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論文名 「Development of Chemiluminescence Method for the Measurements of Chemical Oxygen Demand, Hypochlorite, Ammonium, and Urea in Water」

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## 論文要旨

Chemiluminescence (CL) has been receiving great attention in the environmental analytical chemistry due to its high sensitivity, wide dynamic ranges, simplicity of the apparatus and less burden for maintenance. CL is usually measured in the absence of background light that leads to very low detection limits compared to other optical methods. There are increasing a number of applications of CL for the analysis of various organics compounds and inorganic species.

Water is a very important commodity to human being. Because of the toxicological effects of diverse pollutants found in water, their effluent standards are regulated in many countries. Recently, natural water qualities in Japan have been improved significantly, but the number of fishes has not returned. In some places, excessive treatment disorders balance in aqua system, which decreases the producibility. Therefore, control of water quality - not only reduction of pollutants concentration but also reduction of too much treatment- is important. In order to perform water quality control, it is demanding to put forward the development of reliable, fast, low cost and less labour-intensive methods for water quality monitoring. CL method could be one of the excellent methods to fulfill these required measurement since total cost is not very expensive (low cost performance to continue), and it is easy to operate and compact measurement system. In this study, CL detection methods for some pollutants in water have been developed with the goal of continuous environmental monitoring and effluent control in industrial operations. More specific discussions are outlined below:

In Chapter 1, introduction of CL, chemical oxygen demand, hypochlorite, ammonium, and urea with a review of related literature are summarized.

In Chapter 2, the correlation of 1-step CL COD method with the conventional permanganate COD ( $COD_{Mn}$ ) method is described. Chemical oxygen demand is the important water quality parameter which evaluates the soluble and particulate organic pollutant in water. The measurement of COD by the

conventional method ( $\text{COD}_{\text{Mn}}$ ) is time-consuming and associated with hazardous chemical. In previous study in our laboratory, it was found that when permanganate oxidized organic compounds, the CL originated from excited manganese species was produced. However, the previously developed CL method for COD measurement seems to be ineffective in oxidization of sample due to the very short retention time of sample and reagent in the detection cell. In Chapter 1, the correlation of 1-step CL COD method with  $\text{COD}_{\text{Mn}}$  was examined by comparing the  $\text{COD}_{\text{Mn}}$  values and CL signals of twelve organic compounds: itaconic acid, gallic acid, benzoic acid, methyl propionate, sodium salicylate, fumaric acid, resorcinol, ethanol, benzaldehyde, potassium hydrogen phthalate, oxalic acid, and pyrogallol. Among these organic compounds, six compounds showed no CL. The correlation between 1-step CL COD and  $\text{COD}_{\text{Mn}}$  method was conducted for six detected compounds, the obtained coefficient of determination was  $R^2 = 0.052$ . The CL kinetics of two typical compounds were investigated by using a stop pump experiment, and the results showed that the time for reaching the maximum intensity in the CL kinetic curves of different compounds were different. It means that the reaction rates of permanganate with organic compounds are different in kinds of organic compounds. The correlation between the signal intensity of CL emitted in 1-step CL COD (stop pump peak) and  $\text{COD}_{\text{Mn}}$  method was plotted again, the obtained coefficient of determination was  $R^2 = 0.20$ . In addition, it is revealed that the oxidation yields of organic compounds by  $\text{KMnO}_4$  are different, depending on the chemical structure of the compounds. Moreover, the reaction time of oxidation reaction in  $\text{COD}_{\text{Mn}}$  method is much longer than those in 1-step CL COD method. The bad correlation between the 1-step CL COD and  $\text{COD}_{\text{Mn}}$  was concluded as a result of the difference in reaction rate of different organic compounds and the difference in reaction time between two methods.

