＜論文＞

Development of Real Time Monitor of Chlorine Demand for Combined Sewer Overflow

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Abstract

A novel monitor of chlorine demand for stormwater overflow has been developed. The purpose of this monitor was to try to give an adequate criterion on chlorination control. Oxidation reduction potential (ORP) titration was adopted for measuring breakpoint. As the titration needed several minutes for response time, electric conductivity (EC) was tried to be transformed to chlorine demand in order to decrease response time. However, EC could not be used solely to get chlorine demand because of its deviation from regression line. Therefore combination of ORP titration and EC was adopted to get corrected results of real time measurement.

Key Words; Combined Sewer Overflow, Chlorine Demand, Electric Conductivity, ORP, Titration

1. Introduction

Disinfection of coliform of stormwater overflow is an important treatment for sewage works. Chlorination is the most widely used technique for disinfection because of its simplicity and affordable cost. As inactivation of bacteria depends on total residual chlorine (TRC) and contact time 1), monitoring TRC is preferable to be carried out to check disinfection procedure. But it has been substantially impossible due to lack of adequate on-line monitors. Therefore some researches were reported in order to predict TRC or to make guidelines for dosing chlorine 2)3). Haas et al. proposed empirical equations for microbial inactivation, TRC and contact time 4) with notable comment that they were site specific. Chen et al. studied a kinetic model for simulation of breakpoint curves and proposed an operating guide for wastewater chlorination 5). Their guideline reportedly could reduce dosage of chlorine significantly.

Haas et al. pointed out that it was essential to have a predictive relationship between chlorine residual and chlorine demand 4). Chen et al. also put chlorine demand as the base of their theoretical treatment 5). These papers suggested us to consider chlorine demand as a useful item for disinfection of combined sewer overflow (CSO). Rapid response should be one of prior requirements for chlorine demand measurement because of the short duration of heavy rain.

On the other hand, oxidation reduction potential (ORP) has been adopted as a new indication for disinfection. McPherson described that automatic control with electronic ORP controller could provide immediate breakpoint chlorination of the ammoniated solution 6). Miller reported that chlorine had been overfed in order to ensure safety margin of disinfection before introduction of ORP control. After switching to ORP control, reduction of chlorine usage was more than 40 percent 7). Rao reported that automatic control with ORP reduced chlorine by 32 percent 8). Kim reported that breakpoint treatment using ORP could decrease running cost of a plant 9).

Devkota et al. described ORP could be a surrogate parameter for disinfection for chlorination control purpose 10). They introduced Lund's law that relates ORP and coliform population as a basis of ORP control of disinfection. Their experiments showed that ORP curves had wide upswing region before breakpoint. They considered this region was suitable for automatic control. But they admit that a unique solution for an operating point of chlorine-ammonia reaction was not readily available from ORP control method.

There was no robust and effective chlorine demand monitor for CSO at least in Japan. Difficulties for development of the monitor had two aspects. The first difficulty existed in handling sample solution containing many suspended solids. The second difficulty was in selection of measuring principles in order to meet the requirements for on-line usage.

Handling wastewater in an on-line monitor is very challengeable and it needs practical knowledge and experiences. As difficulties of handling sample solution depend on principles of the measurement, selection of measuring principle should be considered first.

Regarding to the principles of chlorine demand, ORP was studied as an indicator of breakpoint. Somiya et al. compared TRC and ORP for sewerage samples and showed usefulness of ORP for detecting breakpoint 11).

2. Development of chlorine demand monitor

2.1 Selection of measuring principles

2.1.1 Titration

As ORP solely indicates the ratio of oxidant and reductant, titration is preferable method to be adopted for breakpoint measurement. Breakpoint curve is easily obtained directly by titration. And chlorine demand can be calculated by added volume of titrant at the breakpoint. Another advantage of this titration can be related to cleanliness of the system. Stains on the inner wall of the titration chamber could be eliminated by excess addition of sodium hypochlorite. Excess addition is an ordinary step in order to confirm end-point of the titration. Therefore adopting titration seemed adequate for on-line chlorine demand monitor.

One of negative aspects of titration for this monitor is that it needs definite time to complete titration. For this reason titration method can not be considered suitable for a real-time monitor.

2.1.2 Electric conductivity

One possible way to make real-time monitor is using correlation between chemical sensors and conventional titration. If we have significant correlation, we can calculate chlorine demand from indication of the sensor using regression curves. In our preliminary experiment, electric conductivity (EC) showed passable applicability to chlorine demand.

