Introduction of new organic matter indicator and improvement of management system for quality control of drinking water in Korea

By

HWANG, Junyeon

CAPSTONE PROJECT

Submitted to

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ABSTRACT

This paper aims to introduce a new organic matter indicator in order to manage water quality consistently from water resources to drinking water, and to expand the usability of water quality results in Korea's drinking water quality standards.

COD_{Mn} exists as an existing indicator of organic matter, but it has not been used as a water quality indicator several decades ago in foreign countries due to measurement inaccuracy and reliability problems. Water resources sector in Korea recognized these problems about 20 years ago and changed the water quality standard to TOC (Total Organic Carbon) through continuous researches and policy implementation.

However, in the water supply sector, $KMnO_4$ consumption similar to the COD_{Mn} method is still used as an organic matter indicator in the drinking water quality standards, but various problems similar to the COD_{Mn} method may be raised. On the other hand, as TOC is being used for water treatment process management in water treatment plants, it is urgently necessary to realize the organic matter indicator of drinking water quality standards.

This paper reviewed policy trends in the water resource sector, correlation with $KMnO_4$ consumption, TOC water quality standards draft, and environmental and economic impacts. The TOC water quality standard draft was presented as 6 mg/L by comparing the water quality standards of foreign countries and calculating the $KMnO_4$ consumption/TOC ratio of tap water in domestic water treatment plants.

In the future, it is necessary to take a long-term perspective and reflect the TOC in the water quality monitoring items for drinking water and periodically monitor it and introduce an appropriate TOC water quality standard plan.

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1. Introduction

Drinking water is essential public good for people to manage various activities such as daily life, industrial, and agricultural activities. In addition, the types and quantities of pollutants in water resources are increasing due to the advancement of the industrial environment and changes in lifestyle. If drinking water quality will be abnormal, then water supply will be suspended or difficult to use. The damages will be very large and cause social confusion. Therefore, the government should present appropriate drinking water quality standards in accordance with the changing water quality issues and citizens' needs, and waterworks companies should make efforts to supply high-quality drinking water accordingly.

Since there are various pollutants in the raw water, it is not suitable for citizens to drink directly. Organic matters that are typical of pollutants refer a mixture of organic chemicals found naturally in water resources, derived from fauna and flora, microorganisms, and decomposition products of these sources (Chow et al., 1999). Biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) are used as indicators for assessing contamination by organic materials (Korea Environment Institute [KEI], 2008).

When organic matters exist in large quantities in the water system, they consume oxygen in the water, which in turn affect water quality and aquatic ecosystem. Therefore, the government had been making efforts to improve water quality and secure clean water sources by setting water environmental standards for rivers, reservoirs, etc. However, it had been focused on managing organic matters centered on BOD. As a result, COD concentration in major water sources continued stagnation or increase. Since BOD-centered policies were a key management of biodegradable organic matters, measures for non-biodegradable organic matters and non-point pollutants were insufficient, for this situation, the need for countermeasures began to be raised (KEI, 2008).

In addition, there had long been a problem that COD of water environmental standards is insufficient to represent the total amount of organic matters (KEI, 2008). COD is the amount of an oxidizing agent consumed by oxidizing organic matter in water with using an oxidizing agent ($KMnO_4$ or $K_2Cr_2O_7$), expressed as oxygen demand. Due to the lack of oxidative ability, a COD method is difficult to measure all organic matters including non-biodegradable organic materials (Korean Water and Wastewater Association [KWWA], 2018), there are also disadvantages that may include iron ions, nitrite ions, hydrogen sulfide and other reducing matters in water (Ministry of Environment [ME], 2015).

On the other hand, TOC has the advantage of being able to quickly measure more than 90% of organic matters in water, in real time, or within 30 minutes. Already, many countries had recognized COD as an outdated water quality indicator, especially Germany has not used COD by $KMnO_4$ decades ago, since a large-scale study by the Institute for Water, Soil and Air of the German EPA in 1983 found that COD method had a very low oxidation ability and very large numbers of substances had been found (Kang, 2017).

As the advantages and disadvantages of various indicators of organic matters were known, the need for future-oriented organic matters management policies and total amount management of organic matter increased due to the increase of non-degradable organic matters caused by climate change, increased stagnant water, and algae. TOC item was newly introduced from January 2013 to water environment standards of rivers and lakes, and COD method was converted to TOC from January 1, 2018. In addition, it is introducing TOC instead of COD in allowable effluent standards of industrial wastewater from 2021 (Ministry of Environment [ME], 2019).

As we saw earlier, indicator of organic matters in water resources has been replaced by TOC. However, drinking water is still not the case. Drinking water quality standards are specified in the Ministry of Environment Ordinance's "Rule on Drinking Water Quality

Standards and Inspection," which uses $KMnO_4$ demand as an indicator of organic matters. This method is almost similar to the method used to measure COD. Considering the low concentration of organic matters in drinking water compared to raw water in water resources, the concentration of oxidizing agent ($KMnO_4$) is about 1/25 of that of COD and the oxidation time is very short (Ministry of Environment [ME], 2018).

Organic matters which exist in the raw water indirectly affect human health and has a significant impact on the water treatment process. The amount of coagulant usage and sludge production increases, and the ability to remove pathogens decreases due to interference with the disinfectant, in addition, it can reduce sand filter operation time, the efficiency of adsorption or ion exchange processes, and cause biofilms in the water distribution pipes, it could happen pathogens to be attached (Government of Canada, 2019). Organic matters also contributes to the fouling of membranes, serves as precursors for the formation of disinfection by-products of health concern during disinfection/oxidation processes (Own et al., 1998).

