SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDIES OF COMPLEXING OF SOME LANTHANIDE IONS WITH 1, 10-PHENANTHROLINE, ITS 5-METHYL AND 5-NITRO DERIVATIVES, SULFOSALICYLIC ACID, SALICYLIC ACID, AND SALICYLALDEHYDE

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ABSTRACT

SPECTROPHOTOMETRIC AND SPECTROFLUOROMETRIC STUDIES OF COMPLEXING OF SOME LANTHANIDE IONS WITH 1, 10-PHENANTHROLINE, ITS 5-METHYL AND 5-NITRO DERIVATIVES, SULFOSALICYLIC ACID, SALICYLIC ACID, AND SALICYLALDEHYDE

by Bruce D. Powers

Aqueous solutions varying in concentration from 1×10^{-6} M to 1×10^{-4} M of 1, 10-phenanthroline, 5-nitro-1, 10-phenanthroline, 5-methyl-1, 10-phenanthroline, sulfosalicylic acid, salicylic acid, or salicylaldehyde were tested individually as complexing reagents for the following lanthanide ions: La (III), Gd (III), Ho (III), Er (III), Yb (III), Lu (III), and Eu (III), Eu (III) being tested with 1, 10-phenanthroline only. The effect of pH on the absorbance and fluorescence of each reagent solution was examined. The pH of each reagent-lanthanide solution was adjusted to a level where a pH change had the least effect on the absorbance and fluorescence of the reagent solution, still being low enough to keep lanthanide hydroxide formation negligible. Exciting wavelengths tested in fluorescence studies were 265, 297, and 313 mμ. lines from a mercury lamp. There was neither any significant increase nor decrease in absorbance or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to the above reagent solutions. Thus these spectroscopic studies provide no evidence that complexation between the tested lanthanide ions and the organic reagent occurs in aqueous solutions.

Factors which lead to this behavior are: comparatively large size of the lanthanide ions and their unavailability of orbitals for hybrid bonding, the rigid phenanthroline ring system, high dielectric constant of the solvent, and the high amount of stable hydrolysis occurring in dilute aqueous lanthanide ion solutions.

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By

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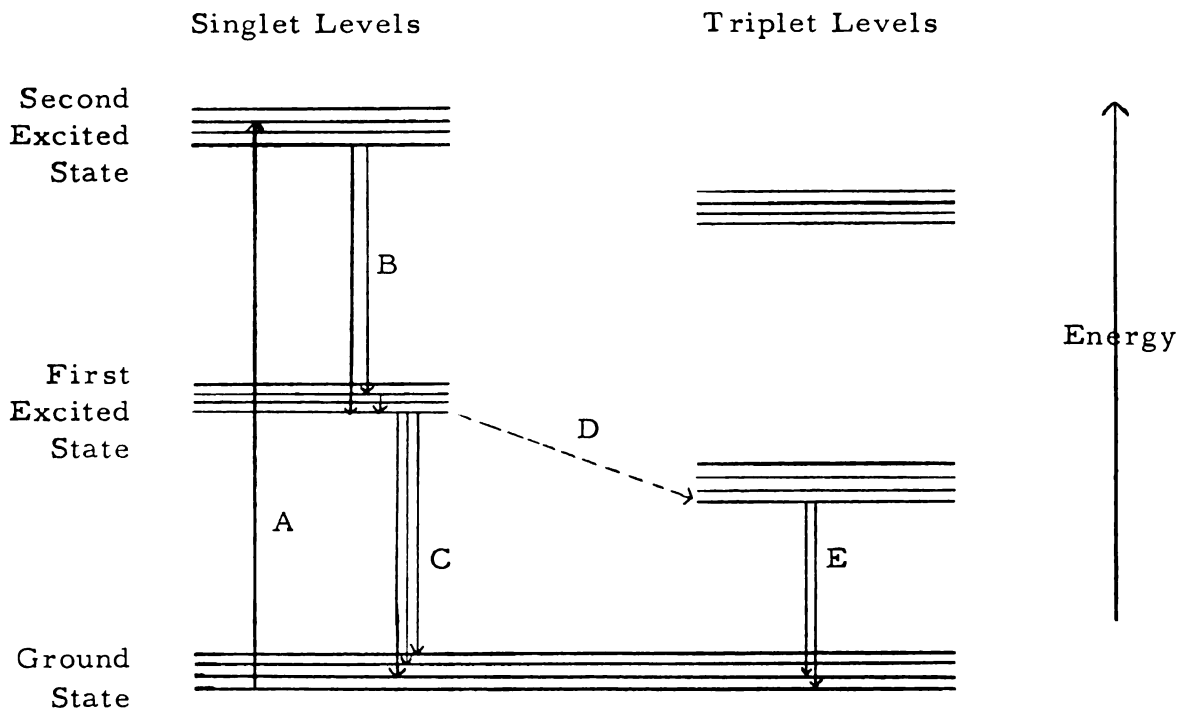
INTRODUCTION

A relatively unentered field to date is the field of fluorometric analysis. When a compound or a complex is excited with relatively high energy radiation, usually ultraviolet radiation, photoluminescence occurs. Photoluminescence is the phenomenon of reemission of radiation after a finite amount of time has elapsed since excitation.

The greatest amount of fluorescence is produced by the exciting monochromatic radiation which is most effectively absorbed by the molecule or complex. After absorption, the energy can be given off by:

1) transfer of kinetic energy to other species,
2) reaction of the excited species with other species in the system,
3) decomposition of the excited species,
4) reemission of energy as light quanta of the same or different wavelength, immediately or after a finite time delay after excitation. The latter is called fluorescence or phosphorexcence.

The difference between phosphorescence and fluorescence is due to the difference in the path that the energy takes in being reemitted. The following is a diagramatic representation of these different paths.



A. . . . A molecule or a group in the molecule in the ground state first absorbs radiant energy and is excited to any one of the excited states; here the second excited state is illustrated. The period of time required is on the order of 1×10^{-12} seconds.

B. . . . Energy may then be given up by any one of many nonradiative transitions, through collisions with encountered species, leaving the molecule or group at the lowest vibrational energy level in the first excited singlet state. This is a singlet $\longrightarrow$ singlet transition.

C. . . . The change shown is a radiative transition to one of the vibrational levels in the electronic ground state. The radiated energy is fluorescence.

D. . . . The transition shown is a radiationless "forbidden" transition of a singlet $\longrightarrow$ triplet type. The triplet state is a metastable state due to the unpairing of electrons normally having paired spins.

E. . . . The metastable triplet state will eventually undergo a triplet $\longrightarrow$ ground state radiative transition. The lifetime of the metastable state is governed by the triplet $\longrightarrow$ singlet transition probability. The radiated energy is phosphorescence.

The exponential expression, $I_f = Q\ I_0\ (1-10^{-abc})$, relates fluorescence intensity I_f to I_0, the incident radiation intensity. In this expression Q, is a proportionality constant whose value depends on the method of measurement and the quantum efficiency, a the absorptivity, b the path length, and c the concentration.

This expression can be transformed to the following exponential series form:

$$I_f = Q\ I_0\ (2.30\ abc - 1.15\ a^2b^2c^2 + 0.38\ a^3b^3c^3 - \ldots)$$

At low concentrations where abc is less than 0.01, the second and third terms become negligible, and the equation resolves to (15, 29, 69):

$$I_f = 2.303\ Q\ I_0\ abc$$

The tripositive lanthanide ions which fluoresce in solution are samarium, europium, terbium, dysprosium, gadolinium, praseodymium, neodymium, cerium, erbium, and lanthanum (42). Lanthanum, gadolinium, and lutetium, with their empty, half full, and full 4f shells, respectively, have a greater tendency to yield fluorescent complexes because the possibility for loss of absorbed energy through intramolecular energy transfer to electrons in these stable 4f configurations is eliminated. When complexed with organic compounds, the lanthanide ions may influence the fluorescence characteristics of the organic reagent.

This project is a part of an investigation of reactions between lanthanide ions and organic reagents, in particular those reagents which form fluorescing complexes (16, 58).

HISTORICAL

Several books which review all phases of fluorescence are available. Most noteworthy is a book by Pringsheim entitled "Fluorescence and Phosphorescence" (42). This book devotes a chapter to lanthanide fluorescence. Another good book is entitled "Fluorescence of Solutions," by Bowen and Wokes (7), which discusses fluorescence theory and fluorescence measurement. A book on the transformation of absorbed radiation into fluorescence light was also written by Bowen and is entitled "The Chemical Aspects of Light" (6).

C. E. White, a worker in the field of fluorescence, reviews the current research in that field every two years for Analytical Chemistry. This series of reviews (60-68) offers a complete listing of references.

One, ten-phenanthroline and its derivatives are just beginning to be used as reagents in aqueous fluorescent analysis. They were tested by Veening and Brandt for the determination of ruthenium (56). The preferred chelating agent, 5-methyl-1, 10-phenanthroline, showed no pH dependence from pH 1 to 13. No fluorescence was noted for 5-nitro-1, 10-phenanthroline. One, ten-phenanthroline was not selected for the greatest amount of research, but was considered to give equally satisfactory results. The investigators concluded that 5-methyl-1, 10-phenanthroline formed a tris complex with ruthenium.

One, ten-phenanthroline and its derivatives have long been known to be complexing agents, and have been used to complex many elements (1, 2, 12, 13, 14, 21, 22, 27, 31, 43, 48, 49, 52, 54, 59, 70). The review by Brandt (8) on complexation with 1, 10-phenanthroline is quite thorough. The complexation of any of the lanthanides by 1, 10-phenanthroline or any of its derivatives was not even mentioned.

Salicylic acid and sulfosalicylic acid are complexing agents in aqueous solution, and have been used to complex many elements (4, 9, 10, 11, 18, 19, 20, 23, 28, 33, 35, 37, 39, 41, 45, 46, 51, 57, 71). Holleck described salicylic acid as a relatively poor complexing agent of europium (26),

but he used sulfosalicylic acid to complex neodymium (24). He also described a colorimetric determination of lanthanides by making a lake of the lanthanides with aurintricarboxylic acid, then adding sulfosalicylic acid to break up the lake to form a colored solution for measurement (25).

Oliver and Fritz made an anionic complex of sulfosalicylic acid with yttrium on an ion exchange column at pH 8-10 (38). Bhattacharya, et al. claimed that a tris complex of Ce(III) was formed with salicylic acid (5).

Very little information is available on the complexation of lanthanides by salicylaldehyde. Kutzmetsova and Sevchenko described luminous complexes formed between a combined reagent of ethylenediamine and salicylaldehyde with europium, samarium or terbium (32). Salicylaldehyde is quite well-known as a complexing agent for other elements (3, 17, 34, 36, 40, 44, 47, 54, 55).

EXPERIMENTAL

Instrumentation

The spectrofluorometer used for this investigation was a modification by Fleck (16) of the instrument constructed by Thommes (53). A block diagram of this instrument is shown in Figure 1. Its components are as follows:

1. The ultraviolet source is a Hanovia S-H high pressure mercury arc lamp powered by a Hanovia 110/120 constant voltage transformer. The mercury lines which were used are the 265, 297, and 303 mμ. lines.

2. The monochromator for the exciting ultraviolet light is a Bausch and Lomb model 33-86-40 grating monochromator. This is attached to the cell compartment by a light tight "0 ring" rubber gasket.

3. The cell compartment is as indicated in Figure 1. Light passes into it from the Bausch and Lomb monochromator through a quartz cylindrical lens. This lens produces a parallel beam of ultraviolet light which illuminates the center of the 20 mm. side of the sample cell.

4. The cells used are a pair of matched clear window silica cells which measure 10 x 20 x 50 mm. These cells were purchased from the Farrand Optical Company. These silica cells are transparent to all ultraviolet radiation used. The cell compartment is made so that the cells are reproducibly positioned within it.

