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Chemiluminescence Reaction of an Iron(III)-Phthalocyanine Complex and Its Application to FIA of L-Tyrosine

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Abstract

Chemiluminescence (CL) of a metal–phthalocyanine complex was studied, and an analytical application of CL detection-flow injection analysis (FIA) of L-tyrosine was developed. The CL reaction of iron (III)–phthalocyanine tetrasulfonic acid (Fe–PTS) was examined using eight metals (Cu, Fe, Ni, Co, Mg, Pd, Pt and Zn)–phthalocyanine complexes. The CL signal immediately appeared, when the Fe-PTS aqueous solution was injected into a hydrogen peroxide solution. Moreover, the influence of foreign substances on the CL system of Fe–PTS was examined. The decrease in the CL intensity of the iron–phthalocyanine complex was caused by adding a reducing agent such as L-tyrosine. The CL detection-FIA of trace amounts of L-tyrosine was then developed using this quenching phenomenon. The calibration curve was obtained in the concentration range 2.5×10^{-7} M to 7.5×10^{-6} M, and the sampling rate was 150 samples h^{-1}. Further, the relative standard deviation (RSD) was 1.20 % (n = 25) for 1.0×10^{-6} M, and the detection limit (3σ) were 8.54×10^{-8} M. The interference of metal ions was able to inhibit using EDTA. Therefore, the interference of L-cysteine was able to inhibit using Zn^{2+}. As an application to a practical sample, L-tyrosine in a supplement was determined. The experimental value is almost the same as the tabulated one (1.0×10^{-6} M) measured by amino acid autoanalyzer at the Japan Food Research Laboratories.

Keywords: Iron–phthalocyanine tetrasulfonic acid, phthalocyanine, chemiluminescence, flow injection analysis, L-tyrosine

1. Introduction

Porphyrins and phthalocyanines are analogous compounds, and these compounds are widely used as dyes, catalysts and organic electroluminescent materials, etc. [1, 2]. In particular, in analytical chemistry, these compounds have been used as highly sensitive reagents for metal ions. Therefore, many highly sensitive spectrophotometric and fluorophotometric methods have been developed using the absorption, fluorescent and phosphorescent properties of porphyrins and phthalocyanines [3-7]. Chemiluminescence (CL) method has some advantages compared to spectrophotometry and fluorophotometry. For example, a high sensitivity, quick response and instrument simplicity are provided. However, CL analysis methods are limited because there are only a few CL substrates with high luminescence intensity. Therefore, a new CL system is desirable.

Nagoshi and Igarashi [8] found a new CL phenomenon of chlorophyll contained in plant leaves by adding a hydrogen peroxide solution in the presence of acetonitrile/water solution. This phenomenon is caused by the decomposition of the chlorophyll containing a fluorescent magnesium complex. Moreover, another CL phenomenon was reported for the iron–chlorophyllin complex which is one of the metal–porphyrin complexes [9]. However, the iron–chlorophyllin complex which exists in the leaves of bamboo grass is a non-fluorescent substance. In this case, it was thought that its porphyrin ring is cleaved by the oxidative reaction with hydrogen peroxide, and the fluorescent decomposition products of the iron–chlorophyllin complex then emit a luminescence because the iron ion which is a paramagnetic metal is released from them.

Phthalocyanines are easily broken at the -C=N- bond in the meso position in comparison to porphyrins having a -C=C- bond. Hence, in this study, the CL phenomenon of phthalocyanine being an artificial synthetic substance was examined in detail. The CL intensity of the iron–phthalocyanine complex decreased on addition of a reducing agent such as L-tyrosine.

L-tyrosine is an important amino acid that functions as a precursor of adrenaline, dopamine, etc., in biological systems. Thus far, various methods have been used to detect L-tyrosine. For example, spectrophotometry in the phenylalanine ammonia-lyase enzyme reaction [10], fluorophotometry in the 1,5-bis(4,6-

dichloro-1,3,5-triazinylamino) synthesis reaction and in the Mo(VI)-phenyl-fluorone quenching reaction [11, 12], CL in the oxidation reactions of $K_3Fe(CN)_6$ and $KMnO_4$ [13-15], cyclic voltammetry in the multiwalled carbon nanotube/4-amino-benzenesulfonic acid film-coated glassy carbon electrode oxidation reaction [16], UV detection of microcolumn electrophoresis [17], HPLC–FL [18] and HPLC–APCI– MS/MS [19] have been reported until now. However, the cases of rapid, simple and highly sensitive analysis of trace amounts of L-tyrosine are few. Therefore, it is very important to develop an automated analysis which can determine rapidly, simply and high sensitively trace amounts of L-tyrosine.