Because of these effects, management of organic matters is very important in the process of water treatment. However, the current $KMnO_4$ consumption is a method to only determine compliance with drinking water quality standard, in fact, mainly TOC is used to determine the concentration of organic matters in raw or treated water in terms of water treatment operations (Yoo et al., 2009). To reduce the amount of organic matters, which is a precursor to disinfection by-products, it is necessary to analyze the TOC concentration for efficient water treatment, such as increasing the amount of coagulant usage and adjusting pH (U.S. Environmental Protection Agency, 2007). In addition, in the case of advanced water treatment, TOC is regularly measured for the evaluation of adsorption efficiency of granular activated carbon.

Many foreign countries such as Japan, the United States, etc. recognized the importance of managing organic matters and set TOC indicator instead of $KMnO_4$ consumption in drinking water quality standards (Government of Canada, 2019). In Korea, it is also necessary to replace the indicator of $KMnO_4$ consumption with TOC based on drinking water quality standards, considering the changes in water environment policies of water resources and the current status of water treatment process management. It is more appropriate that organic matter indicators are unified from the perspective of water resources and waterworks, and from the viewpoint of unified water quality management.

This study aims to provide a policy basis to introduce a new organic matter indicator in drinking water and to improve the organic matters management system. To this end, organic matters indicators based on domestic drinking water quality standards and water quality standards of various foreign countries will be compared and investigated.

Thus, it is expected that a new TOC standard for drinking water will be proposed by investigating $KMnO_4$ consumption and TOC concentration in the raw water and drinking water of water treatment plants. Furthermore, the correlation between the TOC concentration and $KMnO_4$ consumption in drinking water. Additionally, the economic and environmental impacts of replacing TOC on drinking water quality standards will also be considered.

As a result, organic matter management plans applicable to domestic water treatment plants will be presented by analyzing the generation trends of domestic water treatment plants and referring to the organic matter management measures of major foreign countries.

2. Literature review

The improvement of a organic matter indicator in water resources has continued since 2000, supported by related researches and policy improvement efforts. Nevertheless, there are not many studies on the improvement of a organic matter indicator in drinking water, and two papers among them are introduced.

2.1 Case 1: A Study on the Establishment of Total Organic Carbon in Drinking Water Standard (Yu et. al, 2009)

This paper suggested the correlation between the detection range of $KMnO_4$ consumption in drinking water and the concentration of TOC and $KMnO_4$ consumption from raw water to tap water in order to propose the feasibility and reference value of TOC application to drinking water quality standards.

The average concentration of $KMnO_4$ consumption at 12 major water treatment plants nationwide was 8.1 mg/L for raw water and 2.4 mg/L for tap water, and TOC was 2.00 mg/L for raw water and 1.15 mg/L for tap water. The correlation coefficient (r) between $KMnO_4$ consumption and TOC was 0.8, similar for both, and the $KMnO_4$ consumption in tap water was investigated to be about twice that of TOC.

As such, the correlation coefficient and ratio between TOC and $KMnO_4$ consumption are not constant depending on the characteristics of Korea's climate and water sources, so it is judged that it is difficult to set the TOC standard by simply converting it into a ratio. However, when calculating the TOC standard by applying the TOC detection range based on the $KMnO_4$ consumption accumulated through this investigation or applying the ratio that shows a good correlation between $KMnO_4$ consumption and TOC, this study suggested that it is reasonable to set it at 4-5 mg/L.

2.2 Case 2: A Study on Analysis Methods for Natural Organic Matter in Drinking Water "$KMnO_4$ Consumption, TOC and UV254 Absorbance" (Jun et al., 2015)

This paper tried to find the optimal method considering correlation and economic feasibility of test methods such as TOC, UV_{254} absorbance, and $KMnO_4$ consumption of underground water, tap water, and mineral spring water in order to find a measurement method that can replace $KMnO_4$ consumption for quantification of organic matters in drinking water .

Among them, looking at the relationship between TOC and $KMnO_4$ consumption, statistical significance was confirmed in tap water, but the correlation was low, and there was no significance in groundwater and mineral spring water.

Although the correlation coefficient with TOC concentration was evaluated to be low, it was suggested that a reasonable approach is necessary to set the standard for TOC concentration as an alternative to $KMnO_4$ consumption in consideration of the economic feasibility, environmental feature, and automation of the analysis method.

2.3 Comparison of results

To summarize the two papers, $KMnO_4$ consumption and TOC were statistically significant, but the correlation coefficient was high in the first paper but low in the second paper. However, the number of samples surveyed in two papers is not large, with 22 and 102 samples, respectively, and it is judged that water system, water treatment process, and seasonal characteristics should be considered more, and argues that the introduction of TOC is necessary to replace $KMnO_4$ consumption.

3. Water quality standard system and current status

3.1 Domestic water quality standard system

Water quality standards related to water are set by national laws under the jurisdiction of the Ministry of Environment, and the laws and water quality standards according to the water sector can be organized as shown in Table 1.

The water sector can be broadly divided into water resources and waterworks. Water quality standards in the water resource sector exist in the Framework Act on Environmental Policy, the Water Environment Conservation Act, the Sewerage Act.

Water quality standards in the waterworks exist in the Waterworks Act, Drinking water Management Act, and the Groundwater Act. Detailed water quality standards are specified to the attached rules.

