

FLUORESCENCE IN INORGANIC ANALYSIS WITH SPECIAL REFERENCE TO

(A) PHOTOMETRIC ESTIMATION OF ALUMINUM

(B) DETECTION OF THORIUM, ZINC, SILVER, AND COPPER

BY

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INTRODUCTION

The inclusion of fluorescent technique among the tools of the analytical chemist is becoming more and more firmly established as the fundamental principles involved become better understood. Fluorescence is a property of many substances. It is encountered in a great number of the organic products of daily life, such as lubricating oils, milk products, print and paper, wood, paints, textiles, seeds and many others. It appears also among many minerals. Their characteristic emission features, though of a low order of brightness, make possible determination of variations in quality and type. Simple visual examination of the color of the fluorescence emitted when the object is exposed to ultraviolet radiation often reveals the presence of adulteration or contamination with foreign substances. The use of this for routine control is evident.

Other types of fluorescent studies are indicated by investigations such as those of J. T. Randall⁽¹⁾ on the use of low temperatures in the study of fluorescence in solids, of R. G. W. Norrish⁽²⁾ on the relationship of fluorescence to photolysis in gaseous systems, of E. J. Bowen⁽³⁾ on fluorescence efficiency in solutions, and of Joseph Weiss⁽⁴⁾ on photosensitized reactions and the quenching of fluorescence in solution. These are pure research problems, belonging to the realm of chemical physics, seeking to establish the nature of the forces

producing fluorescence in gases, liquids and solids and their fundamental characteristics. Especial interest is attached to artificially prepared products, including both liquid and solid solutions, and also solid inorganic substances, such as sulfides, oxides, tungstates and silicates.

Aside from these two fields of widely differing objectives lies the realm wherein the development of fluorescence or its destruction brought about by chemical reaction is employed as a means for the detection and estimation of metals, as well as of many organic compounds. This realm has not been fully explored and such reactions have met with only limited application due partly to the non-specificity of the fluorescence effects, and partly to the fact that small amounts of impurities present may influence the fluorescent color to a marked degree. In a few instances it has been found possible to detect cations by bringing about a chemical reaction in which the inorganic constituent is tied up with an organic radical producing a fluorescent color or change in fluorescent color. An example of this is the morin test for aluminum.⁽⁵⁾ If a solution of the dye morin is mixed with an aluminum salt and examined under ultra-violet light a greenish fluorescence is visible.

It was with the thought of making the morin aluminum test quantitative by photometric measurement and, if possible, of adding to the number of specific fluorescent tests for the cations that this present investigation was undertaken.

Comprehensive reviews of the applications of fluorescence analysis to a wide variety of industrial and chemical problems of an analytical nature are available in book form as follows:

Fluorescence Analysis in Ultraviolet Light
by J. A. Radley and J. Grant

Lumineszenzanalyse by P. W. Danckwortt

Die Fluoreszenzanalyse in der Mikrochemie
by Max Haitinger

In addition to these reviews an article by Dr. C. E. White, "Fluorescent Analysis of Inorganic Materials"⁽⁶⁾, describes methods, apparatus, and tests particularly adapted to fluorescent studies of inorganic materials.

THEORY OF FLUORESCENCE

Historical

If fluorescence is defined, from an elementary point of view, as being the ability of certain substances to transform incident radiation into radiation visible to the eye, the phenomenon was known to Robert Boyle, who introduced the first fluorescent indicator to distinguish acids and bases from one another by an infusion of "lignum nephriticum".⁽⁷⁾ D. Brewster⁽⁸⁾ and J. Herschel⁽⁹⁾ seem to be the first to have sought an explanation of this phenomenon. Both considered it a type of light dispersion, the former as an "innere dispersion" caused by very small particles of the substance, the latter as an "epipolische dispersion" which after passage through a measurable layer of the fluorescent liquid was robbed of its irradiating effect.

G. G. Stokes⁽¹⁰⁾ classed as fluorescent substances those which under the influence of light became self-luminous. Self illumination proceeds from impinging light rays being changed into radiation of other wave lengths. It was Stokes who first recognized this fact and gave the phenomenon the name it bears, from the fact that it seems particularly characteristic of some varieties of fluorspar or calcium fluoride.

The work of Stokes indicated that fluorescence effects were nothing other than the result of a transformation of one radiant energy into another of definite period and refrangibility: that fluorescent phenomena were connected

with no definite state of aggregation, being most marked in solids and liquids yet also observable in some vapors, e.g. iodine or sodium.

The fluorescence of solutions depends in the first place upon the concentration of the dissolved substance. In general fluorescence is strongest in more dilute solutions. The color frequently changes at higher concentrations. This is caused by the fact that the solution absorbs a part of the emitted fluorescent light. Some substances which fluoresce in the solid state are not responsive to the incident ray when dissolved. This may originate on the one hand in that the fluorescence lies in the ultra-violet region or is so weakened that it is no longer perceptible to the eye; on the other hand it may be that in solid bodies it is brought about by crystalline structure. In the first instance fluorescence is conditioned by chemical constitution of the molecule; in the second instance only by the physical arrangements of one atom with another.

Later investigations, after the period during which Stokes dominated the field, roughly 1850-70, were chiefly concerned with studies about the relationship of fluorescence to chemical constitution. Aside from isolated observations of some authors, R. Meyer⁽¹¹⁾ was the first to study this question in detail. According to him certain atomic groupings were necessary for fluorescence which he called fluorophores, such as the pyron ring and the ring structures

found in anthracene and pyridine. The bare presence of a fluorophore in the molecule was not in itself sufficient for fluorescence. It appeared only if situated between two heavy atomic complexes, especially between benzene nuclei. Thus pyron did not fluoresce whereas alpha, alpha' diphenyl pyron did.

Likewise L. Kaufmann⁽¹²⁾ and co-workers attributed fluorescence to the presence of certain atomic groupings called luminophores. A typical luminophore is the benzene nucleus.

In contrast, J. Stark⁽¹³⁾ emphasized that fluorescence was dependent upon absorption in a band spectrum; it is not always perceptible and can fall in the visible as well as in the invisible light region.

From the complicated structure of most fluorescent organic compounds it is extremely difficult to recognize the essential carrier of fluorescence and numerous examples are found which appear to satisfy each hypothesis. However, exceptions are always found which contradict them.

Laws of Fluorescence

Fluorescence phenomena obey three physical laws:

- (1) Fluorescence is always accompanied by absorption of incident radiation, a principle which must follow from the law of conservation of energy.
- (2) The second law, more generally known as Stokes' law, states in effect that the fluorescent light

is always of greater wave length than the exciting light. This principle has led to a great deal of controversy and has been questioned by several investigators. Lommel⁽¹⁴⁾ in 1877 was the first to point out for certain bodies an unmistakable overlapping of the regions in the spectrum occupied by the exciting light and by the fluorescence which it produced. Later work by Nichols and Merritt⁽¹⁵⁾ of Cornell indicated that Stokes' law held for none of the fluorescent substances examined which included eosin, naphthalin-roth, fluorescein, rhodamin, resorcin-blau, quinine sulphate, chlorophyll, canary glass, green fluor-spar, white fluor-spar, and aesculin. It is generally admitted today that the law is not valid for strongly colored substances.

It has been conjectured that the extra amount of energy required to produce radiation of shorter wave lengths than that of the primary radiation, as is the case for "anti-Stokes'" bodies, originates in the break down of certain atomic heat centers. Definite evidence for this assumption is lacking.

- (3) The distribution of intensities in the fluorescence spectrum and the position of the maximum of the fluorescence band is in all cases independent of the wave length or composition of the exciting light.

Modern Concepts of Fluorescence

Modern thought regarding the fundamental causes of fluorescence phenomena is based upon the existence of discrete energy levels associated with each atom, which serve as stopping places for electrons as the latter are shifted about by various energy radiations. In the case of a gas this effect is known as "resonance radiation". The illumination producing it must have a wave length corresponding to an absorption band of the gas. Through this absorption of energy the atoms or molecules become excited to such an extent that an electron is driven to an outer orbit. The condition for such a state is that $E = h\nu$ where E is the energy of a quantum of the exciting radiation, and ν is the frequency corresponding to the wave length at which energy can be absorbed to excite the atom to resonance. The return of the electron to its normal orbit gives rise to luminescence and is accompanied by energy emission of the same frequency so that there is no change in wave length. This emission is labeled fluorescence if it persists only under excitation by the radiation; it is known as phosphorescence if it exists for an appreciable period after the radiation has been extinguished.