5. To measure the fluorescent light, a Beckman DU with photomultiplier attachment powered by an AC power supply was used. This instrument was modified slightly as indicated in Figure 1,

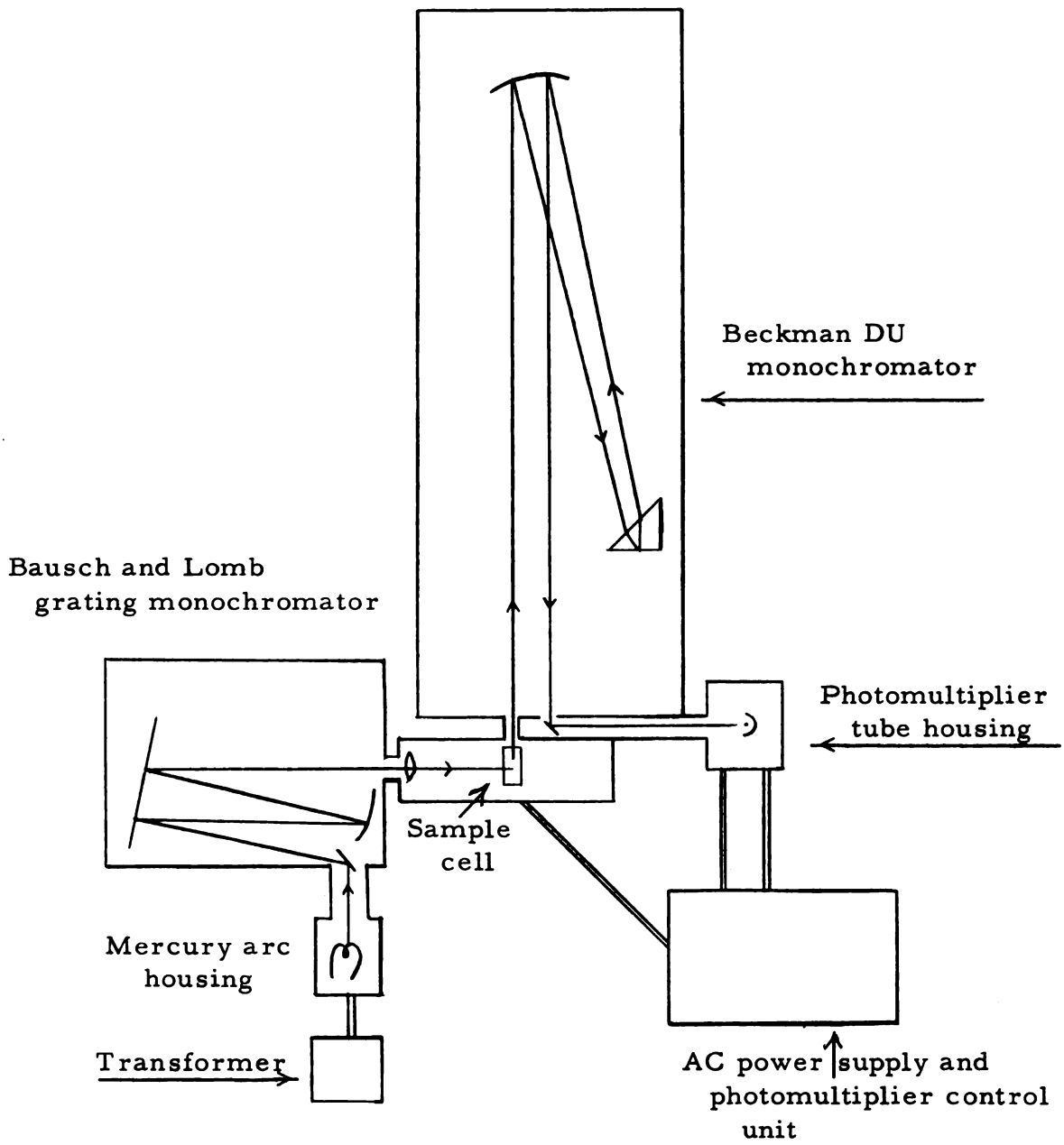


Figure 1. Block Diagram of Spectrofluorometer.

so that the fluorescent light entered from the position the photomultiplier usually occupies and was measured by a photomultiplier at the position usually occupied by the lamp housing.

The spectrophotometer used in absorbance work is a Beckman model DK 2. The cells used with this instrument were matched Beckman 0.988 cm silica cells.

A Beckman model G pH meter equipped with glass-saturated calomel microelectrodes was used in all pH measurements. This instrument was calibrated with a Beckman pH 4 or pH 7 buffer.

The constant temperature bath used was made up of the following components: a Zero Current Relay and a Heater and Circulator for Thermostatic Baths, both by E. H. Sargent and Company of Chicago; controlled by a Princo Magna-Set mercury temperature control, catalogue No. T-260 from Precision Thermometer and Instrument Company.

The light source used for the "Tyndall Effect" was the detached visible light source for the Beckman DU. This was used in a dark room with all other lights out and the solution to be measured silhouetted against a dark background.

Reagents

Ammonium Hydroxide

Baker and Adamson Reagent grade, distilled and stored in a sealed polyethylene bottle.

Ammonium Perchlorate

Baker's Analyzed Reagent.

Dichlorofluorescein

Eastman Kodak White Label.

Erbium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan, labelled purity, 99.9%.

Europium Sesquioxide

Heavy Metals Company, Chattanooga, Tennessee, purity unknown.

Gadolinium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan, labelled purity, 99.9%.

Holmium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan, labelled purity, 99.9%.

Lanthanum Sesquioxide

Heavy Metals Company, Chattanooga, Tennessee, optical grade, 99.9% pure.

Lutetium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan, labelled purity, 99.9%.

Five-methyl-one, ten-phenanthroline

G. F. Smith Chemical Company, Columbus, Ohio, reagent grade.

Five-nitro-one, ten-phenanthroline

G. F. Smith Chemical Company, Columbus, Ohio, reagent grade.

Perchloric Acid

Baker's Analyzed Reagent Grade (70-72%).

One, ten-phenanthroline monohydrate

G. F. Smith Chemical Company, Columbus, Ohio, reagent grade.

Salicylaldehyde

Eastment Kodak White Label. Redistilled under vacuum five times, used immediately.

Salicylic Acid

Unknown source, recrystallized from absolute methyl alcohol.

Sulfosalicylic Acid

Merck and Company, Inc., Rahway, New Jersey, reagent grade.

Water

Distilled water was passed through a "Crystalab Demineralizer" mixed ion exchange column until the meter indicated less than

0.1 ppm. of NaCl, then redistilled from basic solution of potassium permanganate. This treatment was used to make sure all dissolved organic materials were absent.

Ytterbium Sesquioxide

Michigan Chemical Corporation, St. Louis, Michigan, labelled purity, 99.9%.

Preparation of Solutions

Ammonium Hydroxide

Distilled ammonium hydroxide was diluted to approximately 1 N or 0.1 N for pH adjustment of the solutions.

Ammonium Perchlorate

This solution was made by weighing solid ammonium perchlorate and dissolving and diluting to the mark in a volumetric flask to give a 1 M solution.

Dichlorofluorescein

A 0.4 γ per ml. solution was used for standardization of the spectrofluorometer and was made by dissolving the appropriate amount of reagent in 95% ethyl alcohol and diluting to one liter with water.

Lanthanum Perchlorate

Lanthanum sesquioxide was ignited in a platinum crucible at $750^{\circ} \pm 15^{\circ}$ to a constant weight. A calculated amount was then weighed out and placed in a 500 ml. volumetric flask and dissolved in 70-72% perchloric acid. This solution was diluted to 500 ml. and all other solutions were made from this 0.00100 M solution. A solution of gadolinium was also made in the above manner.

Lutetium Perchlorate

Gadolinium Perchlorate

Europium Perchlorate

Ytterbium Perchlorate

Holmium Perchlorate

Erbium Perchlorate

The individual sesquioxides were heated at 750° ± 15° to constant weight. The desired amount of an oxide was weighed out into a volumetric flask and dissolved in the requisite amount of 70-72% perchloric acid. The resulting solution was diluted to the mark. Individual solutions of all of these ions were made so that the final concentrations were 1.0, 0.1, or 0.01 milligrams of the lanthanide sesquioxide per milliliter.

Perchloric Acid

The 70-72% solution of perchloric acid was weighed and diluted to one liter in a volumetric flask to give approximately 5 N, 1 N, or 0.1 N solutions which were used in the adjustment of pH of the various solutions.

One, ten-Phenanthroline and its derivatives

The 1, 10-phenanthroline, 5-methyl-1, 10-phenanthroline and 5-nitro-1, 10-phenanthroline stock solutions were made by placing a weighed amount of the solid reagent to yield a 0.00100 M solution into a 500 ml. volumetric flask, almost filling the flask with redistilled water, heating the flask and contents in a hot water bath to aid dissolution, and diluting to the mark after dissolution had taken place and the solution had been cooled to 25° ± 1°.

A little dilute perchloric acid had to be added to the 5-nitro-1, 10-phenanthroline before dissolution took place.

Salicylaldehyde

This solution was made by weighing out the appropriate amount of reagent, after purification by aspirator distillation five times, into a 500 ml. volumetric flask, adding redistilled water almost to the mark, and then placing the volumetric flask and

contents in a hot water bath to speed up the dissolution. When the reagent had been dissolved and the temperature attained $25^{\circ} \pm 1^{\circ}$, water was added to the mark on the volumetric flask. The concentration, as determined by the weight added, was 0.001275 molar.

Sulfosalicylic Acid

Salicylic Acid

Sulfosalicylic acid and salicylic acid solutions were made by dissolving the appropriate amount of the solid acid in redistilled water in a 500 ml. volumetric flask and diluting to the mark. The final concentration of each was 0.00100 molar.

Experimental Procedures

All experimental work was carried out at room temperature, $26^{\circ} \pm 1^{\circ}$. If the room temperature deviated from this range the flasks containing solutions were placed in the constant temperature bath maintained at $25^{\circ} \pm .02^{\circ}$ for a minimum of one-half hour before making measurements.

Method of sample preparation

Each sample was made by adding 5.00 ml. of the organic reagent solution by pipet, and 5.00 ml. of the lanthanide solution by pipet to a 50.00 ml. glass stoppered volumetric flask. The sample was then diluted to 41-47 ml. with redistilled water added from a separatory funnel equipped with a "Teflon" stopcock. To adjust the solution to the desired pH, the sample was then placed in a 50 ml. beaker, a small "Teflon" covered stirring bar was added. At this point the pH meter electrodes were introduced, and the magnetic stirrer turned on. Minute amounts of acid and/or base were added from medicine droppers with finely drawn

tips until the desired pH was approximated. The resulting solution was returned to the volumetric flask and the sample was diluted to the mark. Exact pH was measured after at least one hour had elapsed in order to make sure that equilibrium had been established.

Method of fluorescence measurement

All measurements of fluorescence in results described in this thesis were made on the spectrofluorometer described on Figure 1. The Beckman DU, its AC Power Supply, and the mercury arc lamp were turned on at least one hour, generally two hours before use to insure a complete warm-up of the instrument. The selector knob on the DU was set to 0.1, the photomultiplier sensitivity knob set on full position, and the monochromator entrance and exit slits set to 2.0 mm. slit width unless otherwise designated.

Standardization was achieved, after allowing time for the instrument to warm up, by placing the 0.4γ/ml. dichlorofluorescein in the silica reference cell in the sample compartment, setting the DU slit width at 0.5 mm. slit, the percent T knob at 50% T, the wavelength scale at 540 mμ., and the exciting wavelength dial at 265 mμ. The shutter was opened, and the sensitivity knob on the DU was then turned until the instrument was at the null position. After this standardization, the instrument was considered "standardized" for a period of about one-half hour. The instrument was then ready for use in fluorescence measurement.

Method of absorbance measurement

All absorbance measurements were made on the Beckman DK 2. Standard operating procedure was used at all times.

Method of pH measurement

A Beckman model G pH meter equipped with glass-saturated calomel micro electrodes was used in all pH measurements. This meter was allowed to warm up for ten to fifteen minutes, then standardized by the use of a Beckman pH 4 or pH 7 buffer solution. When exact measurement of pH was desired, the solution was placed in the enclosed shielded sample compartment. After two to four minutes the pH was read and recorded to the nearest 0.01 pH unit.

EXPERIMENTAL RESULTS AND DISCUSSION

One, ten-Phenanthroline

Absorption spectra for 3×10^{-5} M 1, 10-phenanthroline in 0.1 M NH_4ClO_4, with changing pH were recorded. Figure 2 shows spectra for solutions of pH 3.41 and pH 7.02. A slight shift in the absorbance maximum from 271 mμ. to 264 mμ. is apparent. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table I lists the absorbances of the lanthanide-1, 10-phenanthroline solutions. In each case the blank contained everything the sample solutions contained, with the exception of the lanthanide ion.

Fluorescence spectra for 3×10^{-5} M 1, 10-phenanthroline in 0.1 M NH_4ClO_4 excited by 265 mμ. radiation were recorded and are shown on Figure 3. The fluorescence intensity, I_f, maximum is very close to 420 mμ. for all solutions of pH 4 or less and changes to close to 365 mμ. for all solutions of pH 6 or greater. The fluorescence spectra of this reagent solution containing lanthanide ions were also recorded. Table II lists the fluorescence intensities of the lanthanide-1, 10-phenanthroline solutions.

There is a slight change in the absorbance of ytterbium giving an indication of complexation but this change does not seem to be directly dependent upon concentration. The 5.07×10^{-5} M stock solution shows 0.01 absorbance at 270 mμ. A difference was not noted when the fluorescence spectra of the ytterbium-1, 10-phenanthroline solutions were compared with those of blank solutions.

There was neither any significant increase nor decrease in absorbances or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion additions to 1, 10-phenanthroline reagent solutions. The only exception is ytterbium mentioned above.

