compounds. This is one of the reasons why the trihalomethane problem has been widely recognized.

The official analytical method that is prescribed in the water quality standard and its principle is described as follows.
(1) The purge-and-trip gas-chromatography mass-spectrometry (PT-GC-MS)

Volatile organic compounds are purged from the sample water in their gas phase, driven into the trap tube and concentrated. Next, after they are heated in the trap tube, and if needed, cooled and concentrated again, they are led into a gas-chromatography mass-spectrometer to separate each component. The concentration of volatile organic compounds is obtained as the intensity of the respective mass spectrum and the value of the selective fragment ions.
(2) The head-space gas-chromatography mass-spectrometry (HS-GC-MS)

This method uses a constant amount of the gas in a gas-liquid equilibrium at fixed temperature. The concentration of volatile organic compounds is obtained by the selective ion detection method or the gas chromatography.
(3) The purge-and-trap gas-chromatography (PT-GC)

This method utilizes gas chromatography by using an electron capture detector (ECD) or a flame ionization detector (FID) after pretreatment which is the same as in the PT-GC-MS method.

These methods using gas chromatography excel in respects of generality and sensitivity and are widely utilized in water quality test labs at water purification plants.

However, these methods require complex operations and skill. Pretreatment and measurement takes several hours. These methods are difficult for frequent measurements and unsuitable for continuous monitoring.

Fuji Electric Co., Ltd. developed a trihalomethane analyzer capable of performing continuous and automated measurement. Described below, this product achieved continuous monitoring of the total trihalomethanes.

5. Measures for Reducing Trihalomethane Using the Trihalomethane Analyzer

5.1 The trihalomethane analyzer
(1) Measuring principle

The trihalomethane analyzer, a Fuji Electric product, uses a principle quite different from that of gas chromatography but equals the gas chromatography in sensitivity.

That chlorinated organic compounds and the pyridine derivatives react in strong alkali and emit red light has been known for many years as the Fujiwara Reaction.[1]

Some successful research was conducted to apply this reaction to sensors and the analysis of chlorinated organic compounds.[2][3][4] However, those results were not put to practical use due to the toxicity of pyridine, the instability of the fluorescent substance, and the failure in achieving the same sensitivity as that of the gas chromatography.

Later, Mr. Okumura et al. discovered that by using nicotinamide instead of pyridine and measuring the fluorescence, only the trihalomethane could be detected with sensitivity at the ppb level.[5]

Based upon this research of Mr. Okumura, Fuji Electric developed the trihalomethane analyzer, achieving high sensitivity and automated measurement.
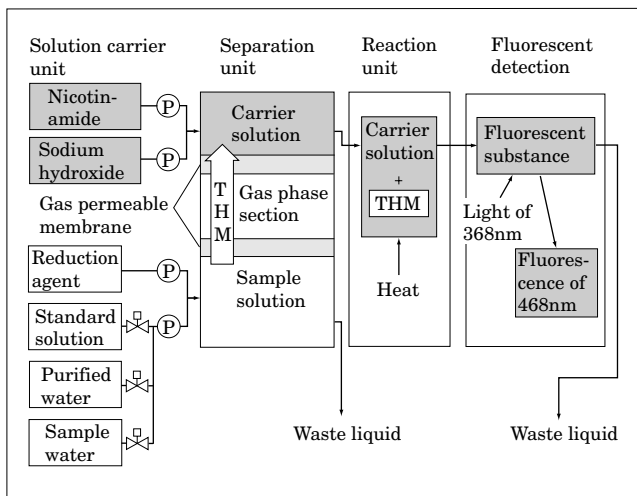
Figure 4 shows the external view of the device and Fig. 5 shows its measuring principle.

Sample water that includes the trihalomethane is led to the separation unit, where only the trihalomethane is extracted into the gas phase section through a gas permeable membrane. The carrier solution, in which nicotinamide is mixed with alkali liquid, is also

Fig.4 External view of trihalomethane analyzer

Fig.5 Measuring principles of the trihalomethane analyzer

Fig.6 Correlation of measurements by trihalomethane analyzer and gas chromatography

$y = 0.96x - 0.79$
$r = 0.9807$
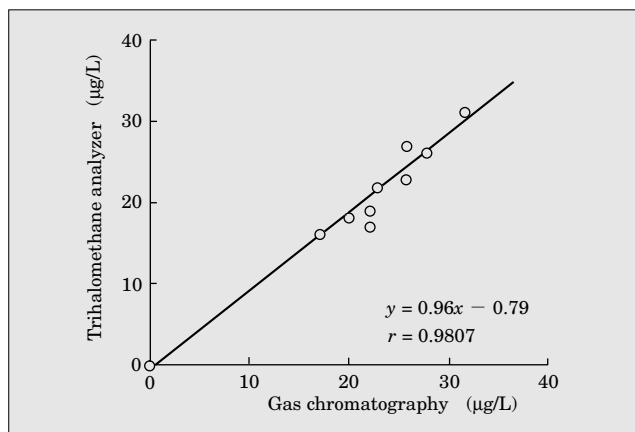
Fig.7 Example of automated operation of trihalomethane analyzer

—○— : Trihalomethane analyzer
● : Gas chromatography

led to the separation unit and dissolves the trihalomethane concentrated in the gas phase section through another gas permeable membrane.