In studying the artificially prepared phosphors two striking characteristics have been noted: (16) first, fluorescence is quite often associated with the presence

of a low concentration of a foreign ingredient; second, fluorescence is not monochromatic although the illuminating radiation may be, but it extends over a broad band of the spectrum and generally is of longer wave length than that of the exciting radiation. These effects are also observed in gases and may be explained in an analogous fashion as being due to the influence exerted by neighboring atoms upon one another.

Thus in the case of pure sodium vapor the luminescence is made up of the D line doublet (5,890 and 5,896 \AA units) resulting from the return of excited electrons from two energy levels lying close together. At very low pressures only one of these lines can be excited as resonance radiation. If the pressure is increased or if a small amount of hydrogen is introduced both lines appear, due to collision of excited atoms with neighboring atoms. Such collisions produce sufficient energy transfer to throw the excited electron into the closely adjacent energy level, the energy difference between the two states corresponding to only 0.01 volt. This system illustrates how sensitive the character of the radiation produced is to the influence of neighboring atoms either of the same or of different species.

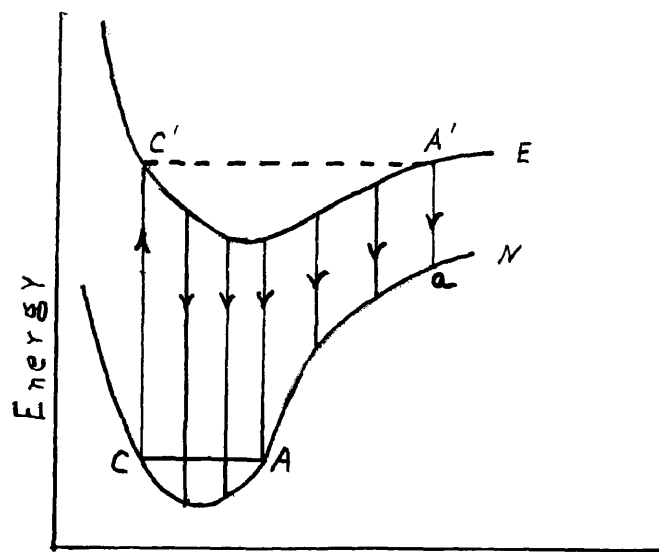
For more complex vapors such as iodine which is in the molecular rather than the atomic state, the two atoms vibrating back and forth and the molecule rotating about the axis uniting the two atoms give rise to various

vibrational and rotational energy states. The usual number of electronic energy levels has been greatly increased. The case has become so complex that the pure resonance spectrum consists of a series of doublets rather than a single line. If now the pressure on the system is increased sufficiently to cause collision of excited molecules with neighboring molecules or if helium is introduced into the system the resulting emission is no longer resolved into lines, but appears as continuous radiation at the location of the expected doublet. The electrons do not return to their normal orbits by a series of definite jumps resulting in clear cut doublets, but return by jumps of different magnitudes to states so close together that continuous bands result. As a counterpart of such collisions the electron loses energy leaving smaller amounts available for light emission. Consequently the emission is displaced toward the longer wave lengths.

The situation represented for sodium and iodine vapors becomes still more complicated as the concentration of atoms and molecules is increased to form the liquid and solid states. The interplay of forces is much more intricate and involved, so much so that groups of electronic levels become packed with lines representing a continuous band of energy. In solids the bands are so far apart in energy content that ordinary methods of producing excited

states can not raise electrons from a normal filled band to an upper unfilled one. If a "localized band" represented by a small amount of impurity is inserted between the two bands some energy states of the impurity will fall in such a position as to allow of excitation by appropriate wave length causing electronic jumps from the localized level to the unfilled band. The result is that luminescence occurs associated purely with the impurity atom. The excited electron falls by steps of thermal interchange to the lowest level of the unfilled band. Therefore the energy emitted on return to its normal state is less than the energy of excitation and the fluorescence is displaced toward the red.

The effect of broadening the emission into a band due to the close packing of the atoms in solids is illustrated by the Franck-Condon principle. (Fig. 1) The distance between atoms (foreign impurities and neighboring atoms) will vary periodically due to thermal vibrations and alternate forces of attraction and repulsion. The potential energies are represented by ordinates of the two curves, N for the normal state and E for the excited state. The principle states in effect that the time of excitation is so short as compared with the time of vibration that transitions between the two states will take place along a vertical line CC'. Vibrations continue between points of equal potential energy in the excited state such as



Distance between atoms

Fig. 1 - Excitation and emission of a phosphor according to Franck-Condon Principle (From G. Fonda, Elec. Engr. 678, Dec. 1938)

C' and A'. The excited state extends over a finite time, and consequently the return of the electron to its normal position is represented as occurring [↑]from any position along the curve E between points C' and A'. The shape of the curves is inherent in the principle as representative of the interplay of forces. As a result, the emitted energy is not equal to the energy of excitation, represented by line CC', but has a succession of lower energy values depending on the point on the curve E from which its return starts.

A localized state might be introduced not only by impurity atoms, but by irregularities in the lattice as a result of non-stoichiometric proportions in the composition of the solid, by various concentrations of allotropic modifications, by the dispersion of active molecules in a solution, or by their adsorption in dispersed form on a solid.

Optimum intensities of fluorescence at critical concentrations have been found to be characteristic of fluorescent dye solutions. Decreases in fluorescence beyond the optimum value are presumably ascribed to the increase in probability of collision between excited and normal dye molecules. An optimum content of foreign metals in inorganic phosphors is apparently also related to this same effect. If this theory is correct, fluorescent tests should be made under conditions of sufficient dispersion to prevent disturbances by collision, which might be accomplished by carrying out observations on adsorbed films, on filter paper, or in solution.

LIGHT SOURCES

The light source should be selected to give conveniently, relatively intense emission of ultraviolet light of all wave lengths; however, the near ultraviolet region comprising wave lengths 3000 to 4000 \AA is of sufficient energy content to excite fluorescence for most analytical work. The intensity should not change with time or working conditions. The source should show no heating effects or objectionable fumes and should be so arranged that it can be enclosed and properly shielded. As the intensity of the fluorescence phenomena is dependent upon the intensity of the excitation source and different types of sources vary widely in intensity, the method or instrument used for excitation must be carefully described. Failure to do this has led to much confusion in the literature in this field.

Although X-rays, cathode rays, and radium rays have been used in isolated instances for fluorescent studies, the most generally applicable sources are the spark or arc discharges between impregnated carbon electrodes or between metallic electrodes such as iron, nickel, cobalt, aluminum, tungsten, zinc, magnesium or cadmium and the quartz mercury vapor lamp. Iron electrodes give light particularly rich in ultraviolet radiation with uniform spectral line distribution. Arcs may be struck in air, in vacuum, in hydrogen, argon or in a metallic vapor

such as that of mercury, bismuth or cadmium. Greater intensities for specific regions of the spectrum are obtained by the use of zinc, magnesium, nickel or cobalt electrodes. Almost all metallic and impregnated carbon electrodes give spectra with greater intensity and number of lines than the mercury arc. The disadvantages of the arc discharge sources include difficulties in maintenance of a constant output, the evolution of heat and obnoxious fumes, and the disintegration of small amounts of hot metal causing darkening of the filter. Table No. 1, taken from Haitinger's data, (17) compares the intensity and number of lines for a number of metal electrodes suggested as applicable for sources of ultra-violet light.

Table No. 1

Percent Total Intensity for the Region 3000-4000 \AA ^o
and the Number of Lines between 2000-4000 \AA ^o and
3000-4000 \AA ^o for Various Metallic Electrodes

Metal	% Total Intensity for 3000-4000 \AA ^o	Number of lines between	
		2000-4000 \AA ^o	3000-4000 \AA ^o
Al	95	28	8
Cd	68	38	11
Cu	69	1368	187
Fe	40	2890	868
Hg	51	78	25
Ni	40	978	309
Pb	55	46	10
W	29	3254	997
Zn	35	3390	1351

Mercury vapor lamps are of many types and designs from those giving point sources of light to larger models used for illuminating purposes. The Genovia analytical model, which is widely used for fluorescent studies, is designed for increased efficiency by being equipped with cylindrical hood and special reflectors for concentrating the radiation. The filter employed to remove visible light is of the nickel oxide type. The suspension is so arranged that the burner and hood may be tilted to start the circuit. The spectral range extends from 1800 to 14,000 \AA . Wave lengths less than 4500 \AA represent two-thirds of all wave lengths present. The principal ultraviolet lines of fluorescent interest consist of two at 3650 and 3654 \AA respectively and one at 3984 \AA . Radiation in the visible is concentrated in a pair of yellow-green lines at 5784 and 5791 \AA and a green line at 5461 \AA .