Table 1. Water sector laws and water quality standards

Field	Water resources			Waterworks		
Law	Framework Act on Environmental Policy	Water Environment Conservation Act	Sewerage Act	Waterworks Act, Drinking Water Management Act	Waterworks Act	Groundwater Act
Enforcement Rule	-	-	-	Rule for drinking water quality standards and inspections	Water Source Management Rules	Rule for Conservation of Groundwater Water Quality, etc.
Water Quality Standards	Water quality Environmental standards for rivers and lakes	Effluent standards, Allowable Effluent standards	Effluent standards	Drinking water quality standards	Raw water (must meet water quality standards)	Groundwater quality standards

* Source : Act, etc. under the Ministry of Environment

3.2 Water quality standards in the field of water resources

As a representative water quality standard in the field of water resources, there are the water quality environmental standards that are stipulated by the Framework Act on Environmental Policy for the purpose of preserving human health and living environment. As regulatory standards to achieve the water quality environmental standards, there are effluent standards and allowable effluent standards, which are based on the Water Environment Conservation Act and the Sewerage Act (National Institute of Environmental Research [NIER], 2000). The water quality environmental standards are necessary to continuously maintain a healthy aquatic ecosystem and water quality suitable for the purpose of clean study.

The water quality environmental standard can be divided into rivers and lakes, and it is divided into health protection items (20 items) that are commonly applied to rivers and lakes and living environment items (stream-7 items, lake-8items). Living environment items are classified into 7 grades according to the water quality, and they are determined in consideration of the physicochemical concentrations of pollutants and the effects on living organisms in the aquatic ecosystem (Environmental White Paper, 2019).

Table 2. [Framework Act on Environmental Policy] Water Quality Environmental Standards

Sortation	Health protection items	Living environment items	
Application	Common to rivers and lakes	River	Reservoir
Item	Cd, As, CN, Hg, Pb, PCB, PCE, Benzene, etc.	pH, BOD, COD*, TOC, SS, DO, TP, Coliform	pH, COD*, TOC, SS, DO, TP, Coliform
Grade		Very good (I a), Good (I b), Slightly good (II), Average (III), Slightly bad (IV), Bad (V), Very bad (VI)	

* COD standards apply until December 31, 2015

** Source: Adapted Table 2 of the Enforcement Decree of the Framework Act on Environmental Policy

The Water Environment Conservation Act aims to preserve the water environment of public waters, such as rivers and lakes, from water pollution. There are standards for effluent standards from public wastewater treatment facilities (7 items) and for allowable effluent standards from wastewater discharge facilities (57 items).

Table 3. [Water Environment Conservation Act] Water Quality Standards

Sortation	Effluent standards	Allowable effluent standards
Application	Public wastewater treatment facility	Wastewater discharge facility
Item	BOD, TOC, SS, TN, TP, Total Coliform Count, Ecotoxicity	57 items including BOD, TOC, SS, Phenol, Cadmium, Ecotoxicity, etc.

* Source: Adapted Tables 10 and 13 of Enforcement Rule of the Water Environment Conservation Act

The Sewerage Act is intended to conserve the water quality of public waters through the sound development of local communities and improvement of public sanitation by appropriately treating sewage and excreta. There are differences in the water quality items applied to each public sewage treatment facility, excreta treatment facility, and private sewage treatment facility.

Table 4. [Sewerage Act] Effluent standards

Sortation	Public sewage treatment facility	Excreta treatment facility	Private sewage treatment facility
Item	BOD, TOC, SS, TN, TP, Total Coliform Count, Ecotoxicity	BOD, TOC, SS, TN, TP, Total Coliform Count	BOD, SS, TN, TP

* Source: Adapted Tables 1-3 of the Enforcement Rule of the Sewerage Act

3.3 Water quality standards in the waterworks sector

Waterworks is a facility used for living or supplying drinking water to citizens. In Korea, all matters such as planning, installation, operation and management are stipulated in the Waterworks Act. In accordance with the Waterworks Act and the Drinking Water Management Act, drinking water quality standards such as tap water, drinking spring water, and drinking deep sea water, etc. are established in the Rule on drinking water quality standards and inspections.

On the other hand, water sources such as rivers and lakes that are used as drinking water sources must be inspected for water quality in accordance with the water source management rules, and the water quality standards are stipulated to meet the water quality environmental standards under the Framework Act on Environmental Policy.

In the case of groundwater, when used as drinking water, drinking water quality standards must be followed, and when used as domestic water, groundwater quality standards must be complied with in accordance with the Groundwater Act and the Rule on Groundwater Quality Conservation.

Table 5. Water quality standards in the Waterworks sector

Sortation	Drinking water	Drinking water Source	Groundwater	
Kinds	Tap water, drinking spring water, drinking deep sea water, etc.	River water, lake water, groundwater, seawater	Drinking water	Water for living and agriculture, etc.
Water quality standards	Drinking water quality standards	Water quality environment standards	Drinking water quality standards	Groundwater quality standards
Item	61 items including microorganisms, $KMnO_4$ consumption, inorganic substances, disinfection by-products, etc.	28 items including heavy metal, BOD, coliform group	50 items including $KMnO_4$ consumption, inorganic matter, disinfection by-product, etc.	20 items including chlorine ion, nitrate nitrogen, heavy metal, etc.

* Source: Adapted Table 1 of the Rule for Drinking Water Quality Standards and Inspections, Table 6 of the Water Source Management Rule, Table 4 of the Rule for Water Quality Conservation, etc. of Groundwater.