Limitation of EC transformation to chlorine demand depends on the fact that EC is a summation of all kinds of electrically charged components as shown in equation (1).

$$\sigma = \Sigma n_i e_i \mu_i \quad \text{---------------------} (1)$$

where

σ : electric conductivity (Sm^{-1})

n_i: number of i-th component

e_i : electric charge of i-th component (C)

μ_i: mobility of i-th component ($m^2s^{-1}V^{-1}$)

Equation (1) can be rewritten as;

$$\sigma = \Sigma p_i + \Sigma q_j \quad \text{------------------} (2)$$

where

p_i: electric conductivity contributed by i-th component that reacts with chlorine (Sm^{-1})

q_j: electric conductivity contributed by j-th component that does not react with chlorine (Sm^{-1})

Equation (2) means that EC consists of related part and non-related part to chlorine demand. Both of them are variables depending on site specific conditions such as weather, time, season, district, etc. Therefore a practical way to make real-time monitor using EC is to make correction of EC by conventional method e.g. titration results. An example of this correction is described in the following section 2.3 of this paper.

2.2 Schematic diagram and overview of the monitor

Figure 1 shows a schematic diagram and figure 2 shows a flow sheet of the titrating unit of the monitor. In order to ensure robustness to sewerage sample solution, some practical ideas have been applied. These ideas were focused on prevention of choking. One of them was adoption of a peristaltic pump for sample solution in order to eliminate check valves in the sampling line. Another example was washing a sample filter by compressed air at the initial step of the titrating sequence.

The detector of ORP was combined platinum electrode with Ag/AgCl reference electrode. Sodium hypochlorite was added by a syringe pump driven by a stepping motor.

2.3 Transformation of EC results to chlorine demand

2.3.1 Practical hypothesis

As shown in equation (2), EC is not related directly to chlorine demand. Therefore some hypotheses were given to transform EC to chlorine demand.

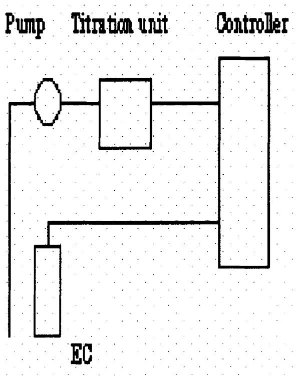
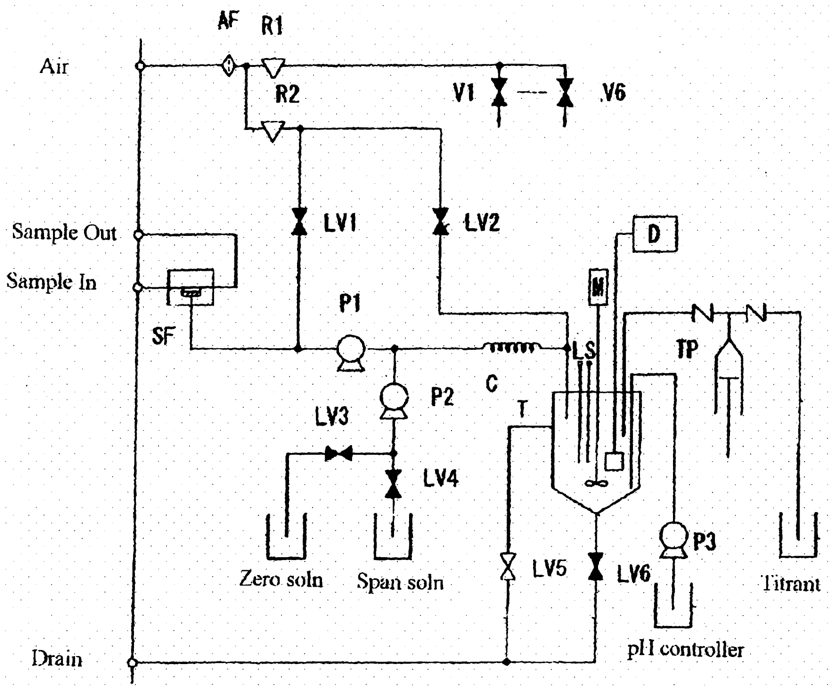


Fig. 1 Schematic diagram of the chlorine demand monitor



SF: Sample filter, AF: Air filter, R: Regulator, V: Air Valve,
LV: Liquid valve, P: Pump, C: Volumetric coil, LS: Level sensor
D: ORP detector, M: Stirrer motor, TP: Titration pump

Fig.2 Titrating unit of the monitor

Hypothesis (A): Σp_i can be written as E_1 and transformed to chlorine demand with only one coefficient as αE_1.
Hypothesis (B): Σq_j can be written as E_2 and transformed to chlorine demand with only one coefficient as βE_2.
Using these hypotheses EC could be transformed by following equation (3);

$$B = a E + b \quad \text{---------------------} \quad (3)$$

Where

B: Chlorine demand (mol dm^{-3})