Then, the carrier solution that dissolved the trihalomethane is led to the reaction unit. The trihalomethane and the nicotinamide produce a fluorescent substance by the Fujiwara Reaction. In the fluorescence detection unit, an exciting ray of 368 nm is applied to the fluorescent substance, which radiates fluorescence of 468 nm, representing the trihalomethane concentration.

The most significant characteristic of this device is that the Fujiwara Reaction occurs without being influenced by substances coexisting in the sample water because only gaseous trihalomethane is extracted from the sample water into the separation unit.

Samples of drinking water from various locations were measured by this trihalomethane analyzer and gas chromatography. The correlation was examined as shown in Fig. 6.

Figure 7 shows a comparison of measurements of trihalomethane concentration over the course of one day. These results verified that the sensitivity of this device is equal to that of the gas chromatography and is suitable for continuos measurement.

(2) Specification

A summary of the trihalomethane analyzer specifications is listed below.

(a) Measuring object: Total trihalomethanes
(b) Measuring system: Measurement of the fluorescence in the reaction of alkaline nicotinamide and trihalomethane
(c) Measuring time: Within 40 minutes approx.
(d) Sample water: Drinking water from the water supply, etc.
(e) Range of measurement: 0 to 200 µg/L (equivalent amount of chloroform)
(f) Ambient temperature: 5 to 40°C
(g) Dimensions: W500 × H440 × D470 (mm)
(h) Power source: 100V ±10V AC at 50/60 Hz
(i) Power consumption: 500VA or less
(j) Mass: 50 kg approx.

5.2 Continuous monitoring system using the trihalomethane analyzer

Using trihalomethane analyzers, continuous monitoring of the total trihalomethanes can be centralized for the processes after feeding chlorine in the water purification plant and in the water distribution network. Figure 8 shows this trihalomethane monitoring

Fig. 8　Flow of water treatment and the trihalomethane monitoring system
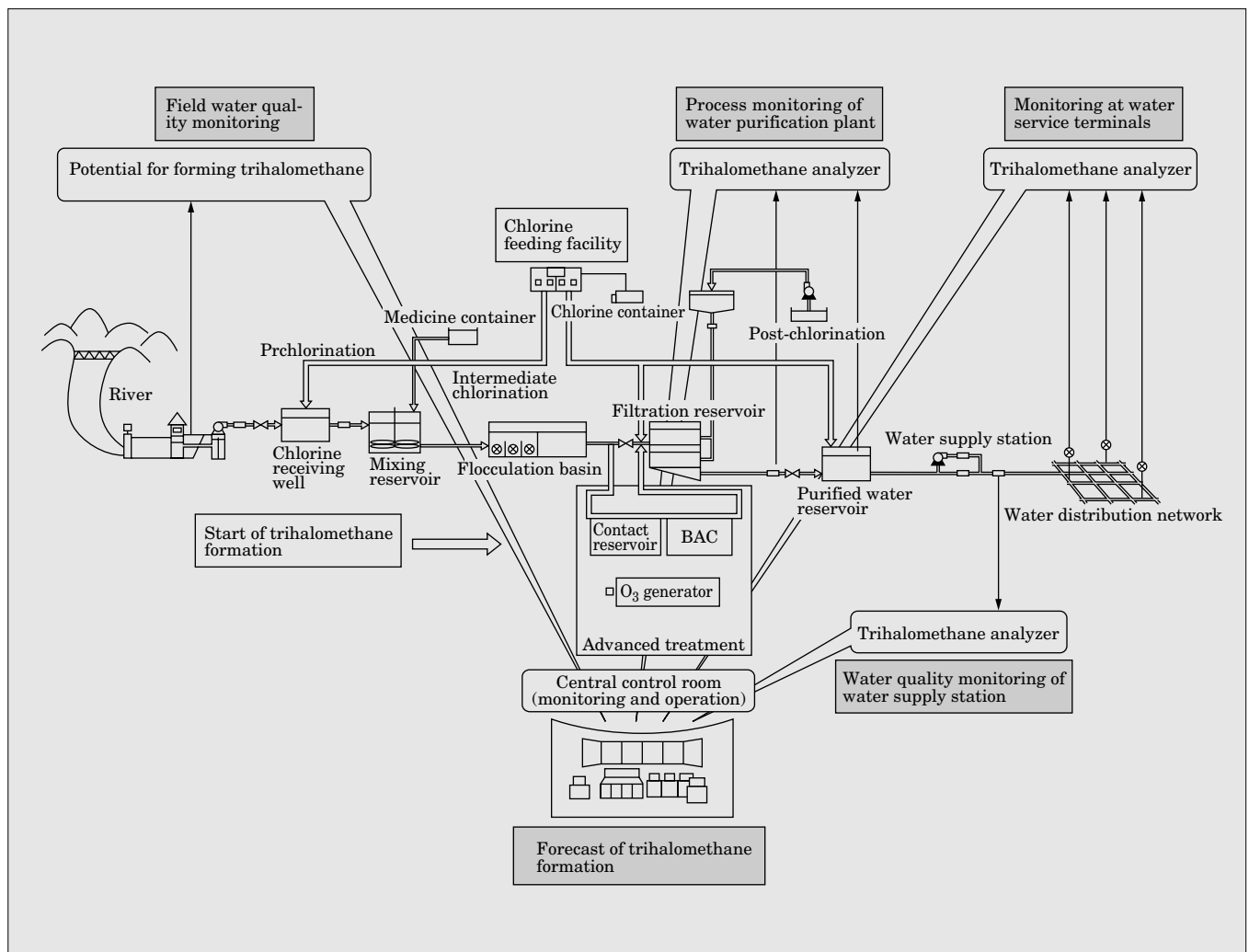
system.