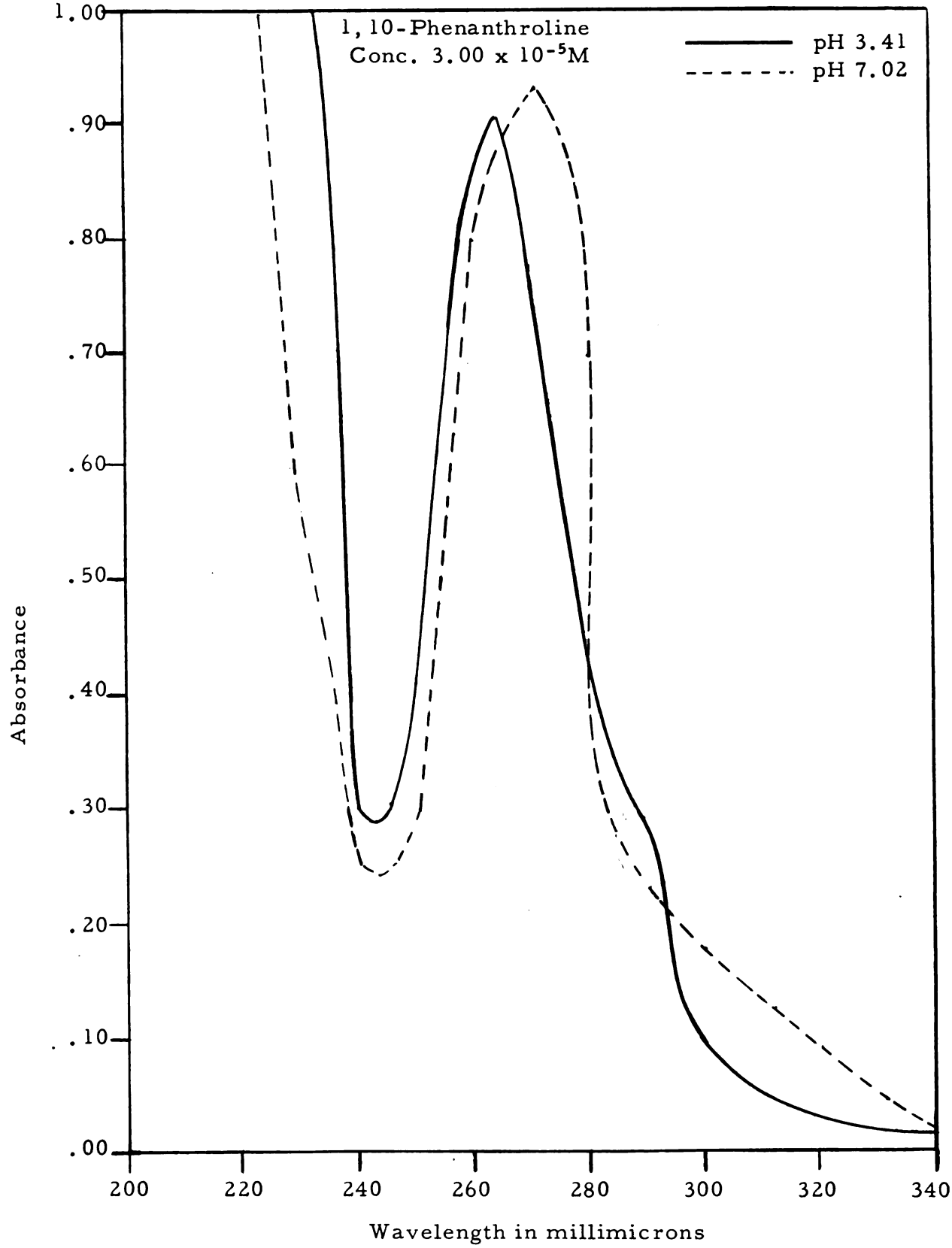


Figure 2. Absorbance Spectra of 1, 10-Phenanthroline at pH 3.41 and pH 7.02.

Table I. Absorbances of Solutions Containing Lanthanide Ions and 1, 10-Phenanthroline

Lanthanide		1, 10-Phenanthroline	Solution		Blank		Absorbance
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance	Maximum in mμ.
La^{+3}	4.00×10^{-6}	3.00×10^{-5}	5.27	0.860	5.43	0.845	265
"	"	"	5.70	0.865	6.01	0.860	"
"	"	"	6.60	0.880	6.60	0.865	"
"	1.00×10^{-4}	1.00×10^{-4}	5.57	1.000	5.52	1.000	286**
"	"	"	6.90	1.000	6.59	1.000	" **
Gd^{+3}	5.52×10^{-6}	3.00×10^{-5}	4.86	0.860	4.47	0.870	269
"	"	"	7.29	0.900	7.02	0.890	265
"	"	"	7.77	0.910*	7.52	0.900	"
"	5.52×10^{-5}	"	6.00	0.895	6.01	0.865	"
"	"	"	6.45	0.905	6.60	0.870	"
Lu^{+3}	5.03×10^{-6}	"	5.14	0.860	5.43	0.845	"
"	"	"	5.74	0.890	6.01	0.865	"
"	"	"	6.54	0.910	6.60	0.870	"
"	5.03×10^{-5}	"	5.46	0.880	5.43	0.845	"
"	"	"	5.95	0.900	6.01	0.865	"
"	"	"	6.38	0.910	6.60	0.870	"
Yb^{+3}	5.07×10^{-6}	"	5.49	0.900	5.03	0.910	270
"	"	"	5.99	0.670	6.01	0.600	275
"	"	"	6.53	0.660	6.60	0.580	"
"	5.07×10^{-5}	"	5.03	0.800	5.03	0.800	"
"	"	"	5.52	0.700	5.43	0.650	"
"	"	"	6.23	0.830	6.01	0.800	270

* Precipitate formed

** Shoulder

Continued

Table I - Continued

Lanthanide		1, 10-Phenanthroline	Solution		Blank		Absorbance
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance	Maximum in mμ.
Eu^{+3}	5.68×10^{-6}	3.00×10^{-5}	5.43	0.860	5.43	0.845	265
"	"	"	6.15	0.890	6.01	0.865	"
"	"	"	6.61	0.885	6.60	0.865	"
"	5.68×10^{-5}	"	5.45	0.860	5.43	0.845	"
"	"	"	5.90	0.870	6.01	0.865	"
"	"	"	6.75	0.890	6.60	0.865	"
Ho^{+3}	5.28×10^{-6}	"	5.82	0.860	5.43	0.845	"
"	"	"	5.96	0.870	6.01	0.865	"
"	"	"	6.37	0.880	6.60	0.865	"
"	5.28×10^{-5}	"	5.50	0.855	5.43	0.845	"
"	"	"	6.59	0.880	6.60	0.865	"
"	"	"	6.63	0.885	6.60	0.865	"
Er^{+3}	5.24×10^{-6}	"	5.40	0.855	5.43	0.845	"
"	"	"	5.90	0.870	6.01	0.865	"
"	"	"	6.37	0.885	6.60	0.865	"
"	5.24×10^{-5}	"	5.22	0.845	5.43	0.845	"
"	"	"	5.86	0.870	6.01	0.865	"
"	"	"	6.32	0.875	6.60	0.865	"

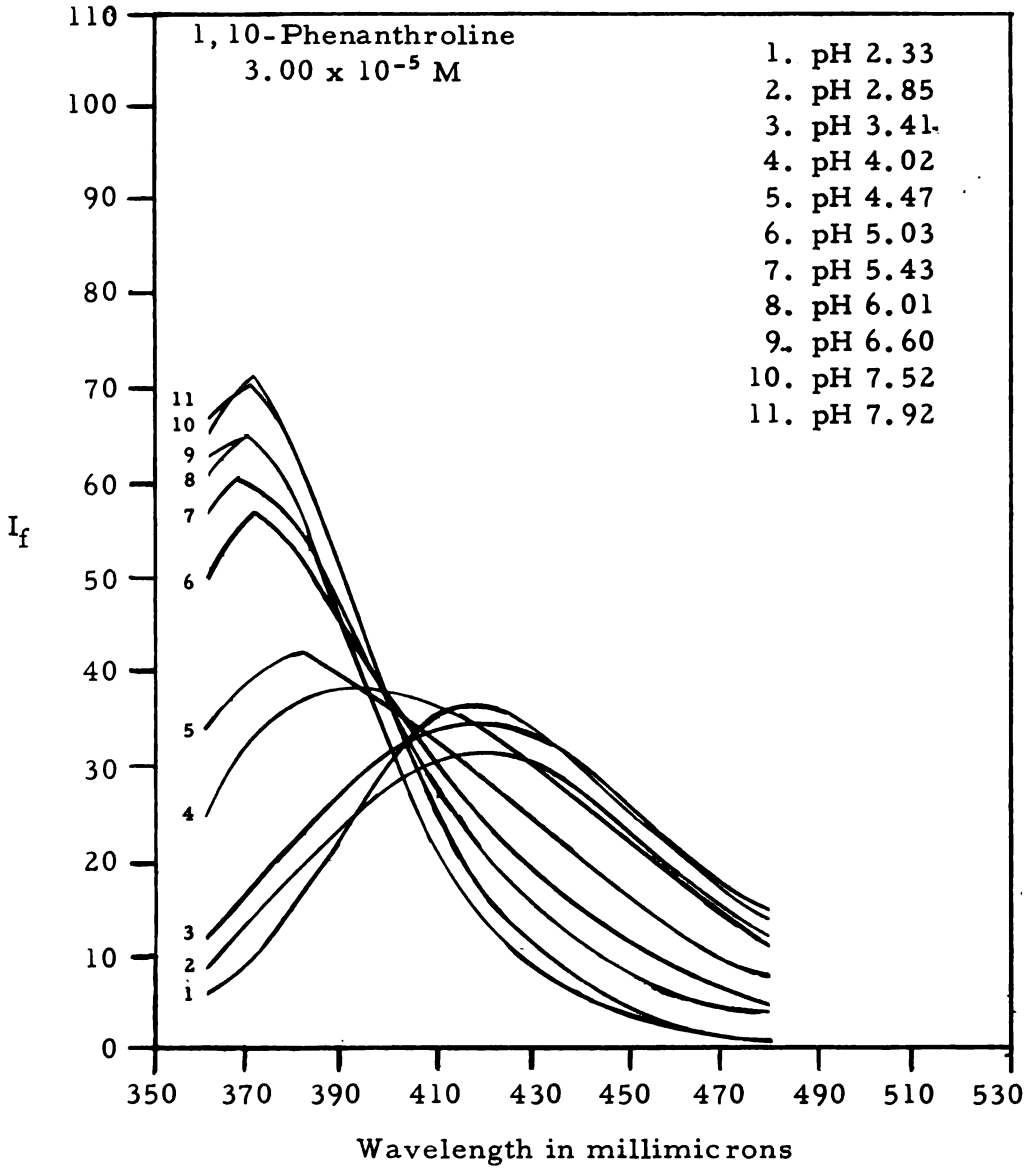


Figure 3. Fluorescence Spectra of 1, 10-Phenanthroline.

Table II. Fluorescence Intensities of Solutions Containing Lanthanide Ions and 1, 10-Phenanthroline

Lanthanide		1, 10-Phenanthroline	Solution		Blank	
Ion	Conc. M	Conc. M	pH	I_f max.	pH	I_f max.
La^{+3}	4.00×10^{-6}	3.00×10^{-5}	5.20	63.5	5.43	60.5
"	"	"	6.13	77.5	6.01	71.0
"	"	"	6.57	76.5	6.60	70.0
"	1.00×10^{-4}	1.00×10^{-4}	5.57	11.5	5.52	12.0**
"	"	"	6.90	13.5	6.59	14.0**
"	"	"	7.66	20.0	7.55	15.5**
Gd^{+3}	5.52×10^{-6}	3.00×10^{-5}	4.86	39.5	4.47	42.5
"	"	"	7.29	69.5	7.52	64.5
"	"	"	7.77	75.0*	7.92	64.5
"	5.52×10^{-5}	"	6.00	74.5	6.01	71.0
"	"	"	6.45	76.0	6.60	70.0
Lu^{+3}	5.03×10^{-6}	"	5.14	54.0	5.03	56.5
"	"	"	5.74	70.5	6.01	71.0
"	"	"	6.54	74.0	6.60	70.0
"	5.03×10^{-5}	"	5.45	65.0	5.43	60.5
"	"	"	5.94	67.0	6.01	71.0
"	"	"	6.38	69.5	6.60	70.0
Yb^{+3}	5.07×10^{-6}	"	5.49	56.5	5.43	60.5
"	"	"	5.99	64.0	6.01	71.0
"	"	"	6.53	68.5	6.60	70.0
"	5.07×10^{-5}	"	5.03	49.0	5.03	56.5
"	"	"	5.52	64.5	5.43	60.5
"	"	"	6.23	70.0	6.01	71.0

* Precipitate formed
** 1.5 mm. slit width

Continued

Table II - Continued

Lanthanide Ion	Lanthanide Conc. M	1, 10-Phenanthroline Conc. M	Solution pH	Solution I_f max.	Blank pH	Blank I_f max.
Eu^{+3}	5.68×10^{-6}	3.00×10^{-5}	5.43	57.5	5.43	60.5
"	"	"	6.15	70.0	6.01	71.0
"	"	"	6.61	71.5	6.60	70.0
"	5.68×10^{-5}	"	5.45	57.5	5.43	60.5
"	"	"	5.90	65.5	6.01	71.0
"	"	"	6.75	72.0	6.60	70.0
Ho^{+3}	5.28×10^{-6}	"	5.82	72.0	6.01	71.0
"	"	"	5.96	74.0	6.01	71.0
"	"	"	6.37	67.5	6.60	70.0
"	5.28×10^{-5}	"	5.50	63.0	5.43	60.5
"	"	"	6.09	68.0	6.01	71.0
"	"	"	6.63	69.0	6.60	70.0
Er^{+3}	5.24×10^{-6}	"	5.40	62.0	5.43	60.5
"	"	"	5.90	70.5	6.01	71.0
"	"	"	6.37	77.0	6.60	70.0
"	"	"	5.22	63.5	5.43	60.5
"	"	"	5.86	78.5	6.01	71.0
"	"	"	6.32	74.5	6.60	70.0

Five-Nitro-one, ten-Phenanthroline

Absorption spectra for 1 x 10^{-4} M 5-nitro-1, 10-phenanthroline in 0.1 M NH_4ClO_4 with changing pH were recorded. Figure 4 shows spectra for solutions of pH 1.98 and pH 7.09. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table III lists the absorbances of the lanthanide-5-nitro-1, 10-phenanthroline solutions. In each case the blank contained everything the sample solution contained, with the exception of the lanthanide ion.