As an outgrowth of the perfection to a commercial stage of high pressure mercury vapor electrical discharge lamps and to the advent of television (which has been made possible by the luminescent cathode ray tube screen) sources of ultraviolet light of much lower original cost and of greater ease of operation are available to the analytical worker. At low pressures, i.e. below 1 mm., a large portion of the energy input is radiated as the resonance line at 2536 \AA . At higher pressures, e.g. above

100 mm. the energy radiated in the visible portion of the spectrum is increased while the resonance radiation is absorbed. In the most recent lamp developments pressures of one-half to one atmosphere are readily utilized by placing the hard glass mercury vapor container within an outer envelope of glass. In addition to the radiation appearing in the visible portion of the spectrum there are present a number of wave lengths lying just below the visible region, most of which are due to the triplet at 3650 \AA . If the lamp is inclosed in order to conveniently filter out the visible light, provision should be made for air circulation in order to keep the temperature from rising.

The high pressure mercury vapor lamps in their present form require from 2 to 5 minutes to reach maximum intensity. Low pressure lamps show no thermal delays connected with their operation, reaching full brilliancy almost instantaneously. However the intensity of such a source is so low that its application is limited.

FILTERS

It is important to know the range of wave lengths transmitted and absorbed by the particular filter being used. "Wood's glass" appearing almost black in ordinary

light but shutting out practically all of the visible spectrum is used extensively in fluorescence work and is standard equipment in a number of lamps. It is essentially a nickel oxide glass with a small amount of copper oxide added to blank out red rays. Commercial filter glasses vary greatly in composition and transmission and absorption characteristics. Consequently reference should be made to manufacturers' catalogs where definite ranges are required.

According to the data of J. Eisenbrand⁽¹⁸⁾ the percentage of various wave lengths passing through 7 mm. thickness of ordinary glass plate is as follows:

Wave length \AA°	% passing through
3860	90
3840	14
3130	under 1

A series of filters transmitting various wave lengths may be constructed from a combination of Wratten dyed gelatin filters, Corning glass, and solutions of nickel and copper sulfates.⁽¹⁹⁾ It must also be borne in mind that the intensity of radiation transmitted will vary inversely with the thickness of the filter.

Materials other than glass have been used successfully to absorb visible rays and transmit ultraviolet. A solution of nitrosodimethylaniline of such strength as to eliminate all blue and most of the violet regions has

been used by Wood⁽²⁰⁾. Combinations of aniline dye solutions or gelatin films impregnated with dyes have been used in many instances although some investigators maintain that dyes generally are too unstable to ultraviolet to be of permanent use.

METHODS OF EXAMINATION

Particle size is of considerable importance, particularly in the case of solids. Generally fluorescence is brighter if the substance is in the powdered state. If the solid presents a fairly large continuous surface, it should be fractured and observations made on freshly broken surfaces. Spotting with dilute acid or alkali and heating are frequently of aid in identification. Use is often made of borax or phosphorous salt beads with good results.

There is little use for the gaseous state in ordinary analytical examinations. As pointed out in the theoretical discussion the fluorescence may be markedly influenced by vapor pressure or the presence of a small amount of impurity. By far the greatest use of fluorescent effects as an analytical tool is met with in liquids and solutions.

The container should be non-fluorescent, and may be placed directly in the path of the radiation for observation. Frequent use is made of filter paper as a medium for carrying out reactions on a small scale.

Yagoda⁽²¹⁾ has developed a technique of confining the spot to a small area by impregnating the paper with paraffin rings. Glass spot plates have been found very satisfactory for micro work. White spot plates usually show a purple fluorescence and black spot plates a green fluorescence. Quartz containers are not necessary where wave lengths below 5000 \AA are not required. If ordinary glass filters are used at the light source, radiation of lower wave length is stopped at this point and the use of quartz for transmitting below 3000 \AA would be unnecessary. Obviously the solvent used should show no fluorescence itself. The liquid or solution should be diluted with a non-fluorescing liquid and examined at progressively increasing dilutions, since there is often an optimum dilution showing a maximum intensity. Observations should be made under both acid and alkaline conditions in searching for identifying characteristics. Generally an increase in temperature will decrease fluorescence.

Fluorescent phenomena can be observed advantageously if the fluorescent material is allowed to crystallize out on the microscope slide and examined under the fluorescent microscope. The form of the crystals and crystal groups, particularly in dark field illumination, may offer new criteria for the identification of unknown samples. Treatment with alkali or acid often produces

a change in fluorescent color and characteristic new crystal forms. The method is adaptable to the investigation of mixed substances, the components of which can be identified by different colored fluorescences.

SURVEY OF SPECIFIC INSTANCES WHERE FLUORESCENT EFFECTS
HAVE BEEN FOUND USEFUL IN INORGANIC ANALYSIS

Inorganic compounds for the most part show no characteristic fluorescent properties. A large number of compounds which have been examined gave a red-violet fluorescence which was not suitable for identification.(22) The metals themselves as well as most salts of the heavy metals do not fluoresce. It is noteworthy that for those metals which exhibit variable valence the compounds in which the metal has the lower valence show more distinctive fluorescence than those compounds in which the metal has the higher valence. Thus cuprous chloride gives a yellow-green fluorescence, mercurous chloride a strong orange fluorescence and thallous carbonate a blue fluorescence while the corresponding salts in which the metals have the higher valence do not fluoresce.

More marked fluorescence phenomena can be observed with the metal salts of organic acids. Table No. 2, taken from the work of Haitinger(23), gives the fluorescent colors of a number of such compounds.

Table No. 2

The Fluorescent Colors of Metal Salts of Organic Acids

Compound	Fluorescent Color
Potassium cyanide	Bright blue
Mercuric cyanide	Bluish white
Barium formate	Blue with violet shade
Calcium formate	" " " "
Nickel formate	Bright carmen red
Thorium formate	Bright blue
Aluminum acetate	Bright blue
Barium acetate	Green with blue tinge
Lead acetate	White with blue tinge
Zinc acetate	Blue with violet shade
Sodium benzoate	Violet
Ammonium salicylate	Bright blue
Barium salicylate	" "
Magnesium salicylate	" "
Sodium salicylate	" "
Strontium salicylate	" "
Zinc salicylate	Bright yellow
Zinc oxalate	Bright green
Potassium hydro tartrate	Blue
Barium succinate	Violet
Potassium succinate	Bluish white
Silver succinate	Bright yellow
Calcium lactate	Bright blue
Strontium lactate	Bright yellow
Sodium oleate	Blue green

Efforts to develop fluorescent tests for identification of cations have met with greater success where the metal ion has been absorbed in an organic compound. A brief description of individual tests reported in the literature for the various metals and other inorganic materials is given below. Since many of these are taken from Japanese literature and have not previously been published in English this review is given in more detail than might otherwise be warranted.

Aluminum

- (a) A test for aluminum sensitive to 1 part in 10^5 has been based on the vivid orange-red fluorescences obtained with aqueous alcoholic solutions of Solochrome Red ERS and Solochrome Violet RS. The test has proved useful in detecting aluminum in sizing materials and adhesives. The fluorescence is observed in an acid solution. Magnesium, calcium, sodium, potassium and ammonium ions do not interfere with the reaction. Zinc gives a dull red fluorescence with both dyestuffs but does not mask the brilliant fluorescence given by aluminum salts. (24)
- (b) An orange red fluorescence produced by Pontachrome Blue Black R (the zinc salt of 4-sulfo-2,2' dihydroxy azonaphthalene) in the presence of aluminum ion is sensitive to one part in 5,000,000 and can be used in the qualitative detection of aluminum in the presence of beryllium and other elements with which it is commonly found. (25)

- (c) The detection of aluminum may be accomplished by treatment with morin whereby a neutral soluble aluminum salt with a green fluorescence is formed.⁽⁵⁾ A more detailed description of this test is given below under experimental work.
- (d) Aluminum gives with oxine (8-hydroxy quinoline) a yellow green fluorescence as does cadmium. The reaction takes place in HOAc, NaOAc, neutral or slightly ammoniacal solutions but is more sensitive with NaOAc. The test may be carried out on filter paper or spot plate. Limit of recognition 0.1 gamma, dilution 1:500,000.⁽²⁶⁾
- (e) Acetic acid solutions containing sodium acetate with cochineal give weak yellow fluorescences. In the presence of aluminum the color shifts to a strong red fluorescence. Limit of recognition 0.1 gamma, dilution 1:500,000.⁽²⁶⁾
- (f) A solution containing sodium acetate and tincture of alkanna in the presence of aluminum gives a yellow brown fluorescence. Without aluminum a weak green fluorescence is observed. Limit of recognition 10 gamma, dilution 1:5,000.⁽²⁶⁾

