Interference of trace metal ions (Mn\(^{2+}\) and Fe\(^{3+}\)) in luminol-H\(_2\)O\(_2\)-metal ion catalyzed chemiluminescent system

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Inhibitory effects of trace metal ions (Mn\(^{2+}\) and Fe\(^{3+}\)) on the intensity of chemiluminescence accompanied by oxidation of luminol with hydrogen peroxide in the presence of Fe(CN)\(_6^{3-}\)catalyst were compared with those for a luminol-H\(_2\)O\(_2\)-Cu\(^{2+}\) system. The chemiluminescent intensity for the Fe(CN)\(_6^{3-}\) system was smaller twentieth than that for the Cu\(^{2+}\) system. However, the decrease in the intensity due to the metal ions found for the Fe(CN)\(_6^{3-}\) system was below 10\% of that for the metal ion free solutions in the metal ion concentration range up to 1\times10^{-6} \text{ mole l}^{-1} \text{ and above } 10^{-5} \text{ mole l}^{-1} the decrease in the intensity seemed to be very smaller than that for the Cu\(^{2+}\) system. This luminol-Fe(CN)\(_6^{3-}\) system may be favorable to determination of H\(_2\)O\(_2\) in clouds and rainwater containing relatively large amount of metal ions.

1. Introduction

Hydrogen peroxide (H\(_2\)O\(_2\)) contributes to atmospheric chemical reactions such as formation of hydroxyl radicals in the gas phase\(^1\) and oxidation of sulfur dioxide to sulfate in water droplets\(^2\). Therefore, the quantitative determination of H\(_2\)O\(_2\) at very low levels in the atmosphere is considered important to understanding the environmental problems of photochemical smogs and acid precipitation. Luminol (5-amino-2,3-dihydro-1,4-phthalaladinedione)-based chemiluminescent systems with catalysts of metal ions\(^3\) and hemin\(^4\) have been developed and applied to field measurements of H\(_2\)O\(_2\). The author recently pointed out that trace amounts of metal ions such as Mn\(^{2+}\) and Fe\(^{3+}\) existing in water droplets greatly diminished the chemiluminescent intensities.\(^5\) Although the mechanism of the interference has not been fully elucidated, it has been inferred that Mn\(^{2+}\) or Fe\(^{3+}\) does not consume H\(_2\)O\(_2\) and there might be certain interactions between luminol/metal catalysts (Cu\(^{2+}\)) and the metal ions.

A luminol-potassium hexacyanoferrate, K\(_2\)Fe(CN)\(_6\), system has been used for measurements of H\(_2\)O\(_2\) in natural water and the optimum concentrations of luminol and Fe(CN)\(_6^{3-}\) were much higher than those in the luminol-Cu\(^{2+}\) system.\(^6\) It is therefore expected that the luminol-Fe(CN)\(_6^{3-}\) system may suffer from less interference than the luminol-Cu\(^{2+}\) system.

2. Experimental

An experimental system used here was the same to the previous one.\(^5\) Stock solutions of luminol (4.5\times10^{-9} \text{ mole l}^{-1}) and a working solution of K\(_2\)Fe(CN)\(_6\) (10^{-4} \text{ mole l}^{-1}) were prepared from the reagent grade chemicals and purified water (treated with ion exchange resins and active carbon). For analysis, the pH and the concentrations of the luminol and Fe(CN)\(_6^{3-}\) solutions were adjusted to the optimum values (pH: 10.5; luminol: 9\times10^{-4} \text{ mole l}^{-1}; and Fe(CN)\(_6^{3-}\): 10^{-4} \text{ mole l}^{-1}) according to the literature.\(^4\) Reagent grade MnCl\(_4\) and FeCl\(_3\) were used as the source of additional Mn\(^{2+}\) and Fe\(^{3+}\) ions. A stock solution of H\(_2\)O\(_2\) (1 wt%) which was titrated with a standard solution of potassium permanganate was made from a 10 wt\% H\(_2\)O\(_2\) solution. The stock solution was diluted to 0.3~1.2 mg l\(^{-1}\) (ppm) solution.
3. Results and Discussion

A good linear relationship was confirmed between the chemiluminescent intensity observed for the metal ion free luminol-Fe(CN)$_6^{3-}$ system and the concentration of H$_2$O$_2$. The detection limit of this analytical system was obtained to be 20 $\mu$g·l$^{-1}$ (ppb) which was larger 20 times than that for the luminol-Cu$^{2+}$ system.