There was no fluorescence detected for 5-nitro-1, 10-phenanthroline solutions, either as the reagent solution or as the reagent solution containing lanthanide ions. Four exciting wavelengths were tested as follows: 265, 297, 313, and 365 mμ. The entire region from just above the exciting wavelength through the entire visible region was scanned with the instrument "wide open."

There was neither any significant increase nor decrease in absorbances nor any change in the shape of the absorbance spectra due to lanthanide ion additions to 5-nitro-1, 10-phenanthroline reagent solutions.

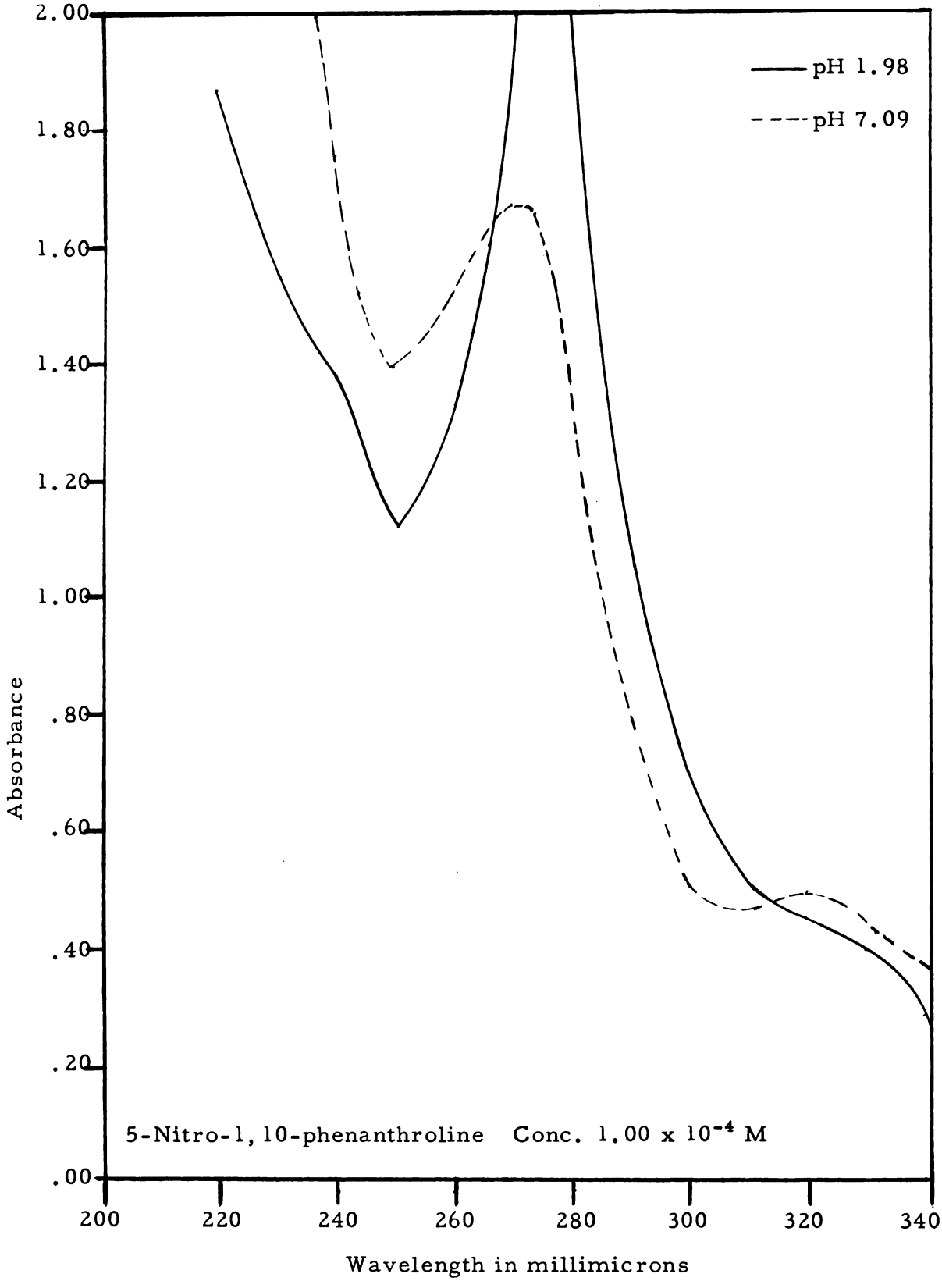


Figure 4. Absorbance Spectra of 5-Nitro-1, 10-phenanthroline at pH 1.98 and pH 7.09.

Table III. Absorbances of Solutions Containing Lanthanide Ions and 5-Nitro-1, 10-phenanthroline.

Lanthanide		5-Nitro-1, 10-Phen.	Solution		Blank		Absorbance
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance	maximum in mμ.
La^{+3}	1.00×10^{-4}	1.00×10^{-4}	1.20	1.000	1.09	1.000	292
"	"	"	7.07	1.670	7.09	1.670	270
Gd^{+3}	5.52×10^{-5}	"	1.98	1.000	1.98	1.000	292
"	"	"	7.07	1.640	7.09	1.670	270
Lu^{+3}	5.03×10^{-5}	"	2.01	0.950	1.98	1.000	292
"	"	"	6.84	1.630	7.09	1.670	270
Yb^{+3}	5.07×10^{-5}	"	1.95	0.950	1.98	1.000	292
"	"	"	7.00	1.610	7.09	1.670	270
Ho^{+3}	5.28×10^{-5}	"	1.92	0.980	1.98	1.000	292
"	"	"	6.93	1.630	7.09	1.670	270
Er^{+3}	5.24×10^{-5}	"	1.93	0.950	1.98	1.000	292
"	"	"	6.68	1.665	7.09	1.670	270

Five-Methyl-one, ten-Phenanthroline

Absorption spectra for 1.00×10^{-4} M 5-methyl-1, 10-phenanthroline in 0.1 M NH_4ClO_4 with changing pH were recorded. Figure 5 shows spectra for solutions of pH 1.90 and pH 8.05. At the high concentration used for fluorescence there was very little pH dependence noted, including the minimum at 245 mμ. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table IV lists the absorbances of the lanthanide-5-methyl-1, 10-phenanthroline solutions at the 245 mμ. minimum. In each case the blank contained everything the sample solution contained with the exception of the lanthanide ion.

Fluorescence spectra for 1.00×10^{-4} M 5-methyl-1, 10-phenanthroline in 0.1 M NH_4ClO_4 excited by 313 mμ. radiation with changing pH were recorded and are shown on Figure 6. The I_f maximum is at 349 mμ. The fluorescence spectra of this reagent solution containing lanthanide ions were also recorded. Table V lists the fluorescence intensities of the lanthanide-5-methyl-1, 10-phenanthroline solutions.

There was neither any significant increase nor decrease in absorbance or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to 5-methyl-1, 10-phenanthroline reagent solutions.

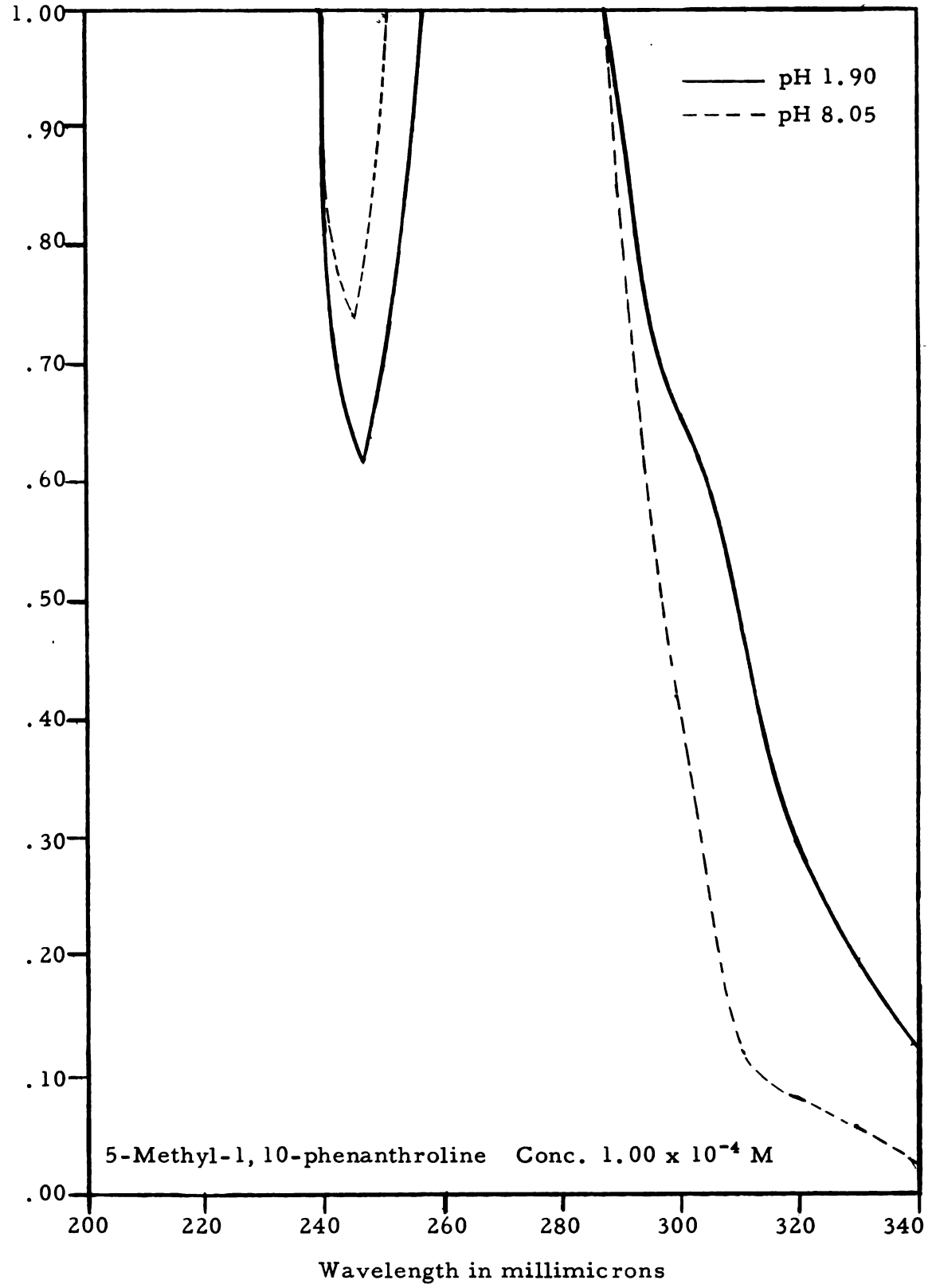


Figure 5. Absorbance Spectra of 5-Methyl-1, 10-phenanthroline at pH 1.90 and pH 8.05.