4. Status and policy direction for organic matter indicators

4.1 Types of organic matters and comparison

Organic matters are not harmful as themselves, except for volatile organic compounds and difficult-to-decompose organic substances, but when organic matters are high, they are converted into carbon dioxide and water through aerobic microbial activity, and dissolved oxygen in water is depleted. In the end, the depletion of dissolved oxygen has a negative effect on water quality and aquatic ecosystem, which can cause damages such as aquatic life death, odor generation, and pathogenic bacteria growth.

Representative water quality items for measuring the content of organic matters or compounds include Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Total Organic Carbon (TOC), The characteristics for this are shown in the Table 6.

Table 6. Comparison of organic matter indicators

Sortation	BOD	COD_{Mn}	COD_{Cr}	TOC
Summary	Measurement of dissolved oxygen consumption by aerobic microorganisms for 5 days	Measure the amount of oxidizing agent consumed by converting the amount of oxygen required by using $KMnO_4$ as an oxidizing agent	Measured by converting the amount of oxidizing agent consumed into oxygen demand by using $K_2Cr_2O_7$ as an oxidizing agent	Measure the amount of carbon dioxide generated during oxidation of organic matter at high temperature
Feature	- long time to measure - Lots of interference - Cannot be measured if it contains non - microbially degradable ingredients	- Simple to measure - Low oxidation rate - Poor reproducibility depending on measurement conditions	- It takes more time than COD_{Mn} - Poor reproducibility at low concentrations - High oxidation rate	- Excellent reproducibility at low concentrations - Short analysis time - Simultaneous analysis - Automation - High equipment cost
Measurement period	5 to 20 days	40 to 50 minutes	3 to 4 hours	5 to 20 minutes
Country of use	Korea, Japan, UK, Australia, Etc	Korea, Japan, etc.	USA, Europe, etc.	USA, Europe, Japan, Korea, etc.

* Source: Ministry of Environment, 2008

BOD is a monitoring item for public waters such as rivers and lakes, and is adopted in most countries. In COD, there are two types of method: Manganese method and Chrome method. Korea and Japan use the manganese method as the standard for water quality environment, but most countries use the chrome method as the COD official method (ME, 2008). TOC is more suitable in terms of representativeness, measurement time, and continuity, and developed countries have been using TOC as an index of organic matter since the past.

As mentioned above, there are three to four measurement methods for organic matter indicators, and Table 7 shows the organic matter indicators used in the water field in Korea. BOD and TOC are used in the field of water resources or raw water, but $KMnO_4$ Consumption is used in drinking water.

$KMnO_4$ Consumption is almost similar to the COD_{Mn} method, but since the concentration of organic matters in drinking water is low, it can be measured by lowering the concentration of an oxidizing agent, and it is a method that can indirectly measure the content of organic matters in a short time.

Table 7. Summary of organic matter indicators in the water field

Field	Water resources			Waterworks		
Water quality standards	Water quality environmental standards for rivers and lakes	Effluent standards, Allowable effluent standards for wastewater treatment facility	Effluent Standards for sewage water quality	Drinking water (tap water, drinking spring water, etc.) water quality standards	Drinking water source (Applying water quality environmental standards)	Ground water quality standards
Organic indicators	Rivers: BOD, TOC Reservoir: TOC	BOD, TOC	BOD, TOC	$KMnO_4$ Consumption	BOD, TOC	-

4.2 Comparison of COD_{Mn} and $KMnO_4$ consumption

Previously, the two measurement methods were similar, but the overall experimental procedure is as shown in Figure 1, and the type of reagents used is about the same, but the concentration and reaction time of the reagents used are different.