In this study, the CL phenomenon of phthalocyanine is discussed and the CL detection-FIA of trace amounts of L-tyrosine is developed using this Fe–PTS CL reaction.

2. Experimental

2.1 Reagents

Iron–phthalocyanine tetrasulfonic acid (Fe–PTS, structure shown in Fig. 1), nickel–phthalocyanine tetrasulfonic acid and copper–phthalocyanine tetrasulfonic acid were obtained from Aldrich (Milwaukee, WI, USA). The metal-free PTS was synthesized and purified by Fukada's method [20]. The other metal–phthalocyanine tetrasulfonic acids were synthesized as follows; the metal-free PTS and a metal nitric salt were added to dimethyl sulfoxide (DMSO) and then mixture was heated to 150 °C for 1 h. The products were obtained by recrystallization using acetone and water. Sodium tetraborate (Borax, Wako Pure Chemicals Industries, Osaka, Japan), was prepared as a pH buffer solution (0.1 M using distilled water). Hydrogen peroxide was prepared as an oxidizing reagent by diluting 30% (v/v) solution (Wako Pure Chemicals Industries, Osaka, Japan) with distilled water. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was obtained from Aldrich (Milwaukee, WI, USA). L-tyrosine was obtained from Tokyo Chemical Industry (Tokyo, Japan) and the practical sample was obtained from medicine (Amino body, Orihiro, Gunma, Japan). All other reagents were of analytical grade.

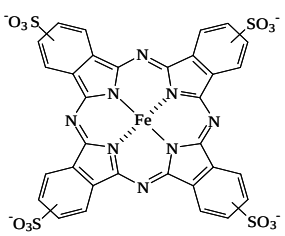

Fig.1 Structure of Fe–PTS

2.2 Apparatus

The absorption spectra were obtained using a V-570 type spectrophotometer (JASCO, Tokyo, Japan). The fluorescence spectra were obtained using an F-4500 type spectrofluorometer (Hitachi, Tokyo, Japan). A 600 type lumicounter (Microtec NITI-ON, Chiba, Japan) was used for the CL measurements. The CL detection of FIA was done using a CL-1525 instrument (JASCO, Tokyo, Japan). This instrument was equipped with two TCI-NOX1000ω (Tokyo Chemical Industry, Tokyo, Japan) double plunger-type pumps. A TM-3 (AS ONE, Osaka, Japan) was used as a thermostat. The injector used was the 100 μL loop injector built into the pump. A PFA (tetra fluoro ethylene-perfluoro alkylvinyl ether copolymer) tube (external diameter: 2.0 mm; internal diameter: 1.0 mm; GL Sciences, Tokyo, Japan) was used for flow tubing and mixing coils.

2.3 Experimental Procedure

2.3.1 Phthalocyanine chemiluminescence (batch method)

A distilled water (340 μL) was injected into a glass cell by using a microsyringe. A 100 μL of pH buffer solution and 40 μL of hydrogen peroxide were added and mixed, and the cell was then placed in the cell holder of the CL detection equipment. An iron–phthalocyanine complex solution (20 μL) was then injected using a microsyringe and the CL signal was measured.

2.3.2 The determination of L-tyrosine (FIA)

The proposed flow system is shown in Fig. 2. The length of the reaction coil (inside diameter = 1 mm) was 3.5 cm. Flow passage A injected the sample solution (100 μL) into a flowing 4.0×10^{-5} M Fe-PTS aqueous solution using the injector (I). Flow passage B adds the 2.0×10^{-3} M hydrogen peroxide aqueous solution, and the flow rate in each flow passage was set at 1.9 mL min^{-1}. The difference in the CL intensity of the sample reaction is indicated by ΔI_{CL} [= CL intensity (blank) − CL intensity (sample)].