In Chapter 3, a new 3-step CL  $\text{COD}_{\text{Mn}}$  method developed for the measurement of COD is reported. In this measurement, a flow injection method was adopted. The 3-step CL  $\text{COD}_{\text{Mn}}$  method is based on the principle of permanganate COD method (JIS K0102). The sample reacted with excess amounts of permanganate under heating, and the remaining permanganate is consumed by pyrogallol. Then, the remaining pyrogallol is detected in the CL detector using permanganate CL reagent (3-step CL  $\text{COD}_{\text{Mn}}$ ). In this method, the difference in timing of CL emission in organic compounds can be neglected since the CL reaction is obtained from only the reaction of permanganate with pyrogallol. Further, this method can take a desired reaction time of permanganate with organic compounds. By using this method, the signals that previously gave no CL signal on 1-step CL COD method were also obtained. The correlation for a number of organic compounds between the 3-step CL  $\text{COD}_{\text{Mn}}$  and  $\text{COD}_{\text{Mn}}$  method showed the correlation of coefficient of  $R^2 = 0.9773$ . The limit of detection was  $0.082 \text{ mg dm}^{-3}$ , using pyrogallol as a standard. This method has been applied for measurement of the real sample from wastewater, wastewater after treatment and river water.

In Chapter 4, the use of potassium dichromate as the oxidizing reagent in the 3-step CL COD is developed. This method is also based on the principle of permanganate COD method (JIS K0102). The sample is reacted with excess amounts of dichromate under heating, and the remaining permanganate is neutralized by a reducing organic compound. Then, the remaining amount of the reducing organic compounds is detected in the CL detector using permanganate CL reagent (3-step CL  $\text{COD}_{\text{Cr}}$ ). Six organic compounds: gallic acid, phenol, pyrocatechol, ascorbic acid, pyrogallol, and potassium hydrogen phthalate were investigated as the reducing organic compounds. The CL kinetics of these compounds with acidic permanganate reagent were studied, and pyrogallol showed the highest signal with the relevant fastest response. Hence, pyrogallol was chosen as oxidizing organic compounds. The enhancement effects of seven metal ions: Cr(III), Mn(II), Cu(II), Ag(I), Fe(II), Fe(III), and Mg(II) were investigated. The result showed that Cr(III), Mn(II), Fe(II), and Fe(III) enhanced the signal. Fe(II) and Fe(III) showed the highest enhance effects, the signals increased 188 and 205 %, respectively. However, Fe(II) made the permanganate reagent become less stable due to the reaction between Fe(II) and permanganate. Hence, Fe(III) was added to the permanganate reagent at the optimum concentration of  $0.45 \text{ mmol dm}^{-3}$ . At higher

concentration of Fe(III) of  $0.45 \text{ mmol dm}^{-3}$ , the CL intensities were almost constant. Therefore, Fe(III) in the sample has no effect on the present method. The correlation between 3-step CL  $\text{COD}_{\text{Cr}}$  method and conventional  $\text{COD}_{\text{Mn}}$  for several organic compounds showed good coefficient of determination,  $R^2 = 0.9594$  ( $n = 16$ ). The limit of detection was  $0.083 \text{ mg dm}^{-3}$ , using gallic acid as a standard. This method was applied to the COD measurement of river water samples.

In Chapter 5, the development of a simultaneous, rapid and continuous measurement method of ammonium and urea in natural water by CL detection is reported. Ammonium, which is mostly from the runoff of agriculture land, is the main forms in the nitrogen cycle, especially in water. Excess amount of ammonium leads to the overgrowth of phytoplankton and algae bloom, which leads to the dissolved oxygen depletion. In addition, high level of urea may cause many health problems like ulcer, cancers, indigestion, acidity and malfunctions of kidney. This method is based on the CL produced by the reactions of hypobromite with ammonium and urea. The CL intensity of urea was stronger than that of ammonium at the same molar concentration. In this study, two pretreatment lines in the flow system were adopted. In the first line, total CL intensity from the reactions of hypobromite with ammonium and urea was measured. In the second line, urea was decomposed to ammonium by urease, and the CL intensity from the reactions of hypobromite with originally existed ammonium and ammonium produced from the decomposition of urea was measured. From these two signals, the concentrations of ammonium and urea in sample water could be calculated. The detection limits of ammonia and urea were  $30.3$  and  $8.9 \text{ } \mu\text{mol dm}^{-3}$  (corresponds to  $0.42$  and  $0.25 \text{ mg dm}^{-3}$  nitrogen of  $\text{NH}_4^+$  and Urea), respectively. The present method was applied to several natural samples.

