The Application of Diarylamine Compounds in Analytical Chemistry. 1. Fluorescence Reactions among 4-(4-Methyl-2-quinolyl)aminosalicylic Acid, Cobalt(II) and Hydrogen Peroxide, and the Fluorimetry of Cobalt(II) by Using Its Fluorescence Reaction†

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The fluorescence reactions among 4-(4-methyl-2-quinolyl)aminosalicylic acid (MQAS) as a diarylamine compound, hydrogen peroxide as an oxidizing agent, and various metal ions such as cobalt(II) were spectrofluorometrically investigated in the presence or in the absence of various surfactants. The MQAS–hydrogen peroxide solution in the presence of trimethylstearylammonium chloride (STAC) as a cationic surfactant was catalytically converted to a fluorescence product by the coexistence of trace amounts of cobalt(II), and its relative fluorescence intensity at 400 nm in the fluorescence reaction product was proportional to the cobalt(II) concentrations. Moreover, a highly selective and sensitive fluorimetric method for the determination of cobalt(II) using MQAS and hydrogen peroxide in the presence of STAC in basic media was proposed. The calibration graph was linear in the range of 0—45 ng cobalt(II) per 10 cm^3 at an emission wavelength of 400 nm, with an excitation wavelength of 320 nm.

Generally, quinoline derivatives such as 8-quinolinol (Oxine) have been used as the solvent-extraction agents, the extraction photometric reagents, and precipitation agents for a wide variety of metal ions,[1-4] but these quinolinol derivatives are relatively lacking in selectivity and sensitivity. On the other hand, it is well-known[5-9] that diarylamine compounds are converted to polycyclic hetero fluorescence compounds by condensation when an oxidation agent and a metal ion, such as palladium or ultraviolet irradiation are used. Akagi et al., have reported[10,11] that 2-anilino-4-methylquinoline derivatives used as diarylamine compounds and a quinoline compound were relatively unstable for light, heat or acid, and were converted into a strong fluorescence material by using the irradiation of ultraviolet rays with a wavelength such as 254 nm, by heating, by using various redox agents or acids: similarly, the product of polycyclic heteroaromatic, *N*-bridgehead compounds[12-14] such as benzimidazo[1,2-*a*]quinolines[12] were converted by ultraviolet irradiation, or by thermal or acid-catalyzed cyclization.

In recent years, the assays of trace amounts of metal ions using various kinetic and catalytic reaction systems[15-18] have been undertaken and used together in the study of environmental pollution or in assisting in the remarkable development of the semiconductor industry, etc. Moreover, the micellar enhancement effects of the coexistence of surfactants on numerous fluorescence reactions between fluorescence agents and metal ions have been investigated, as have color-development systems, and numerous sensitive fluorometric methods have been reported.[19-21]

In the present investigation, with the aim of determining a new fluorescence agent for the assay of trace-metal ions, systematic fluorescence reactions between various quinoline and arylamine derivatives and metal ions were investigated. We observed that the fluorescence reaction between the 2-anilino-4-methylquinoline derivatives and a redox agent such as hydrogen peroxide was remarkably enhanced by the coexistence of trace amounts of cobalt(II) as an oxidation catalyzer in the liquid-oxidation phase. 2-Anilino-4-methylquinoline derivative was then newly converted to a fluorescence product. Especially, the fluorescence reactions among 4-(4-methyl-2-quinolyl)aminosalicylic acid (MQAS), hydrogen peroxide, and cobalt(II) in the presence of trimethylstearylammonium chloride (STAC) was most clear and gave a large fluorescence intensity; this fluorescence intensity was proportional to the cobalt(II) concentration. Accordingly, a new, sensitive and selective fluorometric method for the determination of cobalt(II) was proposed using the fluorescence reactions.

Experimental

Apparatus and Reagents. Spectrofluorometric measurements were performed on a Hitachi model 3000 recording spectrofluorophotometer with 10-mm silica cells and a xenon-arc source. Hitachi-Horiba F-7AD and F-8 pH meters were used for all the pH measurements.