Table IV. Absorbances of Solutions Containing Lanthanide Ions and 5-Methyl-1, 10-Phenanthroline

Lanthanide		5-Methyl-1, 10-Phenanthroline	Solution		Blank	
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance
La^{+3}	4.00×10^{-6}	1.00×10^{-4}	2.71	0.630	2.93	0.630
"	"	"	8.79	0.760	8.05	0.740
"	1.00×10^{-4}	"	1.30	0.630	1.90	0.630
"	"	"	8.38	0.790	9.10	0.750
Gd^{+3}	5.52×10^{-6}	"	2.26	0.610	2.93	0.630
"	"	"	8.70	0.730	8.05	0.740
"	5.52×10^{-5}	"	2.64	0.610	2.93	0.630
"	"	"	8.66	0.745	9.10	0.750
Lu^{+3}	5.03×10^{-5}	"	2.14	0.610	1.90	0.630
"	"	"	8.67	0.730	8.05	0.740
"	5.03×10^{-5}	"	2.41	0.605	1.90	0.630
"	"	"	8.29	0.735	8.05	0.740
Yb^{+3}	5.07×10^{-6}	"	2.19	0.605	1.90	0.630
"	"	"	8.67	0.730	8.05	0.740
"	5.07×10^{-5}	"	2.94	0.600	2.93	0.630
"	"	"	8.37	0.780	8.05	0.740
Ho^{+3}	5.28×10^{-6}	"	2.60	0.595	2.93	0.630
"	"	"	8.65	0.730	8.05	0.740
"	5.28×10^{-5}	"	2.95	0.595	2.93	0.630
"	"	"	8.48	0.785	8.05	0.740
Er^{+3}	5.24×10^{-6}	"	2.67	0.590	2.93	0.630
"	"	"	8.52	0.740	8.05	0.740
"	5.24×10^{-5}	"	2.87	0.600	2.93	0.630
"	"	"	8.56	0.810*	8.05	0.740

*Precipitate formed

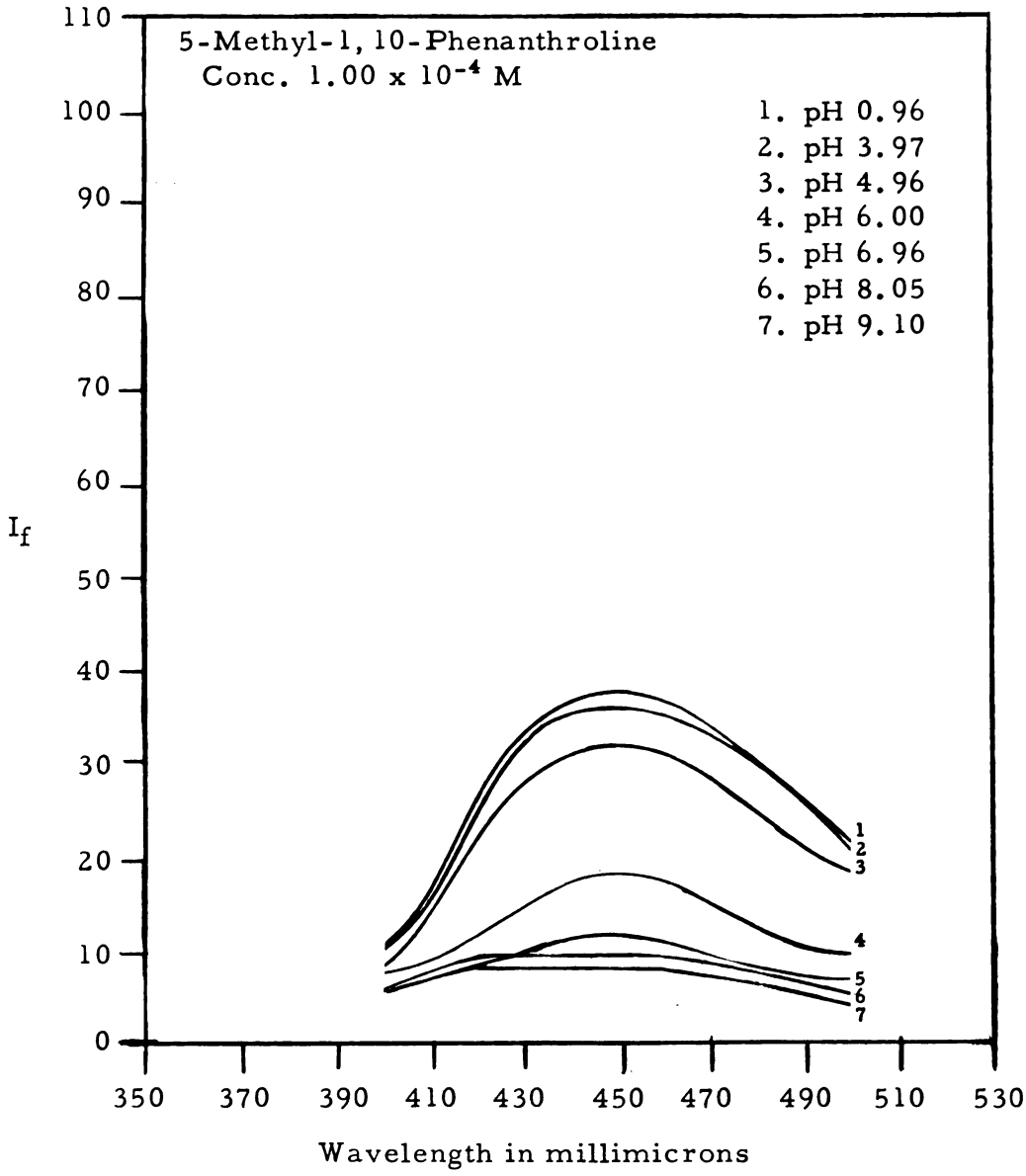


Figure 6. Fluorescence Spectra of 5-Methyl-1, 10-phenanthroline.

Table V. Fluorescence Intensities of Solutions Containing Lanthanide Ions and 5-Methyl-1, 10-phenanthroline

Lanthanide		5-Methyl-1, 10-Phenanthroline	Solution		Blank	
Ion	Conc. M	Conc. M	pH	I_f max.	pH	I_f max.
La^{+3}	4.00×10^{-6}	1.00×10^{-5}	2.71	39.5	2.93	37.5
"	"	"	8.79	10.5	8.05	9.0
"	1.00×10^{-4}	"	1.30	39.5	1.90	37.5
"	"	"	8.38	11.5	8.05	9.0
Gd^{+3}	5.52×10^{-6}	"	2.26	38.0	2.93	37.5
"	"	"	8.70	9.5	8.05	9.0
"	5.52×10^{-5}	"	2.64	39.5	2.93	37.5
"	"	"	8.66	9.5	8.05	9.0
Lu^{+3}	5.03×10^{-6}	"	2.14	39.0	2.93	37.5
"	"	"	8.67	9.5	8.05	9.0
"	5.03×10^{-5}	"	2.41	40.0	2.93	37.5
"	"	"	8.37	11.0	8.05	9.0
Yb^{+3}	5.07×10^{-6}	"	2.19	39.0	1.90	37.5
"	"	"	8.67	9.5	8.05	9.0
"	5.07×10^{-5}	"	2.94	39.5	2.93	37.5
"	"	"	8.37	11.0	8.05	9.0
Ho^{+3}	5.28×10^{-6}	"	2.60	39.5	2.93	37.5
"	"	"	8.65	10.0	8.05	9.0
"	5.28×10^{-5}	"	2.95	39.5	2.93	37.5
"	"	"	8.48	10.0	8.05	9.0
Er^{+3}	5.24×10^{-6}	1.00×10^{-4}	2.67	39.5	2.93	37.5
"	"	"	8.52	10.0	8.05	9.0
"	5.24×10^{-5}	"	2.87	39.0	2.93	37.5
"	"	"	8.56	9.5*	8.05	9.0

* Precipitate formed.

Sulfosalicylic Acid

Absorption spectra for 1.00×10^{-4} M sulfosalicylic acid with changing pH were recorded. Figure 7 shows spectra for solutions of pH 0.95 and pH 4.94. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table VI lists the absorbances of the lanthanide-sulfosalicylic acid solutions at the 245 mμ. maximum. In each case the blank contained everything the sample solution contained with the exception of the lanthanide ion.

Fluorescence spectra for 1.00×10^{-4} M sulfosalicylic acid excited by 313 mμ. radiation using a 1.0 mm. exit slit were recorded and are shown in Figure 8. I_f maximum is very close to 452 mμ. for all solutions of pH 1 or less and changes to close to 410 mμ. for all solutions of pH 5 or greater. The fluorescence spectra of this reagent solution containing lanthanide ions were recorded. Table VII lists the fluorescence intensities of the lanthanide-sulfosalicylic acid solutions.

Due to precipitate formation in aqueous solutions of sulfosalicylic acid solutions containing the lanthanide ion, complexation was thought to be present. All such solutions above pH 6.5 formed a precipitate which settled down or remained suspended. It was assumed that the settled precipitates would be similar to the precipitates which remained dispersed and might be a solid complex of some type. A quantity of test solution was centrifuged, and portions of the precipitate were tested with strong acid and 95% ethyl alcohol. A lanthanide hydroxide is soluble in strong acid, and insoluble in ethyl alcohol. Sulfosalicylic acid is soluble in ethyl alcohol and if a complex was being precipitated, it is presumed that it, too, would be soluble in ethyl alcohol. The portions of the precipitate tested were soluble in strong acid and insoluble in ethyl alcohol. This test may not be absolutely conclusive, but it is indicative that the precipitate is the lanthanide hydroxide.

Some fluorescence quenching occurs in solutions in which the concentration of the lanthanide ion is high and the pH is approximately 6 or higher. This quenching was believed to be due to complexation. Therefore, experiments were performed with Gd(III) in which the mole ratios of reagent to lanthanide ion were varied from 1000/2 to 1/2. The final concentration of sulfosalicylic acid in the test solutions was 1.00×10^{-4} M and that of Gd(III) started at 2.00×10^{-7} M and was increased to 2.00×10^{-4} M. pH was maintained close to 7 since this appeared to be close to the pH which yielded the highest quenching. Precipitation was visually observed in the more concentrated solutions. Solutions in which a solid precipitate had not been observed, were tested for the "Tyndall Effect." Light scattering was observed in all solutions from 2.00×10^{-7} M to 2.00×10^{-4} M in Gd(III), starting with a slight amount of light scattering and increasing with concentration. Later a slight amount of light scattering was observed in a Gd(III) stock solution. It is concluded that the quenching is due to light scattered by lanthanide hydroxide formed at the high pH.

There was neither any significant increase nor decrease in absorbance or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to sulfosalicylic acid reagent solutions.

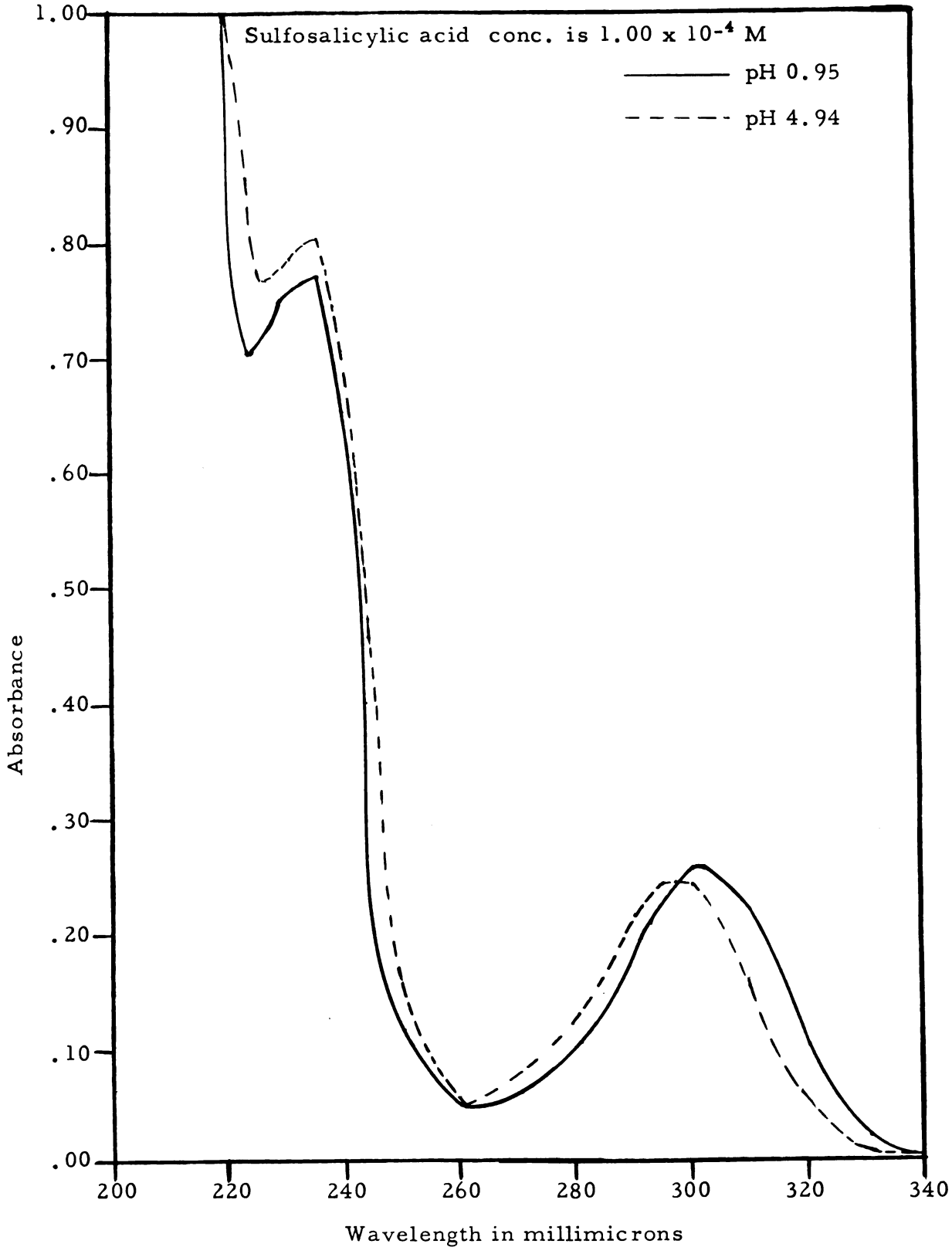


Figure 7. Absorbance Spectra of Sulfosalicylic Acid at pH 0.95 and pH 4.94.