In Chapter 6, a new CL method for the determination of hypochlorite ions is reported. This method is based on the CL emitted from reaction of hypohalite with ammonium ion under alkaline condition. The CL producing from hypochlorite and ammonium was considerably weak compared to those of hypobromite and ammonium. Hence, hypochlorite was rapidly converted to hypobromite through the reaction with bromide in acidic medium. The product of this reaction,  $\text{Br}_2$ , then reacted with excess amounts of sodium hydroxide to form hypobromite ions. Ammonium chloride was used as reagent to detect the hypobromite produced from these above reactions. The flow injection analysis was employed to continuously conduct reagent and carrier water to the system. The interference of common ions in water and heavy metal ions were investigated. These ions showed no CL to this system, the proposed method is selective to the determination of hypochlorite. This method showed a quadratic curve fitting with coefficient of determination,  $R^2 = 0.9989$ . It was found that the CL reaction obeyed 1.5 order for hypochlorite. As a result, calibration graph with 1.5th power of hypochlorite was converted to be linear with same value of coefficient of determination. The limit of detection of  $1 \text{ ppm}$  hypochlorite was obtained for this method, and it showed a good reproducibility with relative standard deviation of  $1.45 \%$  ( $n = 6$ , hypochlorite concentration of  $17.34 \text{ mg dm}^{-3}$ ) with high sample throughput  $50 \text{ samples / hours}$ . This method was suitable for the determination of hypochlorite in commercial products. Moreover, the curve fitting also provided a potential mean to decrease the limit of detection by using standard addition method.

In Chapter 7, conclusion of this thesis and summary of the previous chapters are described.

## 審査結果の要旨

本論文は自然水の水質監視に重要な化学的酸素要求量(COD)、次亜塩素酸、アンモニアおよび尿素の濃度を迅速かつ連続的に測定する簡易測定法の開発に関するもので、従来の簡易測定法の問題点を科学的に解決した研究報告であり、次のような結果を得ている。

- 1) 公定法の COD 測定と同じ原理で測定できる化学発光法の不一致の原因を解明した。化学発光法は室温で数秒反応させた時に生成する化学発光を測定する。そのため、反応速度の遅い物質では、発光のタイミングが合わなかったり、検出できるだけの十分な発光がないことを明らかにした。これを解決するために3段法を提案し、1段目で公定法と相関が出るだけの適当な時間と温度で反応させ、残った過マンガン酸をピロガロールで分解し、さらに残ったピロガロールを過マンガン酸と反応させ、そのときに発生する化学発光光度を測定することで COD を迅速、連続かつ従来よりも正確に評価できるようになった。
- 2) 過マンガン酸を使用した COD は日本で使用されているが、日本以外のほとんどの国では重クロム酸カリウムを用いた方法により COD が測定されている。1) で示した3段法で1段目の過マンガン酸カリウムを重クロム酸カリウムに変更することにより、重クロム酸カリウムを用いた COD 測定に用いることが出来ることを示した。
- 3) 富栄養化の原因物質の1つであるアンモニウムを、COD 測定法で用いた装置を用いて臭素とアンモニウムとの反応により化学発光を生じることを利用した測定法を開発した。また、この方法で問題となる尿素をアンモニアに変化させ、同時に測定することで、尿素が残留した自然水でも測定できる方法となることを示した。
- 4) 水処理等で用いる次亜塩素酸を COD 測定法で用いた装置で測定する方法を開発した。次亜塩素酸とアンモニウムの化学発光は弱い。そこで、臭化物イオンを加えて、次亜塩素酸と反応させて臭素に変化させることで、感度のよい臭素との化学発光を検出することによる、次亜塩素酸測定法を開発した。

以上の諸成果は、種々の汚濁物質濃度を1つの安価な装置で連続かつ迅速にモニタリングする可能性を示したものであり、水質管理の基本となる排出源での随時かつ迅速な測定による排水管理を安価な装置で行うことで、自然水の環境問題の解決に貢献するところ大である。また、申請者が自立して研究活動を行うのに十分な能力と学識を示したものである。