Antimony

- (a) Antimony may be detected in the form of hydrogen antimonide in ultraviolet light with an electrolytic Marsh apparatus at much lower limits than with white

light. The antimony mirror is dissolved in HCl, washed with water, treated with hydrogen sulfide water and compared colorimetrically with a standard solution of tartar emetic. Limit of recognition 1 to 0.1 gamma. (27)

- (b) An aqueous paste of pure calcium carbonate on ignition and treatment with an antimony solution fluoresces sky blue when slowly drawn through a hydrogen flame. The fluorescence is observed before heating to glowing. (28)
- (c) Antimony with a valence of five in acid solution destroys the fluorescence of rhodamine B. Limit of recognition 0.5 gamma, dilution 1:100,000. (26) With a valence of three in HCl solution antimony changes rhodamine B to purple. (29)
- (d) Morin in HCl solution with trivalent antimony gives a strong yellow green fluorescence. Addition of alcohol increases the intensity. Fluorescence is observed even in sunlight. Addition of acetic acid destroys the fluorescence. Limit of recognition 0.05 gamma, dilution 1:1,000,000. (26)

Arsenic

- (a) The mercuric chloride paper used in the Gutzeit test for arsenic under ultraviolet light has a black appearance in the presence of traces of arsenic, insufficient to cause discoloration visible in

ordinary light. Limit of recognition 1 gamma. (30)

- (b) The white precipitate formed with pentavalent arsenic and $(\text{UO}_2)^{2+}$ gives a strong yellow green fluorescence. A neutral solution of arsenate is added to a drop of 0.4 M uranyl nitrate or to a drop of $(\text{UO}_2)(\text{OAc})_2$ 0.05 M on a spot plate. Uranyl sulfate is not satisfactory due to its intense fluorescence and more concentrated solutions of uranyl nitrate should not be used. The presence of arsenic is indicated by formation of a precipitate with strong fluorescence. Phosphates interfere with the test. Limit of recognition 5 gamma, dilution 1:10,000. (26)
- (c) Arsenate and arsenite ions may be detected in alcoholic morin solutions containing HCl or HOAc by production of a yellow green fluorescence. The test is not sensitive. (26)

Beryllium

- (a) The carbonate fusion is dissolved in hydrochloric acid, treated with alcoholic morin solution and then made alkaline with caustic soda. In the presence of beryllium a yellowish green fluorescence appears under ultraviolet light which disappears on acidification or in the presence of aluminum fluoresces a blue green. (31)

Bismuth

- (a) An aqueous paste of pure calcium carbonate on

ignition and treatment with a bismuth solution fluoresces cyanblue when slowly drawn through a hydrogen flame. Limit of recognition 0.0001 gamma. This blue fluorescence is clearly distinguishable from that produced by antimony under the same conditions. (32)

According to the experiments of Gotô, if heating is carried out with a gas flame a purple fluorescence results which does not weaken on prolonged heating. (26)

Boric acid

- (a) The preparation of luminophors with fluorescein as activator giving a vivid green fluorescence even in weak ultraviolet radiation has been recommended for this substance. The optimum concentration of the fluorescein solution is 1:10,000. Below this concentration the color shifts toward the violet, and above it a shift toward the red is noted. Limit of recognition 20 gamma. (33)
- (b) Cochineal tincture produces an orange yellow fluorescence with boric acid at pH 5.8 to 6.9 (phosphate buffer). Limit of recognition 0.5 gamma in 0.025 ml. The reaction takes place much more slowly in the presence of Ag, Hg, As, Sb, Ca, Sr, Ba, K, Na and ammonium ions. Heavy metals interfere and aluminum and magnesium alter the shade of fluorescence. (34)

Bromine

- (a) The change in color brought about by the conversion of fluorescein to eosin by nascent bromine may be used as a qualitative test for 10^{-6} g of bromides even in the presence of chlorides. The reaction is carried out by bringing paper impregnated with a fluorescein solution near the opening of a test tube drawn out into a capillary in which a bromide is being treated with acetic acid and lead dioxide and heated. (35)

Cadmium

- (a) Cadmium sulfide precipitates fluoresce strongly yellow and can be recognized in concentrations of 0.02 mg in 50 ml; this corresponds to a sensitivity of 1:2,500,000. (36)
- (b) Cadmium with oxine (8-hydroxy quinoline) gives a yellow fluorescent precipitate which is more intense in neutral or moderately acid solution. Fluorescent precipitates are also produced with Al, Zn, Ba, Ca, Mg, and Zr. In the presence of acetic acid only Cd, Al, Zn and Zr give fluorescent precipitates so that the number of interfering ions is decreased. Limit of recognition 0.1 gamma, dilution 1:500,000. (26)
- (c) Using pyridine and KI, $\text{Cd}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ is formed which gives a blue white fluorescence. Lead interferes with this reaction. Limit of recognition 0.5 gamma, dilution 1:100,000. (26)

- (d) In neutral solution morin in the presence of cadmium gives a yellow fluorescence. Limit of recognition 1 gamma, dilution 1:50,000.(26)

Chromium

- (a) The fluorescence of acridine in the presence of CrO_4^{-2} in alkaline solution is destroyed. Chromium with a valence of three may be detected by oxidization with bromine water to the higher valence. The test is relatively insensitive but is characteristic.(26)

Copper

- (a) With a neutral or slightly acid solution cupric ion liberates iodine from KI. The iodine liberated will destroy the fluorescence of alpha naphtholflavone. Any oxidizing agent or element that will liberate iodine from KI will give the same reaction. A black purplish precipitate is produced accompanying the disappearance of the fluorescence. Limit of recognition 0.5 gamma, dilution 1:100,000.(26)
- (b) Cupric ion with an alcoholic solution of cochineal made slightly alkaline causes the red fluorescence of cochineal to disappear and produces instead a slightly blue white fluorescence. This is a very sensitive test but is interfered with by lead, platinum and gold. Limit of recognition 0.1 gamma, dilution 1:500,000.(26)

Gold

- (a) Gold also destroys the fluorescence of rhodamine B

as does antimony. The red solution changes to purple with the disappearance of fluorescence. Limit of recognition 2.5 gamma, dilution 1:20,000.(26)

(b) An alkaline, alcoholic cochineal solution in the presence of gold ions loses its red fluorescence and develops a light green fluorescence. If the gold solution is too concentrated the green fluorescence does not develop. Limit of recognition 1 gamma, dilution 1:50,000.(26)

(c) With quinine sulfate and KI in slightly acid solution a brown precipitate forms and the fluorescence of quinine disappears. Limit of recognition 2.5 gamma, dilution 1:20,000.(26)

(d) Neutral or slightly acid solutions of acridine and KI in the presence of gold give a blue purplish precipitate and the fluorescence of acridine disappears. Limit of recognition 2.5 gamma, dilution 1:20,000.(26)

(e) Gold will liberate iodine from KI which will destroy the fluorescence of alpha naphtholflavone. Limit of recognition 0.5 gamma, dilution 1:100,000.(26)

Hydrosulphites

(a) Hydrosulphites will convert resazurin into resorufin in the presence of alkali carbonate and the fluorescence changes from brown, through colorless to red.(37)

Iron

- (a) Dilute solutions of acetic acid containing sodium acetate in the presence of trivalent iron destroy the purple fluorescence of salicylic acid. The solution turns a deep purple color but shows no fluorescence. Limit of recognition 2.5 gamma, dilution 1:20,000. (26)
- (b) Iron liberates iodine from KI which extinguishes the fluorescence of alpha naphtholflavone and gives a blue black precipitate. The reaction is carried out in slightly acid solution. Limit of recognition 0.25 gamma, dilution 1:200,000. (26)

Lead

- (a) The white precipitate $\text{Pb}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ formed with pyridine and KI gives a strong yellow brownish fluorescence. Cadmium is the only other element forming pyridine and KI complexes. The reaction is carried out on a spot plate and approximately 6 minutes are allowed for fluorescence to appear. For small amounts of lead, fluorescence appears only around the edge. Limit of recognition 0.25 gamma, dilution 1:200,000. (26)
- (b) Alcoholic morin solutions give with neutral lead solutions a yellowish green fluorescence. Acidification with acetic acid extinguishes the fluorescence. A few drops of alcohol are added

after mixing the reactants to increase the fluorescence. Limit of recognition 0.25 gamma, dilution 1:200,000. (26)