Table VI. Absorbances of Solutions Containing Lanthanide Ions and Sulfosalicylic Acid

Lanthanide		Sulfosalicylic Acid	Solution		Blank	
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance
La^{+3}	4.00×10^{-6}	1.00×10^{-4}	1.38	0.400	0.95	0.400
"	"	"	4.65	0.440	4.94	0.430
"	"	"	7.47	0.440	7.30	0.440
"	1.00×10^{-4}	"	1.11	0.400	0.95	0.400
"	"	"	3.40	0.440	3.84	0.440
"	"	"	7.68	0.440	7.30	0.440
Gd^{+3}	5.52×10^{-6}	"	1.14	0.400	0.95	0.400
"	"	"	5.34	0.420	4.94	0.430
"	"	"	6.98	0.450	7.30	0.440
"	5.52×10^{-5}	"	1.33	0.400	0.95	0.400
"	"	"	4.67	0.430	4.94	0.430
"	"	"	7.31	0.470*	7.30	0.440
Lu^{+3}	5.03×10^{-6}	"	1.24	0.360	0.95	0.400
"	"	"	5.41	0.410	4.94	0.430
"	"	"	6.40	0.430	6.35	0.450
"	5.03×10^{-5}	"	1.25	0.390	0.95	0.400
"	"	"	5.11	0.430	4.94	0.430
"	"	"	6.57	0.500*	6.35	0.450
Yb^{+3}	5.07×10^{-6}	"	1.27	0.380	0.95	0.400
"	"	"	5.01	0.410	4.94	0.430
"	"	"	6.38	0.430	6.35	0.450
"	5.07×10^{-5}	"	1,29	0.360	0.95	0.400
"	"	"	5.39	0.430	4.94	0.430
"	"	"	6.56	0.730*	6.35	0.450

* Precipitate formed.

Continued

Table VI - Continued

Lanthanide Ion	Lanthanide Conc. M	Sulfosalicylic Acid Conc. M	Solution pH	Solution Absorbance	Blank pH	Blank Absorbance
Ho^{+3}	5.28×10^{-6}	1.00×10^{-4}	1.28	0.380	0.95	0.400
"	"	"	4.81	0.400	4.94	0.430
"	"	"	6.21	0.410	6.35	0.450
"	5.28×10^{-5}	"	1.32	0.380	0.95	0.400
"	"	"	4.77	0.430	4.94	0.430
"	"	"	6.51	0.590*	6.35	0.450
Er^{+3}	5.24×10^{-6}	"	1.33	0.360	0.95	0.400
"	"	"	5.07	0.400	4.94	0.430
"	"	"	6.11	0.440	6.35	0.450
"	5.24×10^{-5}	"	1.31	0.430	0.95	0.400
"	"	"	4.99	0.440	4.94	0.430
"	"	"	5.78	0.480	5.98	0.450

* Precipitate formed.

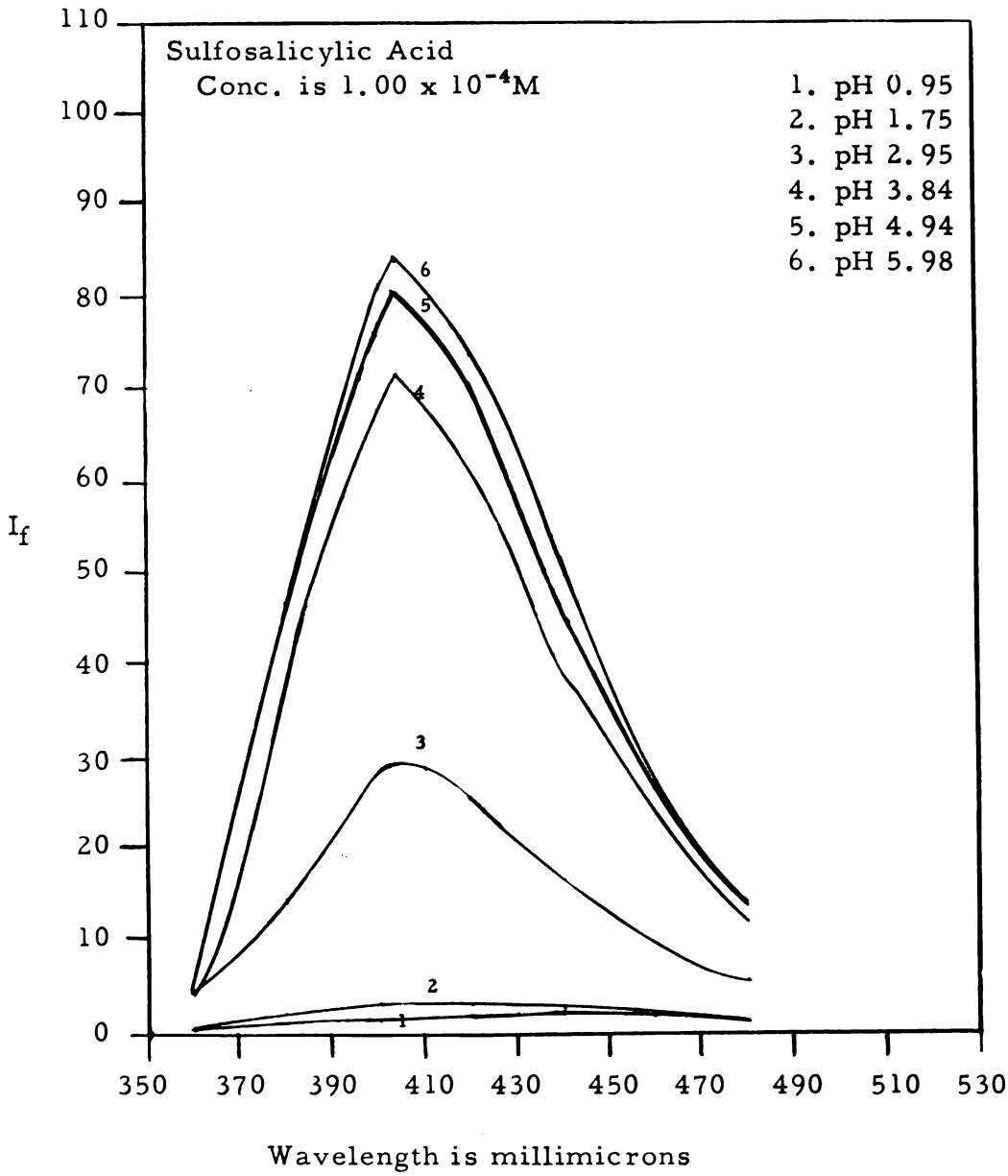


Figure 8. Fluorescence Spectra of Sulfosalicylic Acid.

Table VII. Fluorescence Intensities of Solutions Containing Lanthanide Ions and Sulfosalicylic Acid

Lanthanide		Sulfosalicylic Acid	Solution		Blank		I_f
Ion	Conc. M	Conc. M	pH	I_f max.	pH	I_f max.	max. mμ.
La^{+3}	4.00×10^{-6}	1.00×10^{-4}	1.01	76.5	0.93	76.0	452
"	"	"	4.65	82.0	4.94	81.0	403
"	"	"	7.47	84.0	7.30	80.5	"
"	1.00×10^{-4}	"	0.87	76.0	0.93	76.0	452
"	"	"	3.40	69.5	3.84	71.0	403
"	"	"	7.68	81.5	7.30	80.5	"
Gd^{+3}	5.52×10^{-6}	"	0.87	73.0	0.93	76.0	452
"	"	"	5.34	81.5	4.94	81.0	403
"	"	"	6.98	79.0	7.30	80.5	"
"	5.52×10^{-5}	"	0.97	79.5	0.93	76.0	452
"	"	"	4.67	76.5	4.94	81.0	403
"	"	"	7.31	50.5	7.30	80.5	"
Lu^{+3}	5.03×10^{-6}	"	0.95	79.5	0.93	76.0	452
"	"	"	5.41	78.5	4.94	81.0	403
"	"	"	6.40	81.0	6.35	79.0	"
"	5.03×10^{-5}	"	0.97	77.0	0.93	76.0	452
"	"	"	5.11	78.5	4.94	81.0	403
"	"	"	6.57	54.5	6.35	79.0	"
Yb^{+3}	5.07×10^{-6}	"	0.95	79.5	0.93	76.0	452
"	"	"	5.01	83.5	4.94	81.0	403
"	"	"	6.38	82.5	6.35	79.0	"
"	5.07×10^{-5}	"	0.95	79.5	0.93	76.0	452
"	"	"	5.39	78.5	4.94	81.0	403
"	"	"	6.56	16.5*	6.35	79.0	"

* Precipitate formed.

Continued

Table VII - Continued

Lanthanide Ion	Lanthanide Conc. M	Sulfosalicylic Acid Conc. M.	Solution pH	Solution I_f max.	Blank pH	Blank I_f max.	I_f max. mμ.
Ho^{+3}	5.28×10^{-6}	1.00×10^{-4}	0.95	78.0	0.93	76.0	452
"	"	"	4.81	77.5	4.94	81.0	403
"	"	"	6.21	71.5	6.35	79.0	"
"	5.28×10^{-5}	"	0.92	79.5	0.93	76.0	452
"	"	"	4.77	66.5	4.94	81.0	403
"	"	"	6.51	26.5*	6.35	79.0	"
Er^{+3}	5.24×10^{-6}	"	0.90	79.5	0.93	76.0	452
"	"	"	5.07	77.0	4.94	81.0	403
"	"	"	6.11	73.0	6.35	79.0	"
"	5.24×10^{-5}	"	0.94	79.5	0.93	76.0	452
"	"	"	4.99	64.5	4.94	81.0	403
"	"	"	5.78	54.0*	5.98	84.5	"

Salicylic Acid

Absorption spectra for 1.00×10^{-4} M salicylic acid with changing pH were recorded. Figure 9 shows spectra for solutions of pH 0.67 and pH 4.84. The absorbance maximum is very close to 302 mμ. for all solutions of pH 2 or less and changes to close to 295 mμ. for all solutions of pH 4 or greater. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table VIII lists the absorbances of the lanthanide-salicylic acid solutions. In each case the blank contained everything the sample solution contained with the exception of the lanthanide ion.

Fluorescence spectra for 1.00×10^{-4} M salicylic acid excited by 313 mμ. radiation with changing pH were recorded and are shown on Figure 10. I_f maximum is very close to 452 mμ for all solutions of pH 1 or less and changes to close to 410 mμ. for all solutions of pH 5 or greater. The fluorescence spectra of this reagent solution containing lanthanide ions were recorded. Table IX lists the fluorescence intensities of the lanthanide-salicylic acid solutions.

There was neither any significant increase nor decrease in absorbance nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to salicylic acid reagent solutions. There is a decrease in fluorescence intensities on adding lanthanide ion to reagent solutions but the fluorescence intensity does not vary with concentration of the lanthanide ion.

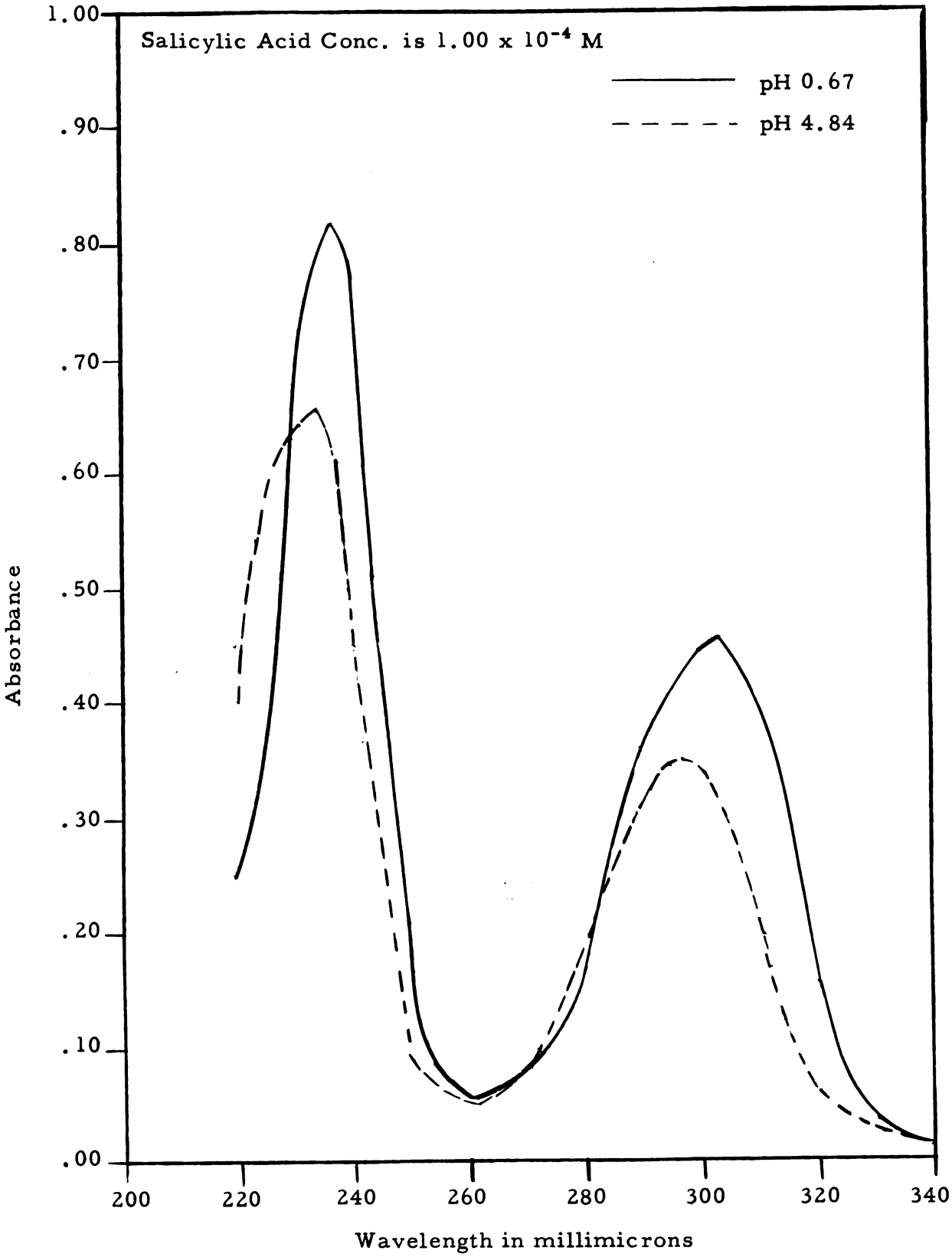


Figure 9. Absorbance Spectra of Salicylic Acid at pH 0.67 and pH 4.84.