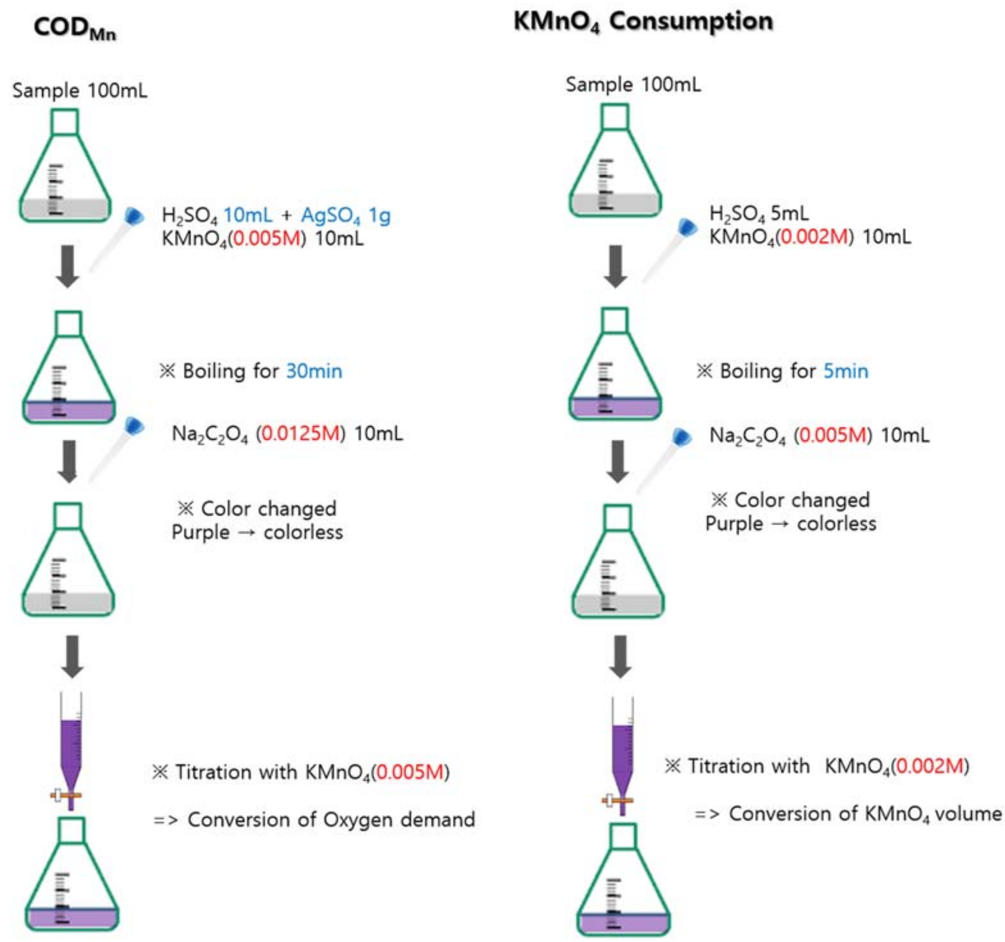

Figure 1. Analysis Process of COD_{Mn} and $KMnO_4$ Consumption

* Source: Adapted from Drinking Water Quality Process Test Standard ($KMnO_4$ Consumption), Water Pollution Process Test Standard (COD_{Mn})

The concentration of $KMnO_4$ used is 0.005M for COD_{Mn} and 0.002M for $KMnO_4$ consumption, which is 2.5 times higher than the concentration of the COD_{Mn} method. And the concentration of $N_2C_2O_4$ is 0.0125M for COD_{Mn} and 0.005M for $KMnO_4$ consumption, which is 25 times higher than the concentration of the COD_{Mn} method. Finally, after titration, COD_{Mn} is converted to oxygen by a separate formula, and $KMnO_4$ consumption is not converted to oxygen like COD_{Mn}, but corrected to the consumed $KMnO_4$ volume to make the final calculation. COD_{Mn} targets raw water with a high probability of having more organic matters, and $KMnO_4$ consumption is targeting drinking water with relatively little organic matters.

4.3 Changes in organic matter indicators in water resources

In the past, COD_{Mn} was mainly used as an indicator of organic matter in Korea's water resources sector. However, as suggested above, the need for changes in the organic matter had been raised due to the shortcomings of COD_{Mn}, algal by-products and non-point pollution sources, and management of total organic matters in the watershed. Accordingly, research and policy efforts have been made to change the organic matter indicator.

Starting with the research of the Ministry of Environment and the National Institute of Environmental Sciences in 2001, a conversion of the organic matter indicator had been continuously proceeding. In 2013, TOC was newly introduced in the Water Quality Environmental Standard of the Framework Act on Environmental Policy, and since 2016, COD_{Mn} has been converted into TOC. In addition, effluent standards and allowable effluent standards in the Water Environment Conservation Act and the Sewerage Act are also being converted from COD_{Mn} to TOC from 2020 and 2021, respectively.

As such, in the water resource sector, TOC, not COD_{Mn}, has been operating as the water quality standard since this year, but $KMnO_4$ consumption is being used in the waterworks sector, it is necessary to consider converting $KMnO_4$ consumption to TOC for unity for organic matter indicators and management of water treatment process.

4.4 Status of organic matter standards in drinking water in overseas countries

Organic matters have the characteristic of showing the amount of carbon-based pollutants, and it is difficult to judge the water quality risk based on the numerical value itself. Therefore, most foreign countries do not have separate drinking water quality standards.

It seems that only Korea and Japan had set $KMnO_4$ consumption, and Japan converted $KMnO_4$ consumption to TOC in 2004, and currently only Korea is setting $KMnO_4$ consumption. Japan converted to TOC in order to make analysis more accurately and theoretically than the existing $KMnO_4$ consumption for organic matters measurement, and has been applied from 5 mg/L initially to 3 mg/L since 2009. In addition to Japan, Norway sets the drinking water quality standard TOC at 5 mg/L.

According to the Drinking Water Quality Guideline of WHO, there is no separate standard for organic matters in drinking water, and the United States does not set a separate TOC standard for drinking water, but when the TOC concentration of raw water exceeds 2 mg/L, water treatment is reinforced. In addition, the EU and the Netherlands do not set a specific value for TOC and present it as No abnormal change.

Table 8. Comparison of indicators of organic matter in foreign countries

Item	Korea	Japan	Norway	United States of America	EU	Netherlands	WHO
$KMnO_4$ consumption (mg/L)	10	- (Changed to TOC, 2004)	-	-	-	-	-
TOC (mg/L)	-	3	5	- (raw water control)	No abnormal change	No abnormal change	-

4.5 Improvement of drinking water quality standards for organic matter indicators

As for domestic drinking water quality standards, the first drinking water quality standards were established at the same time as the “Regulations on Water Quality Standards, Water Quality Inspection Methods, Medical Examinations and Sanitary Measures under the Waterworks Act” in 1963. About 29 water quality items were established and $KMnO_4$ consumption was also included.

According to the 100 years history of waterworks in Seoul (Seoul city, 2008), the first water quality inspection items were listed. This is explained as the same applied standard as the Japan Water Supply Council Agreement Test Method, and it can be seen that the water quality management system of Japan during the Japanese colonial period was similarly applied. The water quality standard for $KMnO_4$ consumption was established at 10 mg/L in 1916, and this water quality inspection system continued even after liberation.