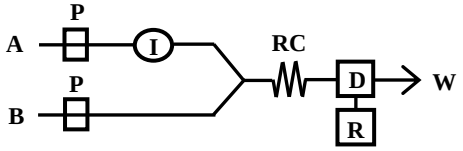

Fig.2 FIA system for determination of L-tyrosine with Fe–PTS solution.
A: 4.0×10^{-5} M Fe–PTS (pH = 10) soln., 1.9 mL min^{-1};
B: 2.0×10^{-3} M H_2O_2 soln., 1.9 mL min^{-1}; P: Pump;
I: Injector (100 μL); RC: Reaction coil (3.5 cm);
D: Detector (CL-1525 instrument); R: Recorder; W: Waste

3. Results and discussion

Phthalocyanine chemiluminescence (batch method)

3.1 The CL of various metal–phthalocyanine complexes

Each CL intensity (I_{CL}) is shown in Table 1. The maximum CL intensity was 1270 by Fe–PTS. On the other hand, for the other metal-phthalocyanine complexes, the CL phenomenon was almost not observed. From these results, Fe–PTS was selected as the CL substrate in this study.

Table 1 CL intensity of metal–PTS complexes

Substrate	I_{CL}
PTS	0
Cu–PTS	0
Fe–PTS	1270
Ni–PTS	0
Co–PTS	1.7
Mg–PTS	0.3
Pd–PTS	0.5
Pt–PTS	0.9
Zn–PTS	0.4

$[Substrate]_T = 2.0 \times 10^{-5}$ M, $[H_2O_2]_T = 6.4 \times 10^{-3}$ M, pH = 10, PMT voltage = −800 V.

3.2 Examination of an oxidizing agent and a pH

The effects of different oxidizing agents (H_2O_2, $NaClO_3$, $NaIO_4$, $KBrO_3$ and oxone) on the CL reaction of Fe–PTS, were examined. As a result, the CL phenomenon was only observed in the hydrogen peroxide aqueous solution. Therefore, hydrogen peroxide which produces the maximum CL intensity was selected as the oxidizing agent in this study. Also, the maximum CL intensity was measured at pH 10. Similar pH dependencies have been reported for other CL systems (luminol CL [21, 22], lucigenin CL [23]).

3.3 Spectral data of Fe–PTS

A sharp CL signal was immediately observed, when the Fe–PTS solution was injected into the hydrogen peroxide solution.

The absorbance changed in the absorption spectra by the CL reaction. It is shown in Fig. 3. Based on this fact, a decrease in absorbance of the iron-phthalocyanine complex at the maximum absorption wavelength was confirmed after the CL. It has been reported that the ring structure of a metal–porphyrin complex changes when the bond at the meso position is broken by photo-oxidation [24]. Therefore, it is presumed that the destruction of Fe–PTS, which is similar to a porphyrin structure, occurs during the CL reaction.

The CL spectrum of Fe–PTS is shown in Fig. 4. The wavelength region of the CL spectrum was almost similar to the luminol CL spectra [25, 26].

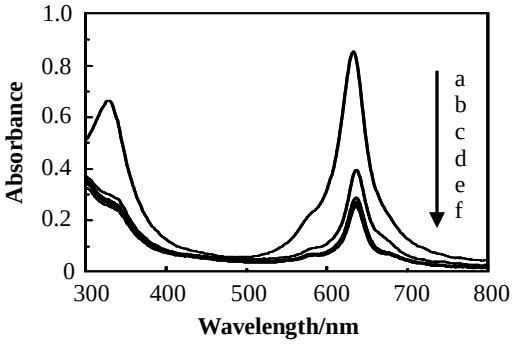

Fig.3 Change of absorption spectra by CL reaction
$[Fe–PTS]_T = 2.0 \times 10^{-5}$ M, $[H_2O_2]_T = 6.4 \times 10^{-3}$ M, pH = 10, Spectral curves a: 0 min, b: 2 min, c: 4 min, d: 6 min, e: 8 min, f: 10 min