All the chemicals used were of an analytical-reagent grade. A working cobalt(II) (1.0×10^{-4} mol dm^{-3}) solution was prepared by the dilution of a 1.0×10^{-2} mol dm^{-3} cobalt(II)—stocked solution using cobalt chloride.[22,23] MQAS was synthesized according to 3-(2-quinolyl)aminobenzoic acid[24] synthesis, while a 1.0×10^{-4} mol cm^{-3} MQAS solution was prepared by dissolving MQAS in methyl alcohol. A 1.0×10^{-2} mol dm^{-3} STAC solution was prepared by dissolving STAC (Kishida Chemical Co., Ltd.) in water. A 0.1% hydrogen peroxide solution was prepared by the dilution of 30% hydrogen peroxide (Mitsubishi Gas Chemical Co., Ltd.). A 2.0×10^{-1} mol dm^{-3} boric acid–sodium hydroxide buffer solution (Sörensen buffer solution: pH 10.0) was used for the pH adjustments. Demineralized water was used

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throughout.

Standard Procedure for the Assay of Cobalt(II). To a solution containing 0—45 ng of a cobalt(II) solution in a 10.0-cm³ standard flask, 2.0 cm³ of a borate buffer (pH 10.0), 1.0 cm³ of a 1.0% STAC solution, 0.15 cm³ of a 0.1% hydrogen peroxide solution, and 1.0 cm³ of a 1.0×10^{-4} mol dm^{-3} MQAS solution were added. The mixture was diluted to volume with water (Solution A), kept at 50 °C for 40 min, and then cooled to room temperature (10—25 °C). The relative fluorescence intensities (R.fl.Int.) of Solution A and of the MQAS solution (Solution B), prepared similarly but without cobalt(II) as a reference, were measured at 400 nm (Em), with excitation at 320 nm (Ex).

Results and Discussion

Fluorescence Reaction among Quinoline Derivatives, Redox Agents, and Metal Ions. The fluorescence reactions among such anilino-4-methylquinolines as MQAS (**I**), 4-(4-methyl-2-quinolyl)aminobenzoic acid (**II**), 4-(4-methyl-2-quinolyl)aminobenzene (**III**) as a diarylamine compound, such metal ions as cobalt(II), copper(II), nickel(II), iron(III), manganese(II), zinc(II), and chromium(VI), and such redox agents as hydrogen peroxide were systematically investigated in the absence or presence of STAC as a cationic surfactant. As is shown in Tables 1 and 2, the combination of MQAS and cobalt(II) in the presence of hydrogen peroxide was best, giving a stable and large fluorescence intensity. Moreover, in the fluorescence reaction between MQAS and hydrogen peroxide, the coexistence of trace amounts of cobalt(II) stimulated the formation of fluorescence products; its R.fl.Int. at 400 nm, with the excitation wavelength at 320 nm, was proportional to the cobalt(II) concentration. In addition, the R.fl.Int. at Em 400 nm of fluorescence products from MQAS in the presence of a cationic surfactant such as STAC was more than about three-times as stable as that in the absence of STAC. Although the clarification of the fluorescence products is necessary, a further investigation of the fluorimetry of cobalt(II) was undertaken by using the fluorescence reaction among MQAS, hydrogen peroxide, and cobalt(II) in the presence of STAC.

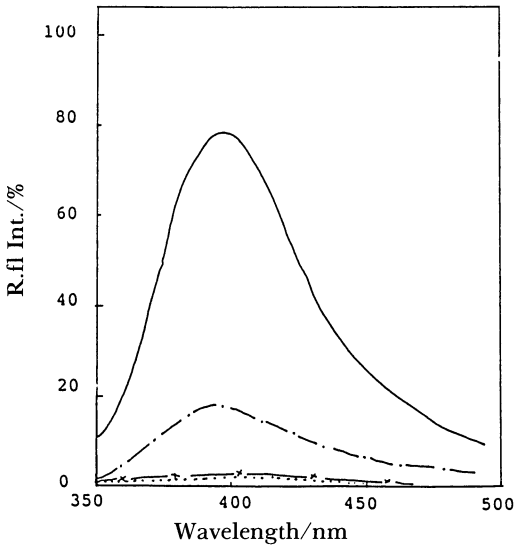

Fig. 1. Emission spectra of MQAS-H_2O_2 and MQAS-H_2O_2-Co(II) solution in the presence or absence of STAC at pH 10.
MQAS; 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; Co(II): 5.0×10^{-8} mol dm^{-3}; Ex: 320 nm. ——: MQAS-H_2O_2-Co(II)-STAC; —X—: MQAS-H_2O_2-STAC; —·—: MQAS-H_2O_2-Co(II); ----: MQAS-H_2O_2.