On the other hand, overseas, it has been judged from the past that it is not suitable to use $KMnO_4$ as an oxidizing agent as an indicator of organic matter, and according to the Institute for water, soil and air of the German EPA (1983), the COD analysis result by the $KMnO_4$ method is, Oxidizing power is very low, there are a very large number of undetectable substances, in addition, the recovery rate is not constant, so it appeared in a range of 0-100%, and most of the 600 kinds of substances investigated at the time were not detected.

The main goals of water treatment in the drinking water sector are removal of turbidity and organic matters. Turbidity is the easiest and most convenient item to measure in real time or directly. The influence of organic matters in the water treatment process is significant. It increases the amount of coagulant injected and the generation of disinfection by-products when treating raw water with a lot of organic matters.

Therefore, a water quality indicator used to monitor organic matters is TOC, and the data on $KMnO_4$ consumption is not utilized as the data for management and operation, and is used only for compliance with drinking water quality standards. TOC enables real-time monitoring and instrument analysis, so a large amount of samples can be analyzed in a short time. Recently, the introduction of advanced water treatment processes such as ozone oxidation and granular activated carbon adsorption is increasing. TOC monitoring is an essential water quality indicator for water treatment and operation efficiency measurement.

As mentioned earlier, the analysis principle and procedure of COD_{Mn} and $KMnO_4$ consumption are very similar, and it is necessary to reexamine the representativeness of $KMnO_4$ consumption as a water quality indicator for organic matters using $KMnO_4$ as an oxidizing agent. Considering this point, it seems reasonable to convert the organic matter indicator of drinking water quality standards to TOC like the water quality standards in the water resources sector.

5. Status of organic matter detection in drinking water

5.1 Domestic $KMnO_4$ consumption detection status

In order to investigate the detection status of $KMnO_4$ consumption in drinking water, the results of $KMnO_4$ consumption in drinking water were investigated for the last 10 years. A summary of the inspection results is shown in Table 9, and total 55,921 inspections were conducted. The number of surveys by water source was the highest in undercurrent, followed by reservoir, river, and groundwater. The average concentration for the total number of inspections was 1.6 mg/L, and the maximum concentration was 10 mg/L or close to all water sources. The level of 95% of the total number of inspections is 3.8 mg/L as shown in Figure 2, and it can be inferred that organic matter management is not adequately responding to some water treatment plants or any period. The average concentration was the highest at 2.3 mg/L in other water sources, and the 95% level was the highest in reservoir at 4.3 mg/L.

Table 9. Domestic drinking water $KMnO_4$ consumption detection status ('11~'20)

Water source	No. of sample	Average	Maximum	Top 95% level
Total	55,921	1.6	10.0	3.8
Undercurrent	20,180	1.5	9.8	3.8
Reservoir	20,110	1.9	9.8	4.3
River	7,845	1.6	9.7	3.2
Groundwater	5,648	0.8	10.0	2.4
Etc.	2,138	2.3	9.0	0.8

* Others: spring water, riverside filtered water, seawater, valley water, etc.

** Source: National Waterworks Information System (www.waternow.go.kr)

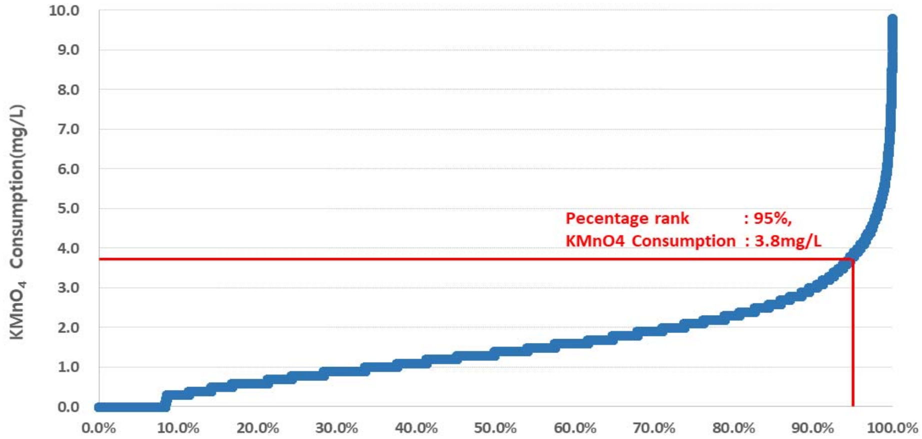

Figure 2. The % rank of $KMnO_4$ Consumption in Total drinking water samples

5.2 Overview of correlation analysis between organic matter indicators

Data on the TOC of domestic drinking water are very difficult to organize. In the case of TOC, since it is not a legal inspection item, the data accumulation on it is not separately systemized and can be found in some research report results.

On the other hand, K-water's multi-regional water treatment plant has some data periodically examined to understand the current status of tap water organic matters, and the correlations were analyzed by organizing them as shown in Table 10. However, there are differences in the number and the timing of inspections by water treatment plants and water treatment methods.

Table 10. Targets of domestic water treatment plant survey

Water source	water treatment plant	Advanced/ Typical	Period	No. of Sample
P Dam (Han River)	S	Advanced	'11.01~'20.12	119
	G1	Advanced	'11.01~'20.12	119
D Dam (Geum River)	C	Typical	'11.01~'14.3 '17.02~'17.12	50
	G2	Membrane filtration	'14.01~'20.3	74
Nakdong River	G3	Advanced	'12.02~'20.12	108
	G4	Advanced	'11.01~'20.12	120
	B	Advanced	'15.02~'20.12	67
I Dam (Upstream Nakdong River)	H	Typical	'11.01~'19.1	97

A total of 8 water treatment plants were analyzed, including 2 plants in the Han River watershed, 2 plants in the Geum River watershed, and 4 plants in the Nakdong River watershed. Although the data period has been set for the last 10 years, there are some differences in that period among water treatment plants, so the number of inspection varies from a minimum of 50 to a maximum of 120.