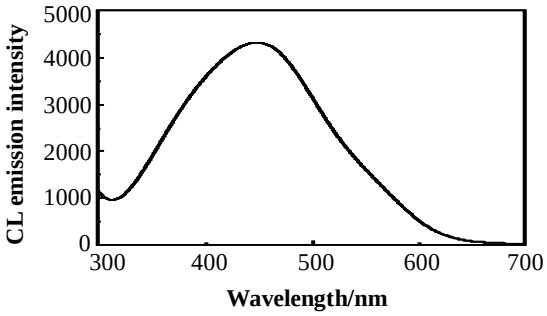

Fig.4 CL spectrum of Fe–PTS
$[Fe–PTS]_T = 2.0 \times 10^{-6}$ M, $[H_2O_2]_T = 6.4 \times 10^{-3}$ M, pH = 10, PMT voltage = 400 V

3.4 Examination of various functions

Function as a catalyst: It is considered that the axial coordinating position of Fe–PTS acts as a catalytic activation point for the CL reaction. Therefore, the catalytic function of Fe–PTS was examined by adding potassium thiocyanate (KSCN). A similar reaction is considered to occur in Fe–PTS. As already reported, the thiocyanate ion (SCN^-) is coordinated to the axial position of the iron-porphyrin complex [9, 27]. The CL intensity decreased with an increase in the KSCN concentration. Based on this result, it is presumed that the axial position of Fe–PTS becomes catalytically inactive because SCN^- coordinates to the axial position of an iron ion. Therefore, the axial coordinating position of Fe–PTS acts as a catalytic activation point in this CL system.

Function as an energy acceptor of the decomposition product: The fluorescence spectrum of Fe–PTS is shown in Fig. 5. The

maximum emission intensity was obtained EM: 450nm, when the fluorescence was measured at EX: 310 nm after the CL reaction. It was confirmed that the fluorescence intensity increased with the reaction time. This is due to the presence of fluorescent substances (phthalimide) in the decomposition products of Fe–PTS. Moreover, the fluorescence-emission wavelength (450 nm) nearly corresponds to the CL-emission wavelength (451 nm). Based on these facts, the compound with fluorescence is generated during the oxidative decomposition of Fe–PTS. It is considered that the decomposition product of the Fe–PTS emits light by receiving the decomposition energy. Therefore, the decomposition product of Fe–PTS acts as an energy acceptor.

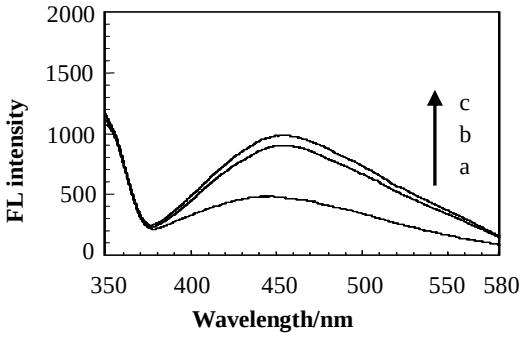

Fig.5 Fluorescence spectral change of Fe–PTS
$[Fe–PTS]_T = 2.0 \times 10^{-5}$ M, $[H_2O_2]_T = 6.4 \times 10^{-3}$ M, pH = 10,
PMT voltage = 950 V, Ex = 310 nm,
Spectral curves a: 0 min, b: 5 min, c: 10 min

3.5 Influence of foreign substances

The CL intensity decreased when an amino acid such as L-cysteine, L-histidine, L-tyrosine and L-tryptophan separately coexisted in this system. It is presumed that L-tyrosine and L-tryptophan inhibit the oxidation reaction with hydrogen peroxide because they have a reducing action [28]. In addition, the CL intensity also decreased when a vitamin such as L-ascorbic acid or a saccharide such as glucose were added. It is presumed that the decreased oxidizing power occurs because L-ascorbic acid and glucose are reducing reagents. On the other hand, the CL intensity increased when Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+} were present. It is considered that these metals act as a catalyst in this CL system, because it has been reported many times that metal ions act as a catalyst in the CL reaction [29].

3.6 The determination of L-tyrosine (FIA)

The FIA flow chart for the CL intensity using the CL reaction of Fe–PTS is shown in Fig. 6. The various conditions with this flow signal were optimized.