Fluorimetry of Cobalt(II). Emission and Excitation Spectra. As is shown in Fig. 1, the fluorescence reaction products among MQAS, hydrogen peroxide,

Table 2. Fluorescence Reaction among 4-(4-Methyl-2-quinolyl)aminosalicylic Acid (MQAS), Hydrogen Peroxide, and Various Metal Ions in the Presence of STAC at pH 10

Metal ions	R.fl.Int. at 400 nm/% STAC	
	Absence	Presence
—	1.8	2.5
Co(II)	19.6	77.3
Cu(II)	3.4	5.0
Ni(II)	3.0	6.4
Fe(III)	2.0	8.5
Mn(II)	1.8	2.6
Cr(VI)	1.8	2.6

MQAS: 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; Trimethylstearylammonium chloride (STAC): 0.1%; Metal ion: 1.0×10^{-6} mol dm^{-3}; Ex: 320 nm; R.fl.Int.: relative fluorescence intensity.

Table 1. Fluorescence Reaction among 2-Anilinoquinoline Derivatives, Hydrogen Peroxide, and Cobalt(II) at pH 10

No.	2-Anilino-quinolines	R.fl.Int. /%			
		Em max	R	R-H_2O_2	R-H_2O_2-Co(II)
I	4-(4-Methyl-2-quinolyl)-aminosalicylic acid	400	0.5	1.8	18.5
II	4-(4-Methyl-2-quinolyl)-aminobenzoic acid	390	4.6	5.1	11.1
III	4-(4-Methyl-2-quinolyl)-aminobenzene	390	4.6	4.8	16.7

Co(II): 5.0×10^{-8} mol dm^{-3}; 2-Anilinoquinoline derivatives, Nos. **I**—**III**, R: 10×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; Ex: 320 nm.

and cobalt(II) in the presence of STAC have an emission maximum wavelength at 400 nm and an excitation wavelength at 320 nm, but the MQAS-hydrogen peroxide solution in the absence of STAC scarcely gave the fluorescence phenomena.

As is shown in Fig. 2, the maximum excitation wavelengths of the MQAS-hydrogen peroxide-cobalt(II) solution (Solution A) in the presence of STAC were obtained at 240 nm and 320 nm, with an emission wavelength at 400 nm.

Because the fluorescence reaction among MQAS, cobalt(II), and hydrogen peroxide in the presence of STAC was remarkably affected by irradiation by such ultraviolet rays as 254 nm, the excitation wavelength at 320 nm instead of that at 254 nm was chosen for further experiments.

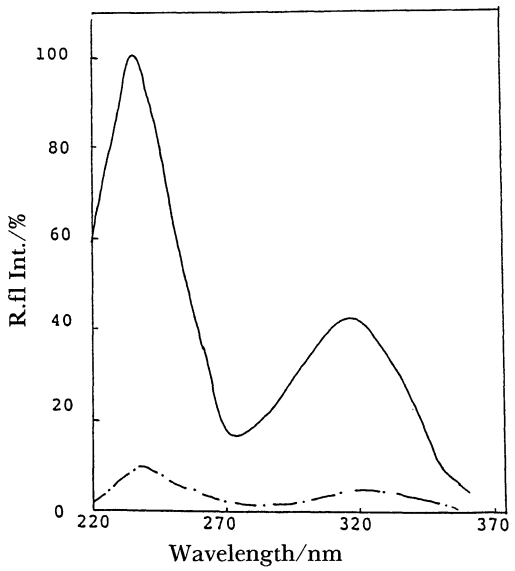

Fig. 2. Excitation spectra of MQAS-H_2O_2 and MQAS-H_2O_2-Co(II) solutions at pH 10.
MQAS: 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; Co(II): 5.0×10^{-8} mol dm^{-3}; Em: 320 nm. —·—: MQAS-H_2O_2; ——: MQAS-H_2O_2-Co(II).