5.3 Correlation analysis results between indicators of organic matter

Table 11 shows the $KMnO_4$ consumption and TOC analysis results for 8 water treatment plants, and Figure 3 shows the detailed status of the correlation. The concentration of organic matters showed the lowest tendency in the Han River watershed for $KMnO_4$ consumption of 1.4~1.5 mg/L and TOC 1.2 mg/L, and the organic matters concentration showed the highest tendency in the Nakdong River watershed such as I Dam.

Table 11. Average concentration and Correlation efficient about $KMnO_4$ Consumption and TOC for Tap water in 8 WTP

Sortation	WTP	Advanced/ Typical	Average concentration (mg/L)		Correlation coefficient	Ratio (A/B)
			$KMnO_4$ consumption (A)	TOC (B)		
P Dam (Han River)	S	Altitude	1.4	1.2 (0~2.12)	0.21	1.20
	G1	Altitude	1.5	1.2 (0.5~1.9)	0.22	1.24
D Dam (Geum River)	C	Normal	2.1	1.3 (0.8~2.0)	0.59	1.61
	G2	membrane filtration	2.1	1.3 (0.8~1.9)	0.61	1.59
Nakdong river	G3	Altitude	2.6	1.8 (0.9~4.6)	0.60	1.47
	G4	Altitude	2.1	1.8 (0.6~3.5)	0.38	1.22
	B	Altitude	2.6	1.7 (1.2~2.2)	0.55	1.51
I Dam (Upstream Nakdong River)	H	Normal	4.7	2.7 (1.8~4.3)	0.73	1.73

Figure 3. Correlation between $KMnO_4$ Consumption and TOC for 8 WTPs

The correlation coefficient also showed a similar tendency to the concentration of organic matter, WTPs with the Han River watershed having the lowest value of 0.21 and WTPs with the Nakdong River watershed being generally high. In particular, H WTP in I Dam, it was the highest at 0.73, and $KMnO_4$/TOC ratio was also the highest at 1.73.

When comparing the advanced and typical water treatment process, there was a difference in the correlation coefficient and organic matters concentration ratio ($KMnO_4$/TOC) in the advanced water treatment process, but the typical water treatment process showed that the correlation coefficients are 0.59 to 0.73 and the organic matters concentration ratio ($KMnO_4$/TOC) are 1.59~1.73 with a higher trend.

To summarize the above results, the correlation coefficient and organic matters concentration ratio ($KMnO_4$/TOC) tend to decrease as the organic matter content is lower. Conversely, in the case of typical water treatment process, the organic matter removal rate is lower than that of advanced water treatment process, so the correlation coefficient and organic matters concentration ratio ($KMnO_4$/TOC) are rather high. The reason for this is presumed due to depending on the difference in the content of oxidizable substances in organic matter.

Additionally, the correlation analysis results for the organic matters concentration ratio ($KMnO_4$/TOC) and the correlation coefficient ($KMnO_4$ vs TOC) show that the higher the correlation coefficient ($KMnO_4$ vs TOC) value, the higher the organic matters concentration ratio ($KMnO_4$/TOC) as shown in Table 4.

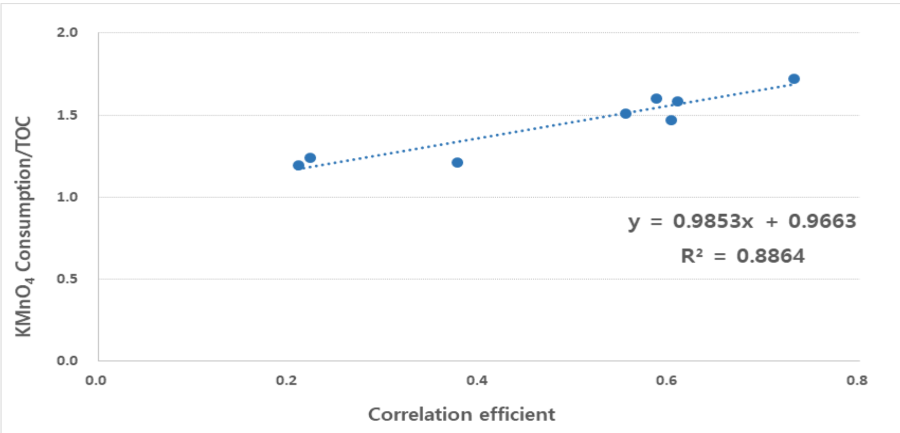

Figure 4. Correlation between ratio ($KMnO_4$/TOC) and correlation efficient

6. Drinking water quality standards draft and policy improvement points

6.1 Proposal of water quality standards draft

Through the inspected organic matters concentration ratio ($KMnO_4$/TOC), it is possible to suggest TOC drinking water quality standards. Although the use of organic matters concentration ratio in the previous literature review, it was applied by the organic matters concentration ratio (COD_{Mn}/TOC) between organic matters when setting the TOC standard in the water resource field.

The $KMnO_4$/TOC ratio is in the range of 1.20 to 1.51 in the advanced water treatment process and 1.59 to 1.73 in the typical water treatment process. As the $KMnO_4$/TOC ratio increases, the correlation coefficient tends to be higher, and the organic matter removal rate is higher due to the characteristics of the advanced water treatment process, so it seems reasonable to use the $KMnO_4$/TOC ratio of the typical water treatment process.