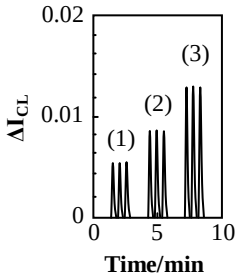

Fig.6 Flow signals of the FIA (PMT voltage: 750 V, gain: 1000)
$[Fe–PTS]_T = 4.0 \times 10^{-5}$ M, $[H_2O_2]_T = 2.0 \times 10^{-3}$ M, pH = 10, 25 °C
Signal: (1) $[L\text{-Tyrosine}]_T = 5.0 \times 10^{-7}$ M, (2) $[L\text{-Tyrosine}]_T = 1.0 \times 10^{-6}$ M,
(3) $[L\text{-Tyrosine}]_T = 5.0 \times 10^{-6}$ M

3.7 Optimization of conditions

Influence of Fe–PTS concentration: The concentration of the Fe–PTS was varied within the range of 8.0×10^{-6} to 8.0×10^{-5} M. The CL intensity increased as the concentration of Fe–PTS increased. The difference in the CL intensity was highest in this range; therefore, the concentration of the Fe–PTS was set at 4.0×10^{-5} M.

Influence of hydrogen peroxide concentration: The concentration of the hydrogen peroxide was varied within the range of 6.0×10^{-4} to 6.0×10^{-3} M. The maximum CL intensity based on the hydrogen peroxide concentration change is observed at 2.0×10^{-3} M. Because the difference in the CL intensity was highest in this range, the concentration of the hydrogen peroxide was set at 2.0×10^{-3} M.

Influence of pH: The pH was varied within the range of 8 to 12. The pH was similar to results of batch method as mentioned above. Hence, because the difference in the CL intensity was highest in this range, the pH was set at 10.

Influence of temperature: A change in the CL intensity was hardly observed between 20 to 40 °C. Because the difference in the CL intensity was highest in this range, the temperature was set at 25 °C.

3.8 Examination of flow rate and reaction coil length

Flow rate and reaction coil length in FIA were examined as follows. The length of the reaction coil (inside diameter = 1 mm) was varied within the range of 3.5 to 50 cm, and the flow rates of Fe–PTS and H_2O_2 were varied within the range of 1.2 to 1.9 mL min^{-1}. The CL intensity was increased, when the length of reaction coil is shorter and the flow rate in each passage is faster. Namely, a shorter reaction time induced a higher CL intensity, because it appears from the results that the CL reaction occurred immediately when the CL substrate was added to the oxidizing reagent. Also, because the difference in the CL

intensity became highest in these ranges, the length of the reaction coil was set at 3.5 cm and the flow rate of the respective passage was also set at 1.9 mL min^{-1}.

3.9 Calibration curve

In the calibration curve of L-tyrosine, the relationship obtained between the concentration range 2.5×10^{-7} to 7.5×10^{-6} M of L-tyrosine and the difference in CL intensity (ΔI_{CL}) was y = 0.0287 ln(x) + 0.4753, where y is ΔI_{CL} and x is the L-tyrosine concentration [M]. The correlation coefficient was 0.990, RSD was 1.20 % (n = 25) at the L-tyrosine concentration of 1.0×10^{-6} M, and the detection limit (3σ) was 8.54×10^{-8} M.

3.10 Influence of foreign substances

The effects of foreign substances on CL intensity are shown in Table 2. As for the allowable limit, the change in time was within ±5 % based on the difference in the CL intensity with the blank when no foreign substances were added. This was compared to the molar ratio with L-tyrosine. Although Fe^{3+} could be present up to 10-fold without affecting the results of the test, Ni^{2+} and Co^{2+} could be present up to 1-fold without affecting the results of the test, and Cu^{2+} could be present up to 0.5-fold without affecting the results of the test. They could be masked up to 50-fold with the addition of EDTA as the masking reagent. Also, L-cysteine could be present up to 0.5-fold without affecting the results of the test. It is reported that L-cysteine and Zn^{2+} form a complex in neutral and alkaline conditions [30]. As a result of experiment, L-cysteine was masked up to 100-fold with the addition of Zn^{2+} as the masking reagent.