In figure, the change in the chemiluminescent intensity due to 0.6 ppm of H$_2$O$_2$ with the concentration of the metal ions observed for both the luminol-Fe(CN)$_6^{3-}$ (as designated by open symbols) and the luminol-Cu$^{2+}$ (as designated by filled symbols) systems. The intensity obtained for the metal ion free solutions was taken as 1.0. It is to be noted that chloride ion seems to have no effects on the chemiluminescent response, based on the experimental results using sodium chloride. It is clear that the degree of the decrease in the intensity due to Mn$^{2+}$ is very smaller for the luminol-Fe(CN)$_6^{3-}$ than that for the luminol-Cu$^{2+}$. The decrease in the intensity for the luminol-Fe(CN)$_6^{3-}$ did not exceed 10% in the Mn$^{2+}$ concentration range up to $1 \times 10^{-6}$ mole·l$^{-1}$. With respect to the interference due to Fe$^{3+}$, little difference was observed between the two chemiluminescent system in the concentration range of $1 \times 10^{-7}$ mole·l$^{-1}$ to $1 \times 10^{-5}$ mole·l$^{-1}$, but above $1 \times 10^{-5}$ mole·l$^{-1}$ the luminol-Fe(CN)$_6^{3-}$ system showed less dependence of Fe$^{3+}$ concentration.

For measurements of trace amounts of H$_2$O$_2$ in aqueous solutions, the luminol-Fe(CN)$_6^{3-}$ system is unfortunately less sensitive than the luminol-Cu$^{2+}$ one, but the interference of the foreign metal ions of Mn$^{2+}$ and Fe$^{3+}$ is found to be smaller for the luminol-Fe(CN)$_6^{3-}$ system. It is thus considered that this chemiluminescent system may have the advantage for the measurements of H$_2$O$_2$ in highly polluted areas where both H$_2$O$_2$ and the metal ion concentrations in clouds, rainwater or natural water are relatively high.

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References


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ヘキサシアノ鉄(III)酸塩, Fe(CN)$_6^{3-}$, を触媒とするルミノールの過酸化水素による酸化反応に伴う化学発光に対する微量金属イオン (Mn$^{2+}$ および Fe$^{3+}$) の妨害効果を Cu$^{2+}$ を触媒とする場合と比較検討した。Fe(CN)$_6^{3-}$ 系では化学発光強度は Cu$^{2+}$ 系よりも20倍以下となった。しかしながら, Fe(CN)$_6^{3-}$系での金属イオンによる発光強度の減少は金属イオン濃度が $10^{-7}$ mole$l^{-1}$ から $10^{-4}$ mole$l^{-1}$ の範囲では金属イオンが無い場合の強度の10%を越えないことおよび $10^{-3}$ mole$l^{-1}$ 以上の濃度範囲でも Fe(CN)$_6^{3-}$ 系での発光強度の減少は Cu$^{2+}$ 系よりもかなり小さいことがわかった。比較的金属イオン濃度が高い雲雨水中の過酸化水素定量には Fe(CN)$_6^{3-}$ 系が適していると思われた。

Key words: H$_2$O$_2$ in water, luminol-based chemiluminescence, Fe(CN)$_6^{3-}$ and Cu$^{2+}$ catalysts, Interference from Mn$^{2+}$ and Fe$^{3+}$

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