Manganese

- (a) An aqueous paste of pure calcium sulfate on ignition and treatment with a manganese solution fluoresces cyanblue when slowly drawn through a hydrogen flame. Limit of recognition 0.001 gamma. (38)
- (b) Manganese in an alkaline solution of rhodamine B on acidification gives a brownish fluorescence which changes slowly into a weak green fluorescence. This applies to the divalent form. If divalent manganese is oxidized in the alkaline solution, on acidification rhodamine B is reduced so that there is no appearance of fluorescence even if made alkaline again. Antimony although extinguishing the fluorescence of rhodamine B shows no evidence of reducing action as does manganese. Cobalt and iron show the same reaction. Limit of recognition 0.1 gamma, dilution 1:5,000,000. (26)

Mercury

- (a) On treating a solution containing mercuric ions with KBr and SnCl_2 a white or blackish precipitate forms. HgBr in the precipitate gives a bright red fluorescence. An excess of SnCl_2 causes the fluorescence to disappear. (26)

- (b) Mercurous ion with HBr forms Hg_2Br_2 which gives the bright red fluorescence. If the reaction is carried out in air the fluorescence must be observed within one or two minutes as it disappears quite rapidly. Limit of recognition 0.5 gamma, dilution 1:100,000. (26)

Molybdenum

- (a) A reduced solution of molybdenum with an alcoholic suspension of coeruleine gives a yellow fluorescence. Limit of recognition 0.025 gamma, dilution 1:2,000,000. (26)
- (b) A neutral solution of molybdenum and an alcoholic morin solution give on mixing a yellowish green fluorescence. Excess alcohol added to the spot reaction increases the intensity. (26)
- (c) Acetic acid solutions containing sodium acetate give with cochineal in the presence of molybdenum a red fluorescence. The test is very sensitive but Al, Zn, Ag, and W give the same reaction. Limit of recognition 0.05 gamma, dilution 1:1,000,000. (26)

Nickel

- (a) In ammoniacal solution nickel destroys the fluorescence of salicylic acid. Limit of recognition 5 gamma, dilution 1:10,000. (26)

Platinum

- (a) Platinum solution added to a solution containing quinine and KI produces a brown precipitate and destroys

the blue fluorescence of the quinine. 0.1% quinine sulfate and 0.3 N KI are used. Limit of recognition 5 gamma, dilution 1:10,000. (26)

- (b) Tetraivalent platinum liberates iodine from KI which destroys the fluorescence of alphanaphthoflavone. A blue black precipitate is formed. Limit of recognition 5 gamma, dilution 1:10,000. (26)
- (c) An alkaline solution of cochineal in the presence of tetraivalent platinum changes the color from purplish red to white and destroys the red fluorescence. The reaction is slow and sufficient time should be allowed before making a final conclusion. Limit of recognition 2.5 gamma, dilution 1:20,000. (26)

Rare earths

Tomaschek and Deutschbein⁽³⁹⁾ have investigated the fluorescence of the rare earths with borax and phosphate beads. Of the cerium family only cerium fluoresces, as a borax bead bright blue. Europium, samarium and gadolinium show especially strong fluorescences when tested in the form of beads, viz. fiery red, reddish yellow and orange yellow respectively. Of the yttrium family dysprosium fluoresces yellow, thulium a weak violet, holmium a very weak yellow. All the above preparations show well defined fluorescent spectra; cerium a continuous spectrum with maximum brightness at 4500 Å°, the others recognizable band spectra of from 3 to 6 bands. No fluorescence was detected for

lanthanum, praseodymium, columbium, erbium and ytterbium. The limits of recognition and limiting concentrations are summarized in the following table: (40)

Table No. 3

Limits of Recognition and Limiting Concentrations
for Detection of the Rare Earths.

Rare Earth	Limit of recognition in gamma values	Limiting Concentration
Cerium	0.4	1:10,000
Samarium	4.5	1: 1,000
Europium	20.0	1: 500
Gadolinium	45.0	1: 100
Terbium	2.0	1: 5,000
Dysprosium	4.5	1: 1,000

Rhenium

- (a) The greenish yellow fluorescence produced by adding a saturated solution of dimethyl glyoxime in alcohol and 3 ml of a 25% solution of stannous chloride in conc. HCl to a 1 ml sample containing rhenium as perrhenate permits the detection of 0.01 mg. (41)

Selenium

- (a) Acid solutions of selenium with acridine and KI give brown precipitates and destroy the fluorescence of acridine. This test is similar to that for platinum and gold but requires an acid solution. Limit of recognition 2 gamma, dilution 1:25,000. (26)
- (b) Acidic selenium solutions with quinine and KI give a brown precipitate destroying the fluorescence of quinine. Limit of recognition 2.5 gamma, dilution 1:20,000. (26)

- (c) Acidic solutions of selenium liberate iodine from KI which combines with alphanaphtholflavone to produce a blue black precipitate destroying the fluorescence of the alphanaphtholflavone. For small amounts of selenium the liquid has a fluorescence but there is no fluorescence in the precipitate. Limit of detection 0.25 gamma, dilution 1:200,000. (26)

Silver

- (a) Neutral or slightly acid solutions of silver destroy the yellow green fluorescence of uranyl sulfate. Mercuric, bismuth, and cadmium ions do not interfere. Less than 1 mg/ml mercurous ion, 1 mg/ml lead ion, 2 mg/ml cupric ion do not interfere. A trace of chloride ion precipitates silver chloride and weakens the fluorescence of uranyl sulfate. Thallium gives the same test as silver. 1/15 molar uranyl sulfate is used. Limit of recognition 1 gamma, dilution 1:50,000. (26)

Sodium

- (a) The precipitation of sodium with zinc uranyl acetate giving greenish yellow fluorescent precipitates permits the detection of smaller amounts of sodium. The reaction is carried out on filter paper. For amounts of sodium under 10 gamma fluorescent specks are noted in from 1 to 4 minutes. Without ultraviolet light 12.5 gamma at a concentration of 1:4,000 are recognizable; with ultraviolet light 2.5 gamma at a limiting concentration of 1:20,000 can be detected. (42)

Sulfites

- (a) Sulfites may be detected by distilling the sample with a little HCl into hydrogen peroxide containing quinine. Sulfur dioxide is oxidized to sulfuric acid causing the quinine to fluoresce. Maximum sensitiveness is about 0.25 mg sulfur dioxide. (43)

Tellurium

- (a) Ignited calcium carbonate on dipping into tellurium solutions and reheating to white heat shows a brilliant red fluorescence. Selenium also gives a slight red fluorescence with this test. Limit of recognition 0.04 gamma, dilution 1:1,000,000. (26)
- (b) Acidic solutions of tellurium with quinine and KI give brown precipitates destroying the fluorescence of quinine as in the case of selenium. The effect of acid is much greater but detection is not as sensitive. One drop each of 0.1% quinine sulfate, 0.3 N KI, and 0.5 N H₂SO₄ are the recommended proportions. Limit of recognition 25 gamma, dilution 1:2,000. (26)
- (c) Acidic solutions of tellurium with acridine and KI give brown precipitates and they destroy the fluorescence of acridine. Limit of recognition 10 gamma, dilution 1:5,000. (26)
- (d) Tellurium reacts the same as selenium with solutions of KI containing alphanaphthoflavone. Blue black precipitates are formed which destroy the fluorescence. Limit of recognition 0.5 gamma, dilution 1:100,000. (26)

Thallium

- (a) Thallium destroys the yellow greenish fluorescence of uranyl sulfate. This applies to thallous ion. Limit of recognition 1 gamma, dilution 1:500,000. (26)
- (b) Trivalent thallium in a neutral or acid solution of rhodamine B changes the color from red to purple, the purple solution showing no fluorescence. To destroy the fluorescence it is unnecessary to make the solution alkaline as with cobalt and manganese. Limit of recognition 0.5 gamma, dilution 1:100,000. (26)
- (c) The red fluorescence of cochineal disappears in the presence of trivalent thallium in alkaline solution. Limit of recognition 0.5 gamma, dilution 1:100,000. (26)

Tin

- (a) Stannous ion produces a yellow green fluorescence with coeruleine in HCl. The reaction is much more sensitive if a small amount of alcohol is added. Limit of recognition 0.02 gamma, dilution 1:2,500,000. (44)
- (b) Ignited calcium carbonate treated with a stannous solution gives a yellow greenish fluorescence. Fluorescence must be observed before a red heat is obtained. Arsenic and antimony interfere with the detection. Limit of recognition 0.02 gamma, dilution 1:1,000,000. (26)
- (c) In HCl solution stannous or stannic ion gives with morin a yellow green fluorescence. Alcohol increases the intensity. Limit of recognition 0.25 gamma, dilution

1:200,000. (26)

Uranyl compounds

Uranyl compounds fluoresce only in the uranyl form, i.e. uranous compounds do not fluoresce. Conversion can easily be accomplished by nitric acid or fusing with borax. In aqueous solutions the yellow green fluorescence is very weak compared to that present in solid forms. In alcohol there is practically no fluorescence. Sulfuric acid increases the intensity whereas halogen acids decrease it. Best results in the detection of uranium compounds are obtained from the preparation of solid solutions. Nichols and Blattery⁽⁴⁵⁾ have used sodium or potassium phosphate, borax, sodium or calcium fluoride as solvents and have established definite ratios of uranium salt to solvent to produce maximum brightness of fluorescence. Sodium and lithium fluorides have been found to be the most satisfactory solvents.⁽⁴⁶⁾

Of numerous investigated elements only columbium gives a fluorescent yellow green on fusion with sodium fluoride.⁽⁴⁷⁾ The fluorescence activated by columbium is much weaker and lies farther in the green than that produced by uranium compounds. If observed in unfiltered iron arc radiation uranium fusions show the characteristic color while columbium fusions appear pale blue.