Table 2 Influence of foreign substances

Foreign substance	[Foreign substance]/[L-tyrosine]
Glutamine, Methionine, Serine, Threonin, Alanine, Glycin, Isoleucin, Glucose, Fructose, Xylose, Saccharose, Raffinose, levulose, Lactulose, Galactose, Nicotinic acid, Nicotinamide, Sodium pantothenate	1000
Asparagine, Lysine, Phenylalanine, Histidine, Leucine, Proline	500
Zn^{2+}, Cysteine*, Valine, Aspartic acid	100
Se^{4+}, V^{5+}, Al^{3+}, EDTA, Ni^{2+*}, Co^{2+*}, Cu^{2+*}, Fe^{3+}, Arginine, Pyridoxine hydrochloride, Thiamine hydrochloride	50
Glutamic acid, Riboflavin, Folic acid	10
Cystine, Tryptophan, Ascorbic acid	5

Tolerance limit is within ±5 % error for CL intensity when $[L\text{-tyrosine}]_T$ is 1.0×10^{-6} M.
*$[EDTA]_T$: 5.0×10^{-5} M was added as a masking reagent.
*$[Zn^{2+}]_T$: 1.0×10^{-4} M was added as a masking reagent.

3.11 Practical applications

3.11.1 The determination of trace amounts of L-tyrosine in a supplement

The L-tyrosine in a supplement containing 20 kinds of amino acid was determined. The sample solution containing L-tyrosine was prepared by dissolving a commercial supplement in distilled water. The determined concentration of L-tyrosine was 0.98×10^{-6} M (supplement concentration 0.18 mg L^{-1}: 1.0×10^{-6} M). Moreover, the RSD was 2.81 % (n=50).

3.12 Comparison with other analysis methods

The comparison between this method and other methods is shown in Table 3. The proposed method proves to be rapid (150 samples h^{-1}), simple, and highly sensitive because the detection limits are almost equivalent to those of fluorophotometry [11] and cyclic voltammetry analyses [16].

4. Conclusion

The CL reaction of a metal–PTS was examined. In conclusion, the maximum CL signal was observed only for Fe–PTS among eight different kinds of metal–PTSs. The CL phenomenon of Fe–PTS is a new CL system using an artificial-synthetic compound. The FIA of trace amounts of L-tyrosine was developed using the CL reaction of a phthalocyanine complex. This method proved to be more rapid, simpler and more precise compared to other methods for the determination of trace amounts of L-tyrosine. Improved sensitivity using micelle sensitization and the applicability to clinical samples will be expected in the near future.

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Table 3 Comparison of proposed method with other methods for L-tyrosine analysis

Analytical method	Determination range (M)	Detection limit(3σ) (M)	Reference
Proposed method	2.5×10^{-7}–7.5×10^{-6}	8.5×10^{-8}	—
Spectrophotometry [a)]	0–6.4×10^{-4}	5.0×10^{-6}	10
Fluorophotometry [b)]	1.1×10^{-7}–1.1×10^{-5}	6.8×10^{-8}	11
Chemiluminescence FIA [C)]	1.0×10^{-8}–1.0×10^{-5}	1.0×10^{-8}	14
Cyclic voltammetry [d)]	1.0×10^{-7}–5.0×10^{-5}	8.0×10^{-8}	16
Microcolumn electrophores [e)]	6.0×10^{-7}–9.0×10^{-5}	2.0×10^{-7}	17
HPLC-FL	5.0×10^{-6}–7.5×10^{-4}	8.0×10^{-7}	18

a) Phenylalanine ammonia-lyase [PAL]/Tris-HCl (pH = 9.5) enzymatic end-point assay system (Microplate).
b) 1,5-Bis(4,6-dicholro-1,3,5-triazinylamino) naphthalene [DTAN]/Sodium citrate-NaOH buffer (pH = 12.0) synthetic reaction system.
c) $KMnO_4$/Sodium polyphosphate (pH = 6.75) oxidation reaction system.
d) Multi-walled carbon nanotubes [MWNTs]/4-aminobenzeresulfonic acid [4-ABSA] film-coated glassy carbon electrode/phosphate(pH = 7.0) electrocatalytic oxidation reaction system.
e) Disodium phosphate (pH = 11.5) containing methanol and acetonitrile microcolumn electrophoresis with the underivatized UV spectrometric detection system.

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