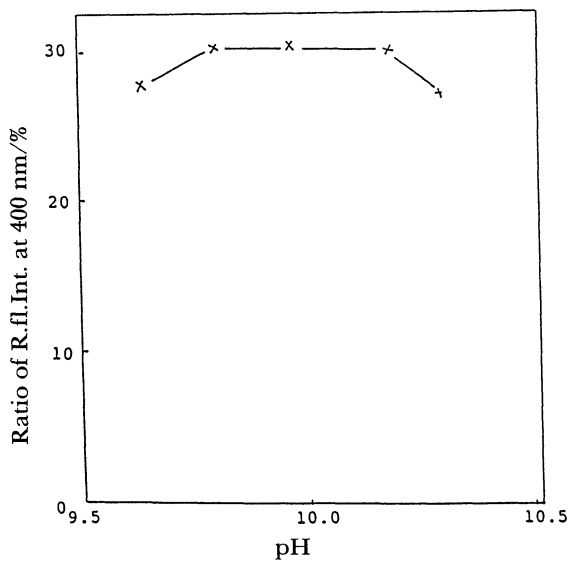

Fig. 3. Effect of pH in the presence of STAC.
MQAS: 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; STAC: 0.1%; Co(II): 5.0×10^{-8} mol dm^{-3}; Ex: 320 nm; Ratio: Ratio of R.fl.Int. of solution A vs. solution B.

Effect of pH. The maximum and almost-constant fluorescence intensity ratio (ratio of R.fl.Int. of the MQAS-hydrogen peroxide-cobalt(II) solution (Solution A) vs. R.fl.Int. of the MQAS-hydrogen peroxide solution (Solution B) at 400 nm was obtained within the limited pH range of 9.8—10.2 using 2.0—3.0 cm^3 of a 2.0×10^{-1} mol dm^{-3} boric acid-sodium hydroxide (Sörensen buffer) solution.

Effect of Redox Agent. The effects of various redox agents were examined by measuring the rate of the R.fl.Int. of the MQAS-redox agent-cobalt(II) solution and the MQAS-redox agent solution. As is shown in Table 3, the R.fl.Int. when hydrogen peroxide was used as the redox agent was largest and gave a reproducible value in various redox agents: hydrogen peroxide, potassium peroxodisulfate, sodium hypochlorite, *N*-bromosuccinimide (NBS), chloramine B, etc. Moreover, the optimum concentration of hydrogen peroxide was finally found to be 0.015% under various conditions—at 50 °C for 20, 40, or 60 min.

Effect of Surfactants. The effects of various surfactants were systematically studied in single or mixed micellar media, using cationic, anionic, amphoteric or nonionic surfactants alone or in combination. The fluorescence intensity of the blank (Solution B), in the presence of a nonionic surfactant, such as poly(*N*-vinylpyrrolidone) (PVP), poly(oxyethylene)-sorbitan monolaurate (Tween 20), and α-(4-(1,1,3,3-tetramethylbutyl)phenyl)-ω-hydroxypoly(oxyethylene) (Triton X 100), or an anionic surfactant such as dodecyl sodium sulfate (SDS) was slightly increased in comparison with that in the presence of sodium *N*-lauroylsarcosine (LS) as an amphoteric surfactant or poly(vinyl alcohol) (PVA) as a nonionic surfactant, or in the absence of these surfactants. Therefore, the ascending effect of the fluorescence intensity of Solution A was relatively small. On the other hand, the rate of R.fl.Int. between Solutions A and B was rela-

Table 3. Effects of Redox Agents

Redox agents	Em	R.fl.Int./%		Ratio[a)]
	nm	R	R-Co(II)	
Hydrogen peroxide	400	5.0	127.6	25.5
Sodium peroxide	400	3.7	48.3	13.1
Potassium peroxodisulfate	395	5.4	5.5	1.0
Sodium hypochlorite	ppt			
Sodium nitrite	395	1.3	1.5	1.2
N-Bromosuccinimide (NBS)	385	2.1	2.1	1.0
Chloramine B	395	2.1	2.1	1.0

MQAS: 1.0×10^{-5} mol dm^{-3}; STAC: 0.1%; Redox agent: 0.06%; pH: 10.0; Co(II): 1.0×10^{-8} mol dm^{-3}. a) Ratio: Ratio of R.fl.Int. of Solution A to Solution B.