E: electric conductivity (Sm^{-1})

a, b: transformation coefficients

2.3.2 Correction of regression coefficients

In order to get precise results, regression coefficients are preferable to be corrected by results of every titration. An example of correction is linear transformation by site-specific conditions as shown in equation (4).

$$(a,b)=\begin{pmatrix} C11 & C12 \\ C21 & C22 \\ - & - \\ - & - \\ Cn1 & Cn2 \end{pmatrix}\times(d1,\ d2,\ -\ -,\ dn)\ \cdots\cdots(4)$$

where

Cij : correction coefficient

d_k: k-th condition value

2.4 Specification

Table 1 shows brief specification of the prototype of the monitor.

Tab. 1 Specification of Chlorine Demand Monitor

Measuring range	0 – 200 mg/L	Correction period	> 10 min	EC sensor	Pt electrode
Sample stream	1	Sample volume	4 mL	Titration vessel	Pyrex 100 mL
Response time	Real time	ORP sensor	Pt, Ag/AgCl	Titration pump	Syringe pump

3. Experiments

Characteristic experiments were conducted with a prototype of the monitor in order to check effectiveness of the ORP titration and EC indication.

3.1 Materials

3.1.1 Sample solution

The monitor was installed in a laboratory of a sewage treatment plant located in the suburbs of Tokyo. Primary effluent was fed to the laboratory and a small polyethylene tank (volume =4 L) was set to soak a sample filter and an EC sensor.

3.1.2 Chemicals

(1) Titrant

Prepared sodium hypochlorite standard solution (280mg/L as Cl_2, DKK-TOA CORPORATION, Japan) was adopted as titrant. Factor of this solution was checked by a pocket chlorine analyzer.

(2) pH controlling solution

10mL of 25g/L KH_2PO_4 solution was added prior to every titration.

(3) Zero solution

Deionized water treated by mixed bed cartridge (G-10, ORGANO CORPORATION, Japan) was used for dilution and washing.

3.1.3 Apparatus

(1) Pocket chlorine analyzer

Model 46700-00 (HACH Company, USA) was used. Measuring method was diphenyl-p-phenylenediamine (DPD).

(2) ATP tester

Model AF-70 (DKK-TOA CORPORATION, Japan) was used for viable cell counting. Counting principle was bioluminescence between ATP (adenosine triphosphate) and luciferase.

(3)Total phosphor and nitrogen analyzer

Ammonia nitrogen of the sample solution was measured by model TNP-10 (DKK-TOA CORPORATION, Japan).

(4)EC meter

A pocket tester for pH and EC model WM-22EP (DKK-TOA CORPORATION, Japan) was used. An EC sensor was platinum electrode model CT-27112B and its cell constant was 252.1m^{-1}.

3.2 Experiments and results

3.2.1 Breakpoint curves

Profiles of ORP and TRC during titration were checked. Figure 3 shows an example of the profiles.

3.2.2 Chlorination versus titration results

Application of chlorine demand to determine chlorination amount could not been found in previous papers.

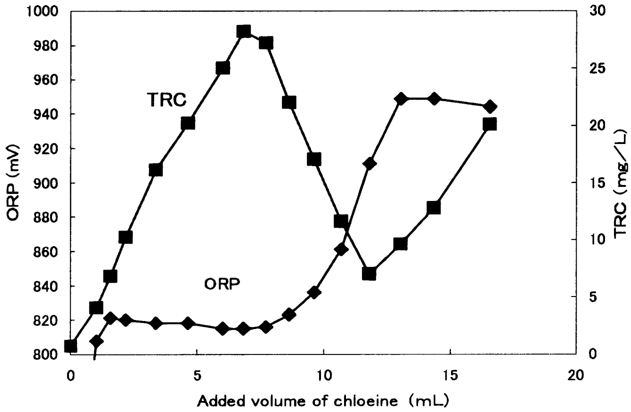


Fig.3 Profile of TRC and ORP during titration

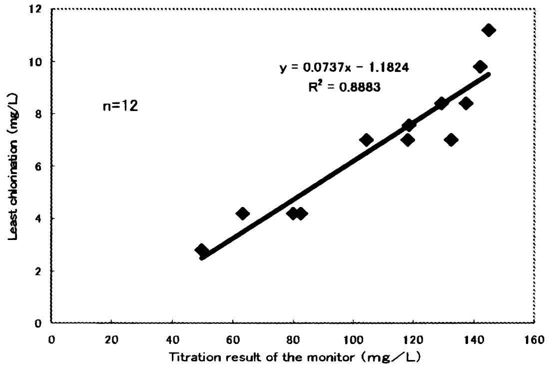


Fig. 4 Least chlorine dose for disinfection vs. titration

Therefore in order to confirm usefulness of chlorine demand on determination of chlorination, chlorination profiles were compared to the results of titration. Added volumes of 280mg/L of hypochlorite solution to 10 mL of primary effluent were plotted. The least added volume for disinfection was determined from the elbow shaped bend of the profile. Figure 4 shows the correlation between the least chlorine dose and titration. This result suggests usefulness of chlorine demand for chlorination.