(1)　Trihalomethane monitoring in the water purification plant

The system measures the biodegradable persistent organic material in the river water as the trihalomethane formation potentials, determines the initial concentration after feeding chlorine, and monitors the concentration in the purified water reservoir, that is, the final outlet for the water purification plant.

In addition, these functions usually help monitor the initial trihalomethane concentration in the water distribution network.

(2)　Trihalomethane monitoring in the water distribution network

This system measures the trihalomethane concentration at the observation site of each water supply station and the main water distribution network to centralize real-time monitoring.　Simulation (to be described later) is used to forecast the trihalomethane increase at the water service terminals.　The trihalomethane concentration can be monitored and forecast at all locations of the water distribution network.

5.3　Forecast of trihalomethane increase in the water distribution network

One of the troublesome points of the trihalomethane problem is that the trihalomethane produced by feeding chlorine into the water purification plant increases in a water distribution network.

Tambo et al. conducted research to quantify the increase of trihalomethane in a water distribution network.　The following equation of increase can be applied.

$$\mathrm{THM} = k\,[\mathrm{Cl_2}]^a\,[\mathrm{TOC}]^b\,[\mathrm{pH}]^c\,[t]^d \cdots\cdots\cdots\cdots (1)$$

Here,

k, a, b, c, d : Constants
$[\mathrm{Cl_2}]$:　　　Available chlorine concentration
$[\mathrm{TOC}]$:　　Total organic carbon
$[\mathrm{pH}]$:　　　pH value
$[t]$:　　　　Chlorine contact time

The dependency of trihalomethane formation on the chlorine feeding volume and the organic matter concentration has been previously described.　The above expression also shows that trihalomethane in-

creases as the pH is higher and the chlorine contacting time is longer.

Each utility which takes necessary precautions against trihalomethane, has experimentally obtained a similar equation so field water will be easier to treat.

Fuji Electric's trihalomethane monitoring system uses the data continuously measured by the trihalomethane analyzers together with data from the above-mentioned equation of increase, the water distribution network, and the water supply operation to forecast the trihalomethane concentration at outlets of the water purification plant, the water supply station and the water service terminals.

5.4 Measures for reducing trihalomethane with continuous monitoring

The following measures for reducing trihalomethane can be implemented by using the trihalomethane continuous monitoring system of Fuji Electric.

(1) Measures for reduction in the water purification plant

　(a) By continuously monitoring the potential for forming trihalomethane in field water and the water after coagulation-sedimentation, it is possible to feed the activated carbon to the field water, optimize the coagulant dosage and change the point of chlorine feeding.

　(b) At the time of chlorine feeding, by determining the amount of initial trihalomethane, it is possible to forecast the trihalomethane concentration at the outlet of the water purification plant, and adjust the chlorine dosage depending upon the chlorine contacting time.

　(c) By monitoring trihalomethane or the potential for forming trihalomethane in the latter stages of advanced treatments (ozonization and feeding the activated carbon), it is possible to evaluate the capability of this treatment to eliminate the potential for forming trihalomethane.

　(d) Based on the trihalomethane concentration in the purified water reservoir, it is possible to forecast trihalomethane increases in the water distribution network, and to promptly feed this information back to earlier stages of the purification treatment.

(2) Measures in the water distribution network

Forecasted increases of trihalomethane in purification plant utilities are verified based on continuous data from each water supply station and typical water service terminals. The following measures can be implemented in case of a rapid concentration rise.

　(a) At points where increases in the trihalomethane concentration are observed, the following water operation measures are possible; it is possible to selectively increase the amount of water supplied from the water purification plant, where the trihalomethane concentration is lower at the outlet, or to feed purified water from an advanced treatment.

　(b) Based on data of the forecast water demand and the flow time, it is possible to plan water operations for reducing trihalomethane.

6. Conclusion

The paper summarized trihalomethane in the water supply, the mechanism that forms trihalomethane and measures for reducing it. Moreover, this paper presented a new trihalomethane analyzer that uses fluorometry and an accompanying monitoring system.

The authors wish to continue their efforts to prevent deterioration of the water environment, and to pursue safety by proposing useful measures for reducing trihalomethane, contributing to research on trihalomethane measurement and improving the trihalomethane monitoring system.

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