Volmar⁽⁴⁸⁾ has used the decrease in fluorescent intensity of uranyl nitrate caused by the presence of

halogen and other ions for microchemical detections. The following increasing series of fluorescence suppression has been established: nitrite, chloride, salicylate, thiosulfate, chromate, ferricyanide, permanganate, sulfide, arsenate, ferrocyanide, thiocyanate, dichromate, bromide, and iodide. Of the cations investigated only silver destroyed the fluorescence which confirms the work of Got6 who used this reaction as a test for silver.

Zinc

- (a) With acetic acid solutions containing sodium acetate, oxine (8-hydroxyquiniline) in the presence of zinc, gives a yellow green fluorescence. Limit of recognition 0.1 gamma, dilution 1:500,000. (26)
- (b) In neutral solutions cochineal produces a red fluorescence with zinc. Limit of recognition 0.1 gamma, dilution 1:500,000. (26)
- (c) Neutral solutions of zinc give a yellow green fluorescence with alcoholic morin. The fluorescence increases if made alkaline but morin itself gives a yellow fluorescence in alkaline solution, hence the test must be carried out in neutral solution. Limit of detection 0.05 gamma, dilution 1:1,000,000. (26)

Concerning the above tests it should be pointed out that a number of these will respond to oxidizing or reducing agents, e.g. any oxidizing agent that will liberate iodine from

KI will destroy the fluorescence of alphanaphthol/3vone. Fluorescent tests which are relatively insensitive, such as those given above for iron, are more of academic interest than utility.

In addition to the applications of fluorescence phenomena to micro-detections of inorganic materials, it has been found that the color change of a number of fluorescent substances with change in the pH value of the solution is critical enough to warrant the use of such materials as fluorescent indicators in inorganic volumetric analysis. This application has met with considerable success, particularly in the titration of colored and turbid liquids. Table No. 4 taken from the work of Radley and Grant⁽⁴⁹⁾ and other workers^(50,51,52,53) lists a number of such indicators with the color change corresponding to a certain pH or pH range.

Table No. 4

Color Change and pH Range of Fluorescent Indicators		
Indicator	Color Change	pH Range
Benzoflavine	Yellow to green	0.3 - 1.7
4-Athoxyacridine	Green to blue	1.2 - 3.2
3,6-Tetramethylidiamino-xanthone	Green to blue	1.2 - 3.4
p-xylenesulfonaphthalein(53)	Colorless to yellow	2.0
Thymol blue(53)	" " orange	2.0
3,6 dihydroxyphthalimide - (1st transition)	Blue to green	Below 2.4
Eosin	Colorless to green	2.5 - 4.5
Betanaphthylamine	" " violet	2.8 - 4.4
Salicylic acid	" " blue	3.0
Alphanaphthylamine	" " blue	3.4 - 4.8
Phloxine	" " yellow	3.4 - 5.0
Erythrosin	" " green	4.0 - 4.5
Fluorescein	" " green	4.0 - 4.5
Quinic acid(52)		4.0 - 5.0
Dichlorofluorescein	Colorless to green	4.0 - 8.0
Betamethyl aesculetin	" " blue	4.0 - 6.2
Resorufin	Yellow to orange	4.4 - 6.4
Acridine	Green to violet	4.9 - 5.1
3,6 dihydroxyxanthone	Colorless to blue-violet	5.4 - 7.6
Litmus(51)	Colorless to blue	5.8 - 7.0
3,6 dihydroxyphthalic-dinitrile	Blue to green	5.8 - 8.2
quinine (1st transition)	Blue to violet	5.9 - 6.1
3,6 dihydroxyphthalimide - (2nd transition)	Green to yellow-green	6.0 - 8.0
Umbelliferone	Colorless to blue	6.5 - 7.6
Orcinolaurin(50)	Red to green	6.5 - 8.0
Phenol red(53)	Greenish yellow to violet	6.8 - 8.4
Magnesium 8-hydroxy quinoline complex	Colorless to golden	7.0
Azolitmin(53)	" " blue	7.0 - 8.0
Rosolic acid(53)	" " violet	7.0 - 8.2
Betamethyl umbelliferone	" " blue	7.1
Na alizarin sulfonate(53)	Light yellow to red	8.0
Coumaric acid	Colorless to green	7.2 - 9.0
Betanaphthol	" " blue	3 - 6
Tumeric tincture(53)	Yellowish green to orange	8.0 - 9.3
Alphanaphtholsulfonic acid	Dark blue to bright violet	8.2

Table No. 4 (cont'd)

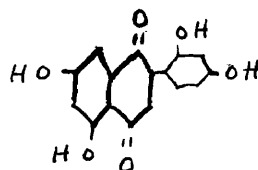
<u>Color Change and pH Range of Fluorescent Indicators</u>		
Indicator	Color Change	pH Range
Aeridine orange	Colorless to yellow-green	8.4 - 10.4
Ethoxyphenylnaphthostilb- azonium chloride	Green to colorless	9 - 11
1-naphthol-2-sulfonic acid	Dark blue to bright violet	9.4
Betanaphtholsulfonic acid	Dark blue to bright violet	9.5
Quinine (2nd transition)	Violet to colorless	9.5 - 10.0
6.7 dimethoxyisoquinoline (51)		9.5 - 11.0
Coumarin	Weak green to bright green	9.8 - 12.0
Alphanaphthionic acid	Azure blue to green	12 - 13
Betanaphthionic acid	Azure blue to violet	12 - 13
Cotarnine	Yellow to white	12.5

EXPERIMENTAL

(A) Photometric Estimation of Aluminum by the Morin Reaction

The discovery by Goppelsroeder⁽⁵⁴⁾ in 1867 of the fluorescent phenomenon produced by aluminum in the presence of morin under excitation by ultraviolet light has been studied by Schantl⁽⁵⁾ with reference to its use for the detection of aluminum in microchemical work. This portion of the present investigation is an attempt to establish this reaction upon a systematic quantitative basis through accurate measurement of the fluorescent light transmitted by solutions of varying aluminum concentration.

Morin, a tetrahydroxy flavonol of the following structural formula



is obtainable from fustic extract and may be crystallized in the pure state in slender yellowish white prisms. It is insoluble in cold water, dissolves in increasing amounts in hot water, ether, alcohol and acetone; it is slightly soluble in chloroform, insoluble in benzene, petroleum ether, and carbon disulfide. For the present investigation a solution of the crystallized material in 95% alcohol was used.

The fluorescence produced is of a yellowish green color

and consists of a green and red band extending over wave lengths 4500 to 6300 $\text{m}\mu$. Acids such as nitric, sulfuric and hydrochloric destroy the fluorescence. Acetic acid exerts a characteristic effect in increasing the intensity of the fluorescence and shifting the wave length further toward the red end of the spectrum. In alkaline solutions morin gives a faint yellow fluorescence.

Evidence has been presented by Behantl⁽⁵⁾ that maximum fluorescent brightness is obtained from solutions containing dyestuff and aluminum in the ratio of 5 mols of morin to 1 of aluminum, corresponding to the compound $\text{Al}(\text{C}_{15}\text{H}_9\text{O}_7)_3$. This evidence has been confirmed (Table No. 5) and to solutions studied quantitatively morin was added to satisfy or exceed this relationship. Thus a solution containing 1 mg aluminum will require 33 mg of morin to give maximum fluorescence.

Table No. 5

<u>Volume of 0.1% Morin Solution Required to Produce Maximum Visual Intensity for 5 and 10 ml Volumes Respectively of an Aluminum Solution Containing 100 mg Al/l.</u>				
	(1)	(2)	(3)	Calculated
5.0 ml. Aluminum Soln.	17.3	17.0	17.5	16.7 ml.
10.0 ml. " "	34.1	35.0	34.2	33.4 ml.