Table 4. Effects of Various Surfactants

Surfactant	R.fl.Int. at max Em /%			Ratio[a]
	Em/nm	R	R-Co(II)	
—	395	1.8	18.5	10.3
STAC	400	2.5	77.2	30.9
HTAC	400	2.7	52.8	19.6
DTAC	395	1.5	20.6	13.7
Zp	395	2.4	54.1	22.5
SDS	395	5.3	9.8	1.9
LS	395	2.3	2.5	1.1
PVA(n=2000)	395	1.6	4.9	3.1
PVP(K=30)	405	8.4	11.1	1.3
Tween 20	410	14.5	20.0	1.4
Triton X 100	410	16.6	20.6	1.2

MQAS: 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; pH: 10.0; surfactant: 0.1%; Co(II): 5.0×10^{-8} mol dm^{-3}; Ex: 320 nm. a) Ratio: Ratio of R.fl.Int. of solution to Solution B.

Table 5. Effects of Lighting of Ultraviolet Rays in the Presence or Absence of STAC

No.	Rays	Surfactant	R.fl.Int./%			Ratio[a]
			Em/nm	R	R-Co(II)	
A	UV[b]	STAC	400	3.1	9.7	3.1
	UV[b]	—	395	2.5	5.3	2.2
B	—	STAC	400	1.6	8.0	5.0
	—	—	395	0.6	4.5	7.4
C	—	STAC	400	2.5	77.2	30.9
	—	—	395	1.8	18.5	10.3

MQAS: 1.0×10^{-5} mol dm^{-3}; H_2O_2: 0.015%; STAC: 0.1%; Co(II): 5.0×10^{-8} mol dm^{-3}; pH: 10.0; Ex: 320 nm. a) Ratio: Ratio of R.fl.Int. of solution to Solution B. b) UV, ultraviolet: 254 nm. Nos. A and B: without heating procedure; No. C: standard procedure.

Table 6. Effects of Foreign Ions

Foreign ion	Added			Ratio[a]
	as	μg/10 cm^3	molar ratio	
—	—	—	—	30.9
Fe(III)	Sulfate	0.28	10	26.4
Fe(II)	Sulfate	0.28	10	30.4
		2.79	100	22.5
Mn(II)	Chloride	2.75	100	30.9
Ni(II)	Nitrate	5.87	200	30.9
		29.34	1000	20.0
Cu(II)	Sulfate	0.16	5	23.1
Zn(II)	Chloride	6.54	200	30.9
Al(III)	Nitrate	26.98	2000	30.9
Ti(IV)	Sulfate	0.96	40	30.9
Sn(IV)	Sulfate	2.96	50	30.9
Cr(VI)	Chromate	2.60	100	30.8
Mo(VI)	Molybdate	47.97	1000	30.5
CN^-	Potassium	0.01	1	30.9
		0.13	10	20.5
S^{2-}	Sodium	16.03	1000	29.7
F^-	Sodium	1900	200000	30.5
Citrate	Sodium	10.51	100	30.9

Co(II) taken: 5.0×10^{-8} mol dm^{-3}; H_2O_2: 0.015%; STAC: 0.1%; pH: 10.0; Ex: 320 nm; Em: 400 nm; MQAS: 1.0×10^{-5} mol dm^{-3}. a) Ratio: Ratio of R.fl.Int. of solution to Solution B.

tively large and well reproducible in the presence of a cationic surfactant such as STAC, as is shown in Table 4.

Especially, the coexistence of STAC as a cationic surfactant provided the optimum conditions (STAC, hexadecyltrimethylammonium chloride (HTAC), benzyldimethyltetradecylammonium chloride (Zephiramine, Zp), dodecyltrimethylammonium chloride (DTAC), etc.); its optimum amount was a final concentration of over 0.05%.

Effect of Reagent Concentration. The effect of the concentration of MQAS on the fluorescence reaction was also examined. Although the fluorescence-forming reaction was affected by the MQAS, hydrogen peroxide, and cobalt(II) concentrations, a constant ratio between the R.fl.Int. of Solutions A and B was obtained at a final hydrogen peroxide concentration of 0.015% and at 5.0×10^{-6} mol dm^{-3} over MQAS in the presence of a final STAC concetnraiton of 0.1%. Accordingly, all further investigations were carried using final concentrations of 1.0×10^{-5} mol dm^{-3} MQAS, 0.015% hydrogen peroxide, and 0.1% STAC.

Effects of Temperature and Standing Time. As the fluorescence reaction was based on the kinetic action caused by the coexistence of cobalt(II), this reaction was enormously influenced by the temperature and the heating time. A standing time of over 40 min at 50 °C was optimal, and its fluorescence intensity was stable and well reproducible. Accordingly, the heating at 50 °C for 40 min was used as the procedure for the assay of cobalt(II).