When applying the $KMnO_4$/TOC ratio of 1.59~1.73 of the typical water treatment process, considering that the drinking water quality standard for $KMnO_4$ consumption is 10mg/L, the TOC drinking water quality standard draft is 5.8~6.2mg/L, so it is reasonable to determine about 6mg/L. This TOC value is slightly higher than the TOC drinking water quality standard of 5 mg/L in Norway and Japan among foreign countries.

If the TOC water quality standard draft is designated as 6 mg/L, the maximum TOC concentration of 8 water treatment plants is 4.6 mg/L, which is expected to satisfy the TOC water quality standard draft. The 95 % level is 3.8 mg/L, and when converted to TOC, a level of about 2.4 mg/L is expected to be detected.

However, the TOC level of 6mg/L is rather high compared to other countries, so when considering the improvement of tap water quality and reduction of disinfection by-products, one of the goals of the future drinking water management policy is to reduce the organic matter content by expanding and introducing advanced water treatment processes.

6.2 Environmental impacts and economic assessment

If the water quality indicator is changed, the cost required for inspection may change, so it is necessary to review it. According to NIER(2010), a method for calculating the basic unit of cost for each test item by dividing it into 1 unit and 10 units was suggested.

It can be calculated in two ways by applying the test material cost, labor cost, and expenses as follows. The first method is "material cost + direct cost + indirect cost" and the second method is calculated as "material cost + direct cost + direct labor cost".

The comparison result of $KMnO_4$ consumption and TOC is shown in Table 12. When analyzing 10 or more items, the test time is 0.78 times for TOC compared to $KMnO_4$ consumption. It was investigated that the cost of TOC is 2.15~6.93 times higher than that of $KMnO_4$ consumption.

In terms of economic feasibility, the $KMnO_4$ consumption measurement method is more advantageous than TOC, but if automatic sample injection is possible, the first method of TOC is judged to be more advantageous for analyzing a large number of samples because the cost decreases as the number of samples increases.

Table 12. Comparison of test time and cost

Sortation			TOC (A)	KMnO4 consumption (B)	Remark (A/B)
Test time (hr)	1 unit		1.25	1.08	1.16
	10 unit		2.00	2.58	0.78
Cost for each test (won)	1 unit	1 way	33,834	13,929	2.43
		2 way	43,172	22,021	1.96
	10 units	1 way	191,592	27,656	6.93
		2 way	101,018	46,954	2.15

In addition, considering the environmental impacts, about 120mL is generated per case in the $KMnO_4$ consumption measurement method, but in the TOC measurement method, there is no wastewater generated due to the addition of reagents, which is environmentally advantageous. If the wastewater treatment cost is calculated considering the laboratory wastewater treatment cost of 150,000 won/ton, a wastewater treatment cost of 18 won per one measurement of $KMnO_4$ consumption occurs, and when measuring $KMnO_4$ consumption, sulfuric acid is added and heated to generate waste acid. It is also necessary to consider the cost of gas treatment.

Additionally sulfuric acid is an accident-preparing material, and separate thorough laboratory safety management is required according to the Chemicals Control Act. Although TOC may be somewhat disadvantageous in terms of economic feasibility, it can be judged as environmentally friendly compared to $KMnO_4$ consumption. Considering that almost all drinking water inspection stations currently have TOC analysis equipment, it is necessary to review them from an integrated perspective, such as future-oriented water quality management and data utilization for water treatment process management rather than economic feasibility..

6.3 Waterworks policy suggestions

In the present era, TOC is judged to be a more reasonable water quality indicator than KMnO4 consumption in organic matters management. However, $KMnO_4$ consumption clearly has the advantage that it can be used as an inexpensive and easy organic matter indicator in the case of water treatment plants with poor laboratory operating conditions.

Nevertheless, as mentioned above, $KMnO_4$ consumption has a limit as an organic material indicator itself, so it is necessary to proceed with the change to TOC. The domestic drinking water management system is operating separate water quality monitoring items. Water quality items judged to have an effect on drinking water can be monitored for a long period of time and added to the drinking water quality standards.

If the organic matter indicator of drinking water is changed to TOC immediately, confusion may occur in the field. Therefore, it is considered reasonable to designate drinking water as a water quality monitoring item for the next several years, conduct monitoring once a month, and derive a reasonable water quality standard draft after accumulating long-term data.

7. Conclusion

Previously, the reasons for the need to introduce a TOC indicator, policy trends in the water resources sector, correlation with $KMnO_4$ consumption, TOC water quality standards draft, and environmental and economic impacts were analyzed.

COD_{Mn} is mainly used in the water resource field in Korea, but in foreign countries has not been recognized as an organic material indicator form the past. Based on this, the organic matter indicator change to TOC was completed thanks to research and policy efforts over a long period of time in the field of water resources in our country.

Korea is the only country that uses $KMnO_4$ consumption, which is an indicator of organic matter in drinking water, as the drinking water quality standards in a method similar to COD_{Mn} in principle and procedure. In actual water treatment plants, TOC is being used as an organic matter indicator for water treatment process management such as coagulation, activated carbon adsorption, and ozone oxidation processes.

In order to present the TOC water quality standard draft, 6 mg/L was presented through comparison of water quality standards in foreign countries and the calculation of $KMnO_4$ consumption/TOC ratio through $KMnO_4$ consumption and TOC correlation analysis. However, a stronger TOC water quality standard draft should be introduced for long-term TOC monitoring and future-oriented improvement of drinking water quality.

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