3.2.3 EC and ammonium versus titration results

In order to get countermeasures to achieve rapid measurement, EC and ammonia concentration were compared to the titration. Figure 5 shows the result. Both of EC and ammonia showed passably good correlation to the titration respectively. Correlation coefficient between EC and titration was more than 0.9. This result leads us to try to adopt EC as a real time sensor for chlorine demand due to its simplicity.

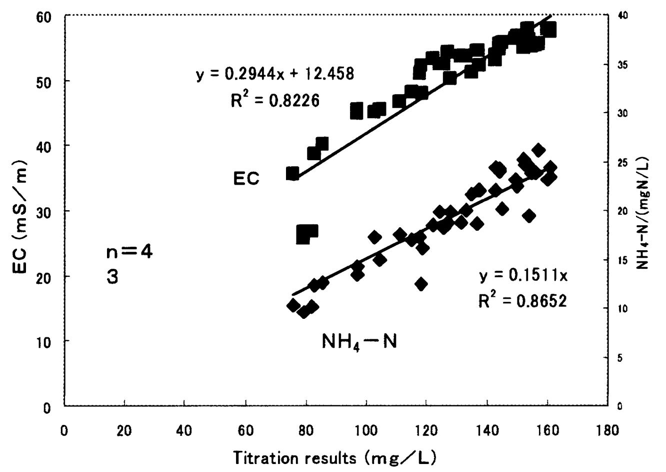


Fig. 5 EC and NH_4-N vs. titration results

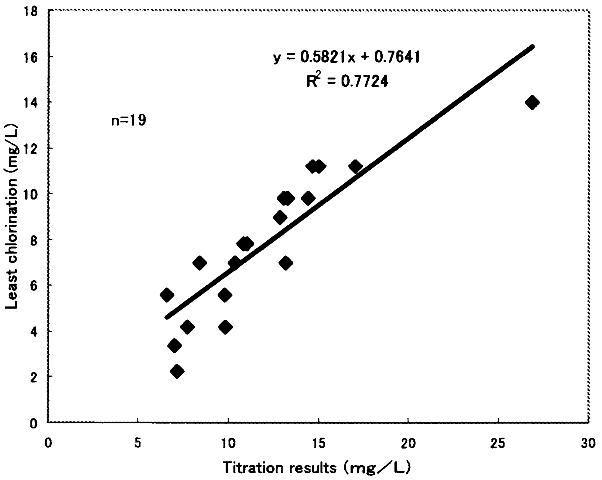


Fig.6 Least chlorination for disinfection vs. titration of first jump

3.2.4 First jump of titration

The first jump of ORP titration corresponds to chlorine demand only contributed by fast reactions with chlorine, while the second jump shows the breakpoint of the sample solution. Figure 6 shows the comparison between these jumps. A passably good correlation can be found.

4. Discussion

4.1 EC and chlorine demand

As described in section 2.3, limitation of EC transformation to chlorine demand depends on deviation from the practical hypotheses. These deviations can be considered as site specific. In case of rainfall, all the n_i of equation (1) is considered to be diluted equally. Therefore it is reasonable to expect positive correlation between EC and chlorine demand for wide range of measurement including rainy days and non-rainy days.

For narrow range measurement, dilution effect can not be expected. As site specific factors dominate correlation, transformation of EC to chlorine demand becomes difficult. Therefore every titration data must be used to correct transformation coefficients.

4.2 ORP controlling

As described in the first section of this paper, ORP reportedly could be used solely for chlorination control. However, those researches were applied only to final effluent and low ammonia conditions. Contrary, primary effluent and stormwater overflow contains high ammonia nitrogen. Therefore ammonia is preferable to be taken into account for chlorination i.e. breakpoint can be meaningful to be measured. But it is notable that this measurement does not mean breakpoint chlorination. Actual criterion for chlorine dose can be determined using breakpoint as an important factor.

5. Conclusion

EC and ORP titration were applied to measure chlorine demand. Correlation coefficient between wide range of EC and titration was more than 0.9. Frequent correction using ORP titration could be a possible way to transform EC to chlorine demand accurately.

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