Table VIII. Absorbances of Solutions Containing Lanthanide Ions and Salicylic Acid

Lanthanide		Salicylic Acid	Solution		Blank		Absorbance
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance	max. in mμ.
La^{+3}	4.00×10^{-6}	1.00×10^{-4}	1.05	0.830	0.67	0.820	237
"	"	"	4.74	0.660	4.84	0.650	232
"	"	"	7.40	0.660	6.73	0.650	"
"	1.00×10^{-4}	"	1.05	0.820	0.67	0.820	237
"	"	"	3.67	0.650	4.34	0.650	232
"	"	"	7.44	0.650	6.73	0.650	"
Gd^{+3}	5.52×10^{-6}	"	1.10	0.830	0.67	0.820	237
"	"	"	5.70	0.650	5.35	0.650	232
"	"	"	7.30	0.650	6.73	0.650	"
"	5.52×10^{-5}	"	1.06	0.830	0.67	0.820	237
"	"	"	5.41	0.650	5.35	0.650	232
"	"	"	7.11	0.650	6.73	0.650	"
Lu^{+3}	5.03×10^{-6}	"	1.04	0.820	0.67	0.820	237
"	"	"	5.65	0.650	4.34	0.650	232
"	"	"	6.80	0.650	6.73	0.650	232
"	5.03×10^{-5}	"	1.02	0.830	0.67	0.820	237
"	"	"	6.28	0.650	6.73	0.650	232
"	"	"	7.20	0.650	6.73	0.650	232
Yb^{+3}	5.07×10^{-6}	"	0.94	0.820	0.67	0.820	237
"	"	"	4.45	0.650	4.34	0.650	232
"	"	"	7.10	0.650	6.73	0.650	232
"	5.07×10^{-5}	"	0.93	0.810	0.67	0.820	237
"	"	"	5.33	0.660	5.35	0.650	232
"	"	"	7.10	0.670	6.73	0.650	232

Continued

Table VIII - Continued

Lanthanide Ion	Lanthanide Conc. M	Salicylic Acid Conc. M	Solution pH	Solution Absorbance	Blank pH	Blank Absorbance	Absorbance max. in mμ.
Ho^{+3}	5.28×10^{-6}	1.00×10^{-4}	0.95	0.810	0.67	0.820	237
"	"	"	5.64	0.650	5.35	0.650	232
"	"	"	6.44	0.650	6.73	0.650	232
"	5.28×10^{-5}	"	0.93	0.820	0.67	0.820	237
"	"	"	5.60	0.660	5.35	0.650	232
"	"	"	6.70	0.660	6.73	0.650	232
Er^{+3}	5.24×10^{-6}	"	0.91	0.810	0.67	0.820	237
"	"	"	5.13	0.650	5.35	0.650	232
"	"	"	7.01	0.650	6.73	0.650	232
"	5.24×10^{-5}	"	0.94	0.800	0.67	0.820	237
"	"	"	5.17	0.650	5.35	0.650	232
"	"	"	5.94	0.650	5.35	0.650	232

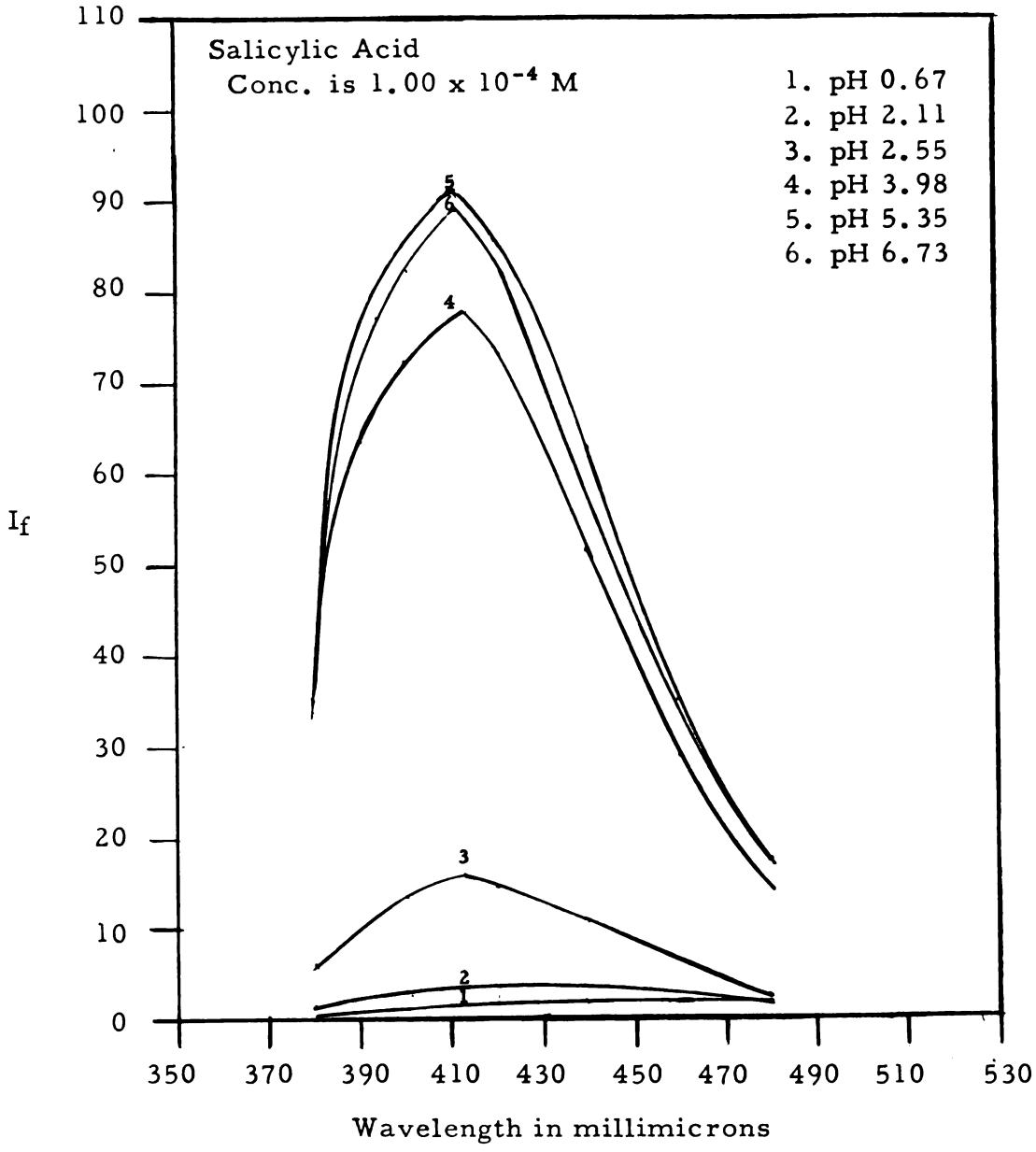


Figure 10. Fluorescence Spectra of Salicylic Acid.

Table IX. Fluorescence Intensities of Solutions Containing Lanthanide Ions and Salicylic Acid

Lanthanide Ion	Lanthanide Conc. M	Salicylic Acid Conc. M	Solution pH	Solution I_f max.	Blank pH	Blank I_f max.	I_f max. in mμ.
La^{+3}	4.00×10^{-6}	1.00×10^{-4}	0.67	40.5	0.67	47.5	450
"	"	"	4.74	80.0	4.84	88.5	410
"	"	"	7.40	80.0	6.73	89.0	"
"	1.00×10^{-4}	"	1.05	40.5	0.67	47.5	450
"	"	"	3.67	66.0	3.98	78.0	410
"	"	"	7.44	76.5	6.73	89.0	"
Gd^{+3}	5.52×10^{-6}	"	1.10	41.0	0.67	47.5	450
"	"	"	5.70	77.0	5.35	91.0	410
"	"	"	7.30	78.5	6.73	89.0	"
"	5.52×10^{-5}	"	1.06	39.5	0.67	47.5	450
"	"	"	5.41	80.0	5.35	91.0	410
"	"	"	7.11	72.5	6.73	80.0	"
Lu^{+3}	5.03×10^{-6}	"	1.02	39.0	0.67	47.5	450
"	"	"	5.65	79.5	5.35	91.0	410
"	"	"	6.80	78.0	6.73	89.0	"
"	5.03×10^{-5}	"	1.04	39.0	0.67	47.5	450
"	"	"	6.28	80.5	6.73	89.0	410
"	"	"	7.20	76.5	6.73	89.0	410
Yb^{+3}	5.07×10^{-6}	"	0.94	44.5	0.67	47.5	450
"	"	"	4.45	89.0	4.84	88.5	410
"	"	"	7.10	89.0	6.73	89.0	"
"	5.07×10^{-5}	"	0.93	44.0	0.67	47.5	450
"	"	"	5.33	86.0	5.35	91.0	410
"	"	"	7.10	32.0	6.73	89.0	"

Continued

ıble IX - Continued

Lanthanide Ion	Conc. M	Salicylic Acid Conc. M	Solution pH	Solution I_f max.	Blank pH	Blank I_f max.	I_f max. in mμ.
Ho^{+3}	5.28×10^{-6}	1.00×10^{-4}	0.95	44.0	0.67	47.5	450
"	"	"	5.64	88.5	5.35	91.0	410
"	"	"	6.44	90.5	6.73	89.0	"
"	5.28×10^{-5}	"	0.93	44.0	0.67	47.5	450
"	"	"	5.60	83.5	5.35	91.0	410
"	"	"	6.70	66.0	6.73	89.0	"
Er^{+3}	5.24×10^{-6}	"	0.91	42.5	0.67	47.5	450
"	"	"	5.13	82.0	5.35	91.0	410
"	"	"	7.01	83.5	6.73	89.0	"
"	5.24×10^{-5}	"	0.94	42.5	0.67	47.5	450
"	"	"	5.17	81.5	5.35	91.0	410
"	"	"	5.93	82.0	5.35	91.0	"

Salicylaldehyde

Absorption spectra for 1.275×10^{-4} M salicylaldehyde with changing pH were recorded. Figure 11 shows a spectrum for a solution at pH 3.91. Absorption spectra of this reagent solution containing lanthanide ions were also recorded. Table X lists the absorbances of the lanthanide-salicylaldehyde solutions at the 255 mμ. maximum. In each case the blank contained everything the sample solution contained with the exception of the lanthanide ion.

Fluorescence spectra for 1.275×10^{-4} M salicylaldehyde excited by 313 mμ. radiation with changing pH were recorded and are shown on Figure 12. The I_f maximum is at 510 mμ. The fluorescence spectra of this reagent solution containing lanthanide ions were recorded. Table XI lists the fluorescence intensities of the lanthanide-salicylaldehyde solutions.

There was neither any significant increase nor decrease in absorbance or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to salicylaldehyde reagent solutions.