Effects of Ultraviolet Rays. Fluorescence-forming reactions among MQAS, hydrogne peroxide, and cobalt(II) were influenced by ultraviolet rays. As is shown in Table 5, the fluorescence reaction by irradiation of ultraviolet (254 nm) at room temperature (=Condition A) showed a larger intensity than that without lighting at room temperature (=Condition B). However, the fluorescence intensity of a blank (MQAS-hydrogen peroxide solution) under Condition A was also larger than that under Condition B, and the analytical sensitivity under Condition A was inferior to that under Condition B. Accordingly, for the assay of cobalt(II), a proposed standard method (=Condition C) was used without any irradiation.

Calibration Graph and Recovery. The calibration curve for cobalt(II) was linear over the range from 0 to 45 ng of cobalt(II) per 10 cm^3. For 30 ng of cobalt(II) in 10 cm^3, the coefficient of variation, as estimated for 5 replicates, was 1.3%.

Effects of Diverse Ions. The influences of diverse ions on the determination of 5.0×10^{-8} mol dm^{-3} of cobalt(II) (9 ng) were examined. The tolerance limit was taken as the amounts that caused errors of about ±3% in the R.fl.Int. values. Although the coexisten-

ces of copper(II), iron(III), etc. gave negative errors in the presence of a 2-fold or 10-fold excess over cobalt(II), nickel(II), manganese(II), and zinc(II) were permitted in a 100—200-fold excess over cobalt(II). Moreover, aluminium(III), chromium(VI), and molybdenum(VI) did not entirely interfere. Also, almost no anions interfered, although cyanide, iminodiacetate ions gave a negative error when were present in 4-fold excess over cobalt(II). Thus, the proposed method is very selective and sensitive. The results for foreign ions are given in Table 6.

Applications. The proposed fluorimetric method was applied to the assay of cobalt(II) in cyanocobalamine (vitamin B_{12}): the recovery tests were very good (99.5% —104.5%), as good as in previous reports.[22,23]

Conclusion

Firstly, the fluorescence formation reaction among 2-anilinoquinoline, 4-(4-methyl-2-quinolyl)aminobenzoic acid, or MQAS as the diarylamine compound, various metal ions (such as copper(II), cobalt(II), manganese(II), and palladium(II)), and redox agents (such as hydrogen peroxide, sodium hypochlorite, sodium nitrite, chloramine B, NBS, and potassium peroxodisulfate) were systematically investigated. Especially, MQAS as a 2-anilinoquinoline derivative was easily converted to a fluorescence product by an oxidation-reaction using hydrogen peroxide in the coexistence of cobalt(II): its fluorescence intensity was proportional to the concentration of the trace amounts of cobalt(II). In addition, the formation of micellar media using STAC as a cationic surfactant was effective for the fluorescence reaction with MQAS. Although further investigation is necessary, cobalt(II) may be oxidized to cobalt(III) by hydrogen peroxide; probably the formation of a cobalt(III)-peroxo complex and the subsequent oxidation fluorescence reaction is enhanced by the coexistence of cobalt-hydrogen peroxide. As to the composition of the fluorescence product, it was considered that the majority of the fluorescence products may be of the MQAS oxidation type; the formation of quinonimine or quinone derivatives was most common, while the cyclized products of MQAS were very small in quantity; while the fluorescence spectra of the proposed method were obviously distinct from the spectra of the N-bridgehead compounds of diarylamines.[12-14]

Secondly, from a systematic investigation of these fluorescence reactions, a simple, rapid, sensitive, and selective spectrofluorimetry of cobalt(II) was proposed which does not need solvent extraction; the fluorimetry of cobalt(II) was perfected by measuring the ratio of R.fl.Int. to MQAS-hydrogen peroxide-cobalt(II) and MQAS-hydrogen peroxide solutions (Solutions A and B) in the presence of STAC at the emission wavelength of 400 nm and with the excitation wavelength of 320 nm. The calibration graph was linear in the range of 0—45 ng of cobalt(II) per 10 cm^3, and the interference of foreign ions were very small. Moreover, the proposed method was applied to the assay of cyanocobalamine preparations: these results were relatively good.

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