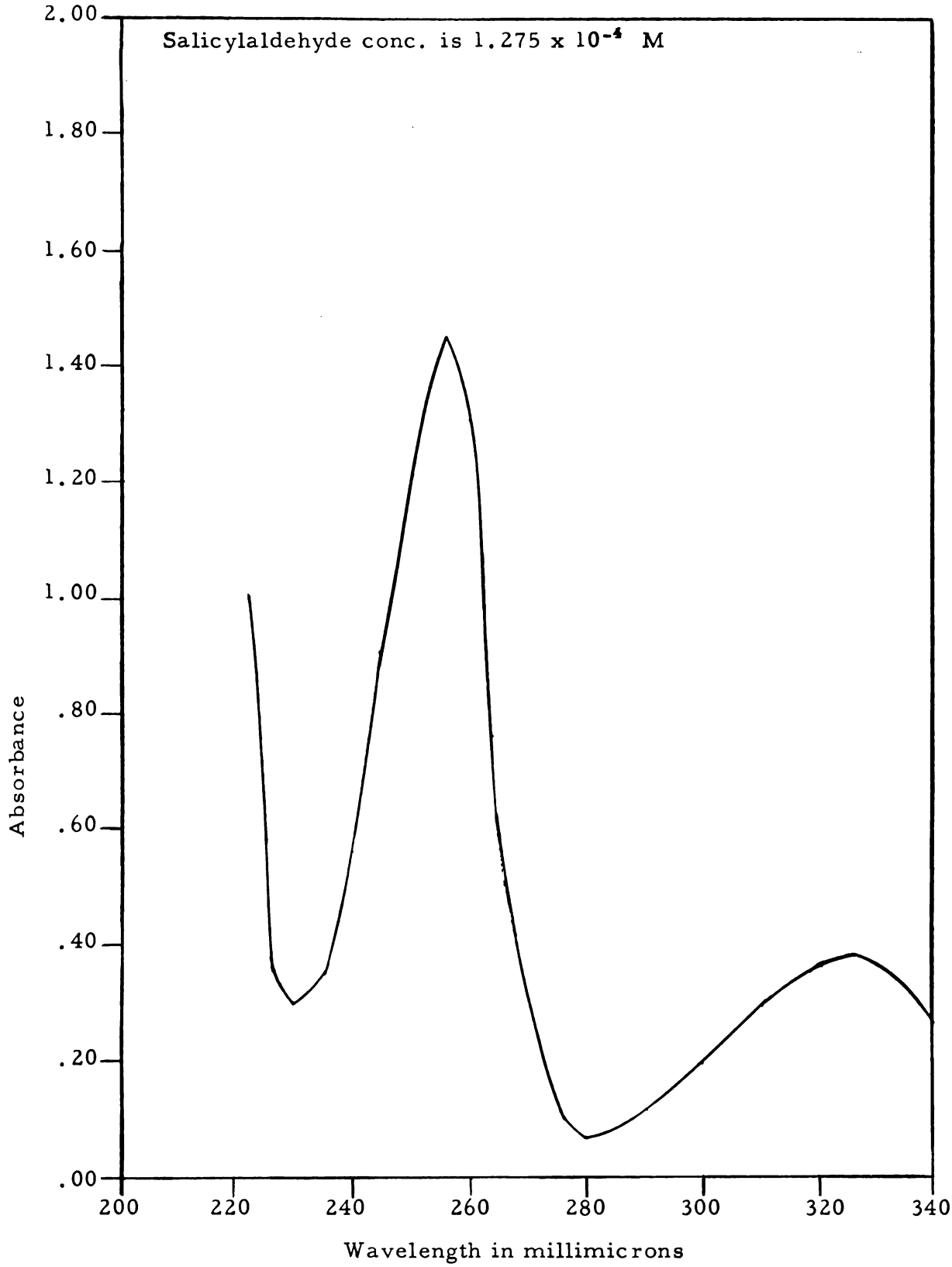


Figure 11. Absorbance Spectrum of Salicylaldehyde at pH 3.91.

Table X. Absorbances of Solutions Containing Lanthanide Ions and Salicylaldehyde

Lanthanide		Salicylaldehyde	Solution		Blank	
Ion	Conc. M	Conc. M	pH	Absorbance	pH	Absorbance
La^{+3}	4.00×10^{-6}	1.275×10^{-4}	4.37	1.52	3.91	1.44
"	1.00×10^{-4}	"	3.44	1.47	3.91	1.44
Gd^{+3}	5.52×10^{-6}	"	4.37	1.50	3.91	1.44
"	5.52×10^{-5}	"	4.33	1.47	3.91	1.44
Lu^{+3}	5.03×10^{-6}	"	4.64	1.50	3.91	1.44
"	5.03×10^{-5}	"	4.11	1.49	3.91	1.44
Yb^{+3}	5.07×10^{-6}	"	4.32	1.49	3.91	1.44
"	5.07×10^{-5}	"	4.43	1.47	3.91	1.44
Ho^{+3}	5.28×10^{-6}	"	3.94	1.51	3.91	1.44
"	5.28×10^{-5}	"	4.16	1.47	3.91	1.44
Er^{+3}	5.24×10^{-6}	"	3.85	1.50	3.91	1.44
"	5.24×10^{-5}	"	4.21	1.47	3.91	1.44

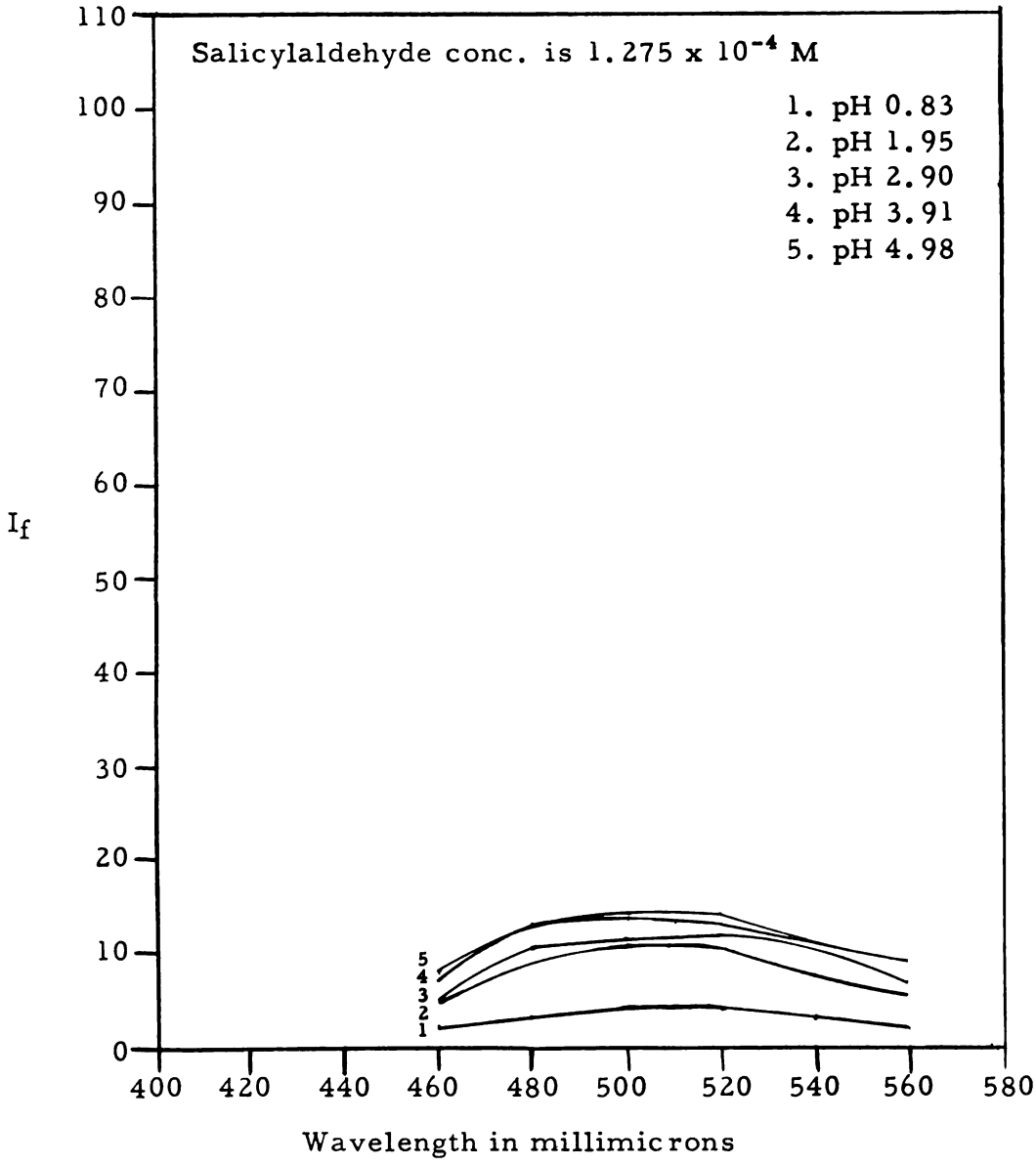


Figure 12. Fluorescence Spectra of Salicylaldehyde.

Table XI. Fluorescence Intensities of Solutions Containing Lanthanide Ions and Salicylaldehyde

Lanthanide		Salicylaldehyde	Solution		Blank	
Ion	Conc. M	Conc. M	pH	I_f max.	pH	I_f max.
La^{+3}	4.00×10^{-6}	1.275×10^{-4}	4.37	13.0	3.91	13.0
"	1.00×10^{-4}	"	3.44	12.5	3.91	13.0
Gd^{+3}	5.52×10^{-6}	"	4.37	12.5	3.91	13.0
"	5.52×10^{-5}	"	4.33	12.0	3.91	13.0
Lu^{+3}	5.03×10^{-6}	"	4.64	12.0	3.91	13.0
"	5.03×10^{-5}	"	4.11	11.5	3.91	13.0
Yb^{+3}	5.07×10^{-6}	"	4.32	11.5	3.91	13.0
"	5.07×10^{-5}	"	4.43	12.0	3.91	13.0
Ho^{+3}	5.28×10^{-6}	"	3.94	11.5	3.91	13.0
"	5.28×10^{-5}	"	4.16	12.5	3.91	13.0
Er^{+3}	5.24×10^{-6}	"	3.85	12.0	3.91	13.0
"	5.24×10^{-5}	"	4.21	12.5	3.91	13.0

CONCLUSIONS

Aqueous solutions varying in concentration from 1 x 10^{-6} M to 1 x 10^{-4} M of 1, 10-phenanthroline, 5-nitro-1, 10-phenanthroline, 5-methyl-1, 10-phenanthroline, sulfosalicylic acid, salicylic acid, or salicylaldehyde were tested individually as complexing reagents for the following lanthanide ions: La (III), Gd (III), Ho (III), Er (III), Yb (III), Lu (III), and Eu (III). (Eu (III) being tested with 1, 10-phenanthroline only.) The effect of pH on the absorbance and fluorescence of each reagent solution was examined. The pH of each reagent-lanthanide solution was adjusted to that level where, a pH change had the least effect on the absorbance and fluorescence of the reagent solution, and the pH was still low enough so that the lanthanide hydroxides did not form to any discernable extent. The exciting wavelengths tested in the fluorescence studies were the 265, 297 and 313 mμ. lines from a mercury lamp. There was neither any significant increase nor decrease in absorbance or fluorescence intensities nor any change in the shape of either the absorbance or fluorescence spectra due to lanthanide ion addition to the above reagent solutions. Thus the spectroscopic studies provide no evidence that complexation between the tested lanthanide ions and the organic reagents occurs in aqueous solutions.

It is generally recognized (30, 50) that lanthanide ions form ionic complexes. Factors limiting the complexation of the lanthanide ions are: (a) the spatial unavailability of 4f orbitals for hybridization in the formation of strong covalent bonds, (b) the comparatively large size of the ions which limits the space into which they can fit for close contact with the complexing species.

The fused phenanthroline ring is quite a rigid structure in which there is little or no possibility of change in the distance between the 1, 10 nitrogens. An inorganic ion of compatible radius can be complexed. If an ion is too large, no complexation can occur. A well-known example of metal ion complexation with 1, 10-phenanthroline is that of Fe (III).

Its ionic radius is 0.64 Å. The radius of La (III) is 1.16 Å (30). This difference in size accounts for the difference in complexating behavior with the phenanthrolines tested.

The 1, 10-phenanthroline, 5-nitro-1, 10-phenanthroline, and 5-methyl-1, 10-phenanthroline reagents contain a small partially negative charge on the 1, 10 nitrogens due to the unbonded electrons. In the two derivatives, this effect is enhanced by the positive inductive effect of the 5-methyl group and inhibited by the negative inductive effect of the 5-nitro group. On the basis of this basicity, complexation with the lanthanides might be expected. Since complexation apparently does not occur, the size of the ion is a more significant factor. Complexing of the lanthanides with other organic nitrogen containing compounds by bonding to the nitrogen are known, even though the tendency to do so is slight. Some of those mentioned are antipyrene with bonding believed to be to the methyl substituted nitrogen, 8-quinolinol, and pyramidone (30). It is interesting to note that none of these contained a fused ring system as does 1, 10-phenanthroline.

One other contributing factor is that of the dielectric constant of the solvent. A high dielectric constant solvent favors the dissociation of ionic species. Formation of ionic complexes in water would not be as extensive as in a medium of lower dielectric constant.

The solvent molecules surround and tend to shield the attraction for the lanthanide ions by the effect of the partially negative oxygen in the water molecule. Obviously the competition between the solvent and the complexing agent for the lanthanide ion is in favor of the water.

Complexing groups in the salicylic family are not as rigidly fixed as in the phenanthrolines but apparently complexes still do not form. Dimensions could still be a limiting factor as well as the solvent effects and characteristics of the lanthanide ions.

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