GENERAL EXPERIMENTAL DETAILS

A General Electric high pressure 4H mercury vapor tube inclosed within another glass tube was used as a source of

near ultraviolet radiation comprising wave lengths from 3000 to 4000 \AA . This lamp was mounted in front of a small opening in a wooden box. A small electric fan was also mounted in the box to prevent overheating during long periods of use. Wood's glass placed over the opening was used as a filtering medium.

Intensity values were obtained by use of a Zeiss Pulfrich photometer. This instrument employed two cells in one of which was placed the standard solution and in the other the unknown. Observations were made at right angles to the source of ultraviolet light. Fluorescence appearing in the two cells was observed simultaneously through an eyepiece as a circular divided field. Filters in the eyepiece permit isolation of bands about 25 millimicrons wide in various regions of the spectrum. The intensity of the unknown or calibration solution was determined by reducing the intensity of the beam from the standard solution by means of a variable aperture in the objective. When the two fields were matched the intensity was read from a calibrated drum as a percentage value. Cells 2.0 x 1.8 cms. were used, arranged so that the thickness penetrated was the 1.8 dimension.

Standard aluminum solutions were prepared by dissolving potassium aluminum alum crystals in warm distilled water. Intermediate concentrations for calibration curves were obtained by dilution. Fustic extract, of good quality, was

used as a source of morin.

THE QUANTITATIVE METHOD

The following detailed instructions were evolved as calibrations and determinations were carried out over a period of several months.

- (1) The amount of alcoholic morin solution required to react with the aluminum content should be added as part of the volume of the standard aluminum solutions as they are made up. In carrying out determinations on solutions of unknown aluminum content morin should be added to a separate portion of the solution until maximum brightness is obtained in order to determine the minimum amount of morin which must be added. An excess of morin solution has no detrimental effect on the measurements. The dilution value must be taken into consideration in calculating the amount of aluminum present in the original solution.
- (2) For concentrations of aluminum above 10 mg/l more reproducible readings are obtained by centrifuging off a small amount of brownish flocculent material which appears at the higher aluminum concentrations.
- (3) Care must be taken that exactly the same volumes are compared in the two cells.
- (4) The cells must be placed in the same relative position with regard to the prisms and to the source of ultraviolet radiation for each observation in

preparing calibration curves. A satisfactory method of accomplishing this is to clamp to the stage of the photometer a piece of cardboard in which holes have been cut into which the cells fit tightly. Having once adjusted the height of the cells from the prisms, no change should be made in the setting during the course of a set of observations. The cells can be emptied by suction through a capillary glass tube and filled by pipette readily without disturbing their position. The cells must be kept optically clean at all times.

- (5) The source of radiation should be set in such a position in relation to the photometer that equal intensities are obtained in the two fields when the same solution is placed in both cells. This adjustment must always be made before making observations unless a permanent set-up is available.
- (6) The final reading should be an average of several readings taken as equality in intensity is approached both from the dark and bright sides.
- (7) When working with low aluminum concentrations and weak fluorescent intensities a drop of acetic acid added to both cells will often permit more accurate readings.

EXPLANATION OF TERMS USED

The fundamental equation used in these measurements to

show the dependence of fluorescence upon concentration is the relationship proposed by Perrin. (55)

$$\phi = \phi_0 e^{-K \cdot c}$$

$$\text{or } K = \frac{1}{c} \log \frac{\phi_0}{\phi} \text{ in logarithmic form}$$

where

c = concentration of solution contained in cell in g/l

$\phi = \frac{F}{c}$ where F is the measured fluorescent intensity

ϕ_0 = specific fluorescence factor which is approached with increasing dilution, i.e. is a constant obtained from the ratio F/c where c is in the range in which fluorescence is directly proportional to concentration. (See Table No. 6)

K = a constant

The fluorescent intensity relationship is the same as that for light absorption which is given by ^{the} Lambert-Beer's law. This states that the light absorption is proportional to the thickness of the cell, to the concentration of the dissolved substance in mol/l, and to a constant varying from substance to substance and known as the molecular light absorption coefficient.

$$D = \log \frac{I_0}{I} = \epsilon \cdot c \cdot d$$

D = density

$\log \frac{I_0}{I}$ = extinction

c = concentration of solution contained in cell (in mols/l)

d = thickness of cell in cm.

ϵ = molecular extinction coefficient

For any wave length the value of ϵ should be constant at all dilutions and all stratum thicknesses. This constancy is a criterion of adherence to Beer's law.

ANALYTICAL RESULTS

The curves obtained for fluorescence vs. concentrations are typical of fluorescent solutions. At low concentrations, Graphs 2 and 3, a straight line relationship between fluorescent intensity and concentration is obtained. For concentrations above 100 mg/l the fluorescence and concentration are not directly proportional but follow an exponential relationship proposed by Perrin, (55) as indicated by the constancy of K . (See Table No. 6 and Graph 1) It is noted that the specific fluorescence factor ϕ is constant for increasing concentration up to a concentration of approximately 0.10 g/l. A plot of $\log \frac{\phi_0}{\phi}$ values against concentration, Graph 4, shows the adherence to Beer's law.

The method followed for calculation of the molecular extinction coefficient is outlined as follows:

$$D = \log \frac{I_0}{I} = \log \frac{I_0}{I_0 - I_{\text{abs.}}}$$

where D = density

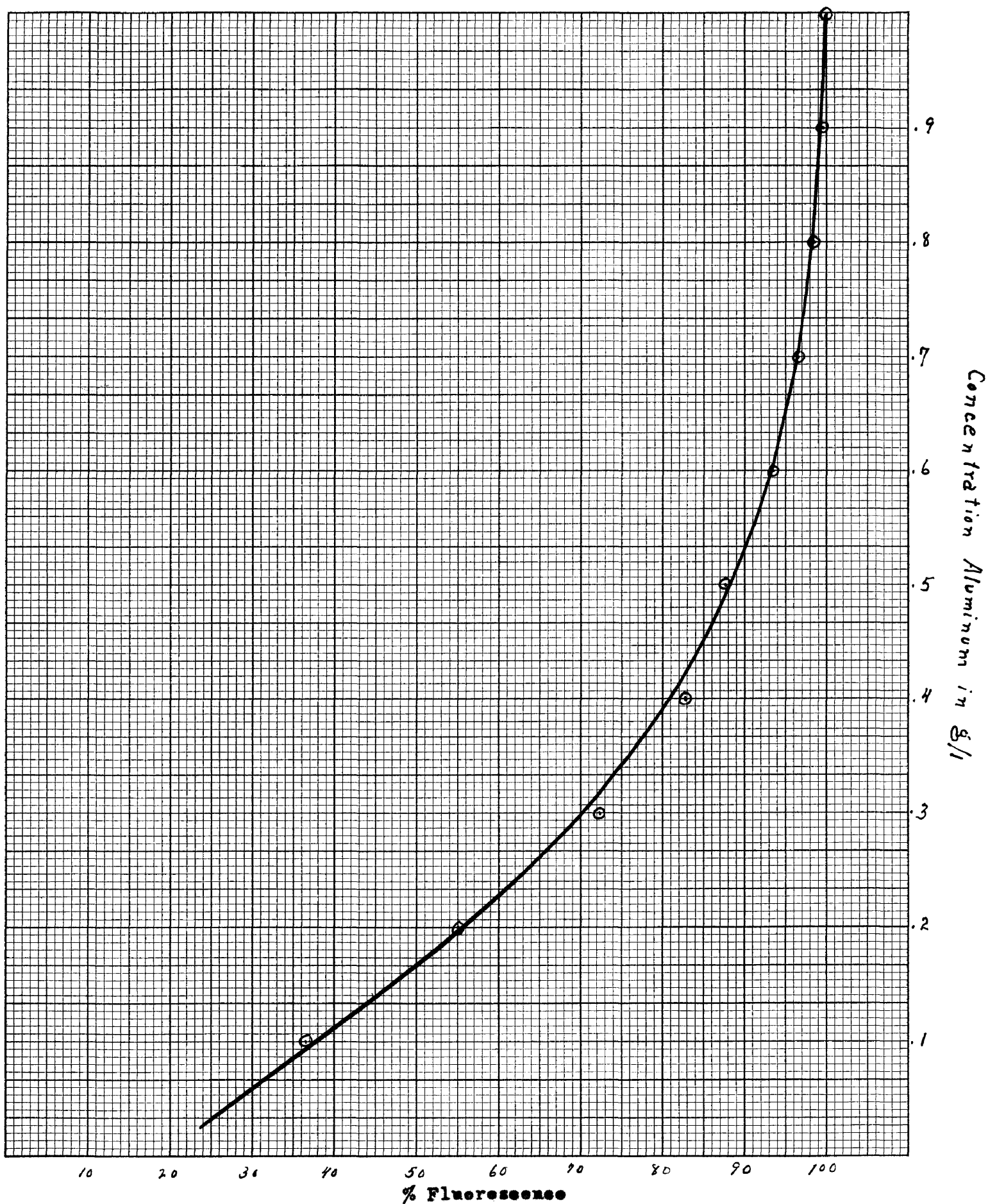
I_0 = intensity of primary radiation

I = " " radiation from fluorescing solution

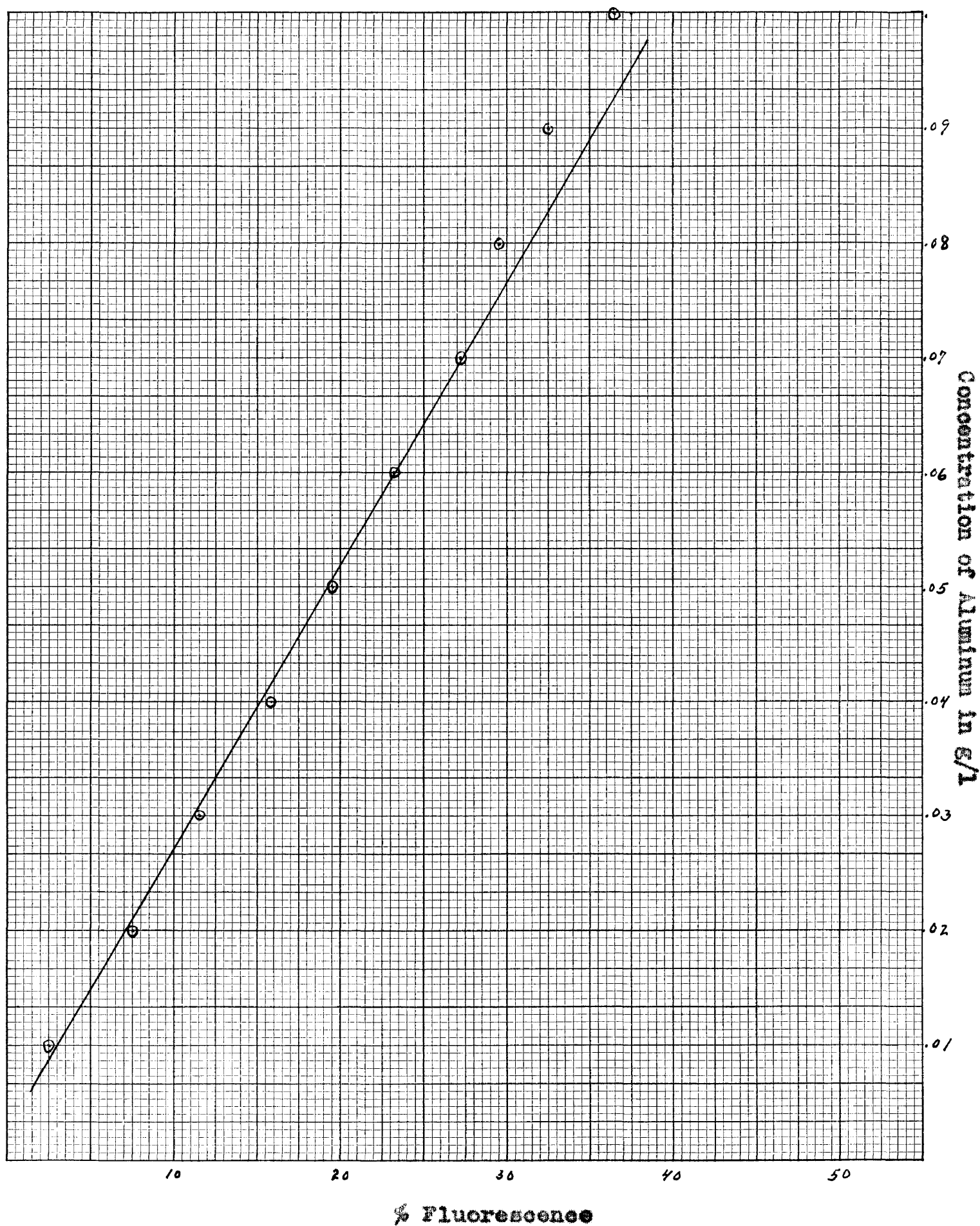
$I_{\text{abs.}}$ = intensity absorbed by solution

Since the fluorescent intensity F is directly proportional

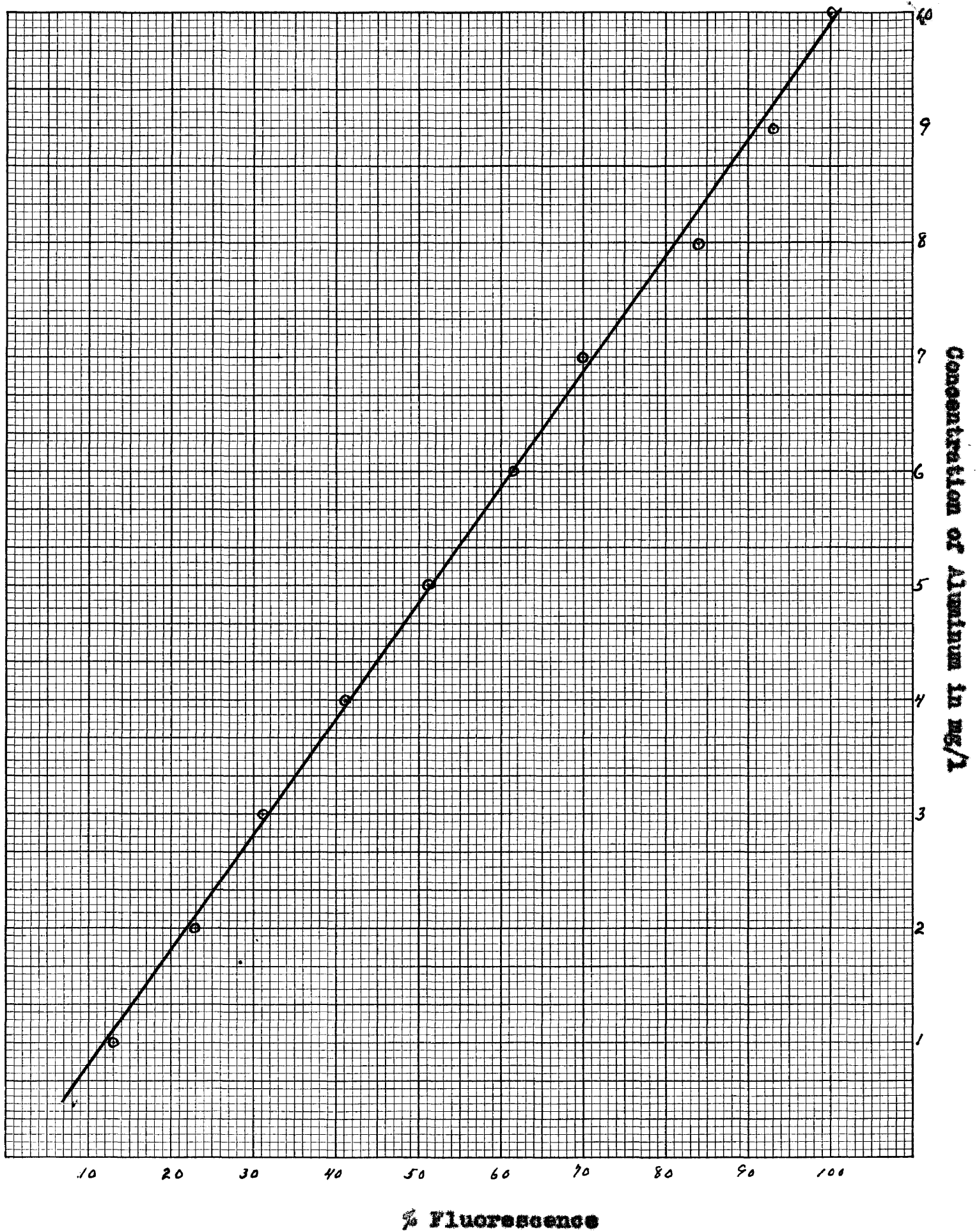
Graph No. 1
% Fluorescence vs. Aluminum Concs. from 0.1 g/l to 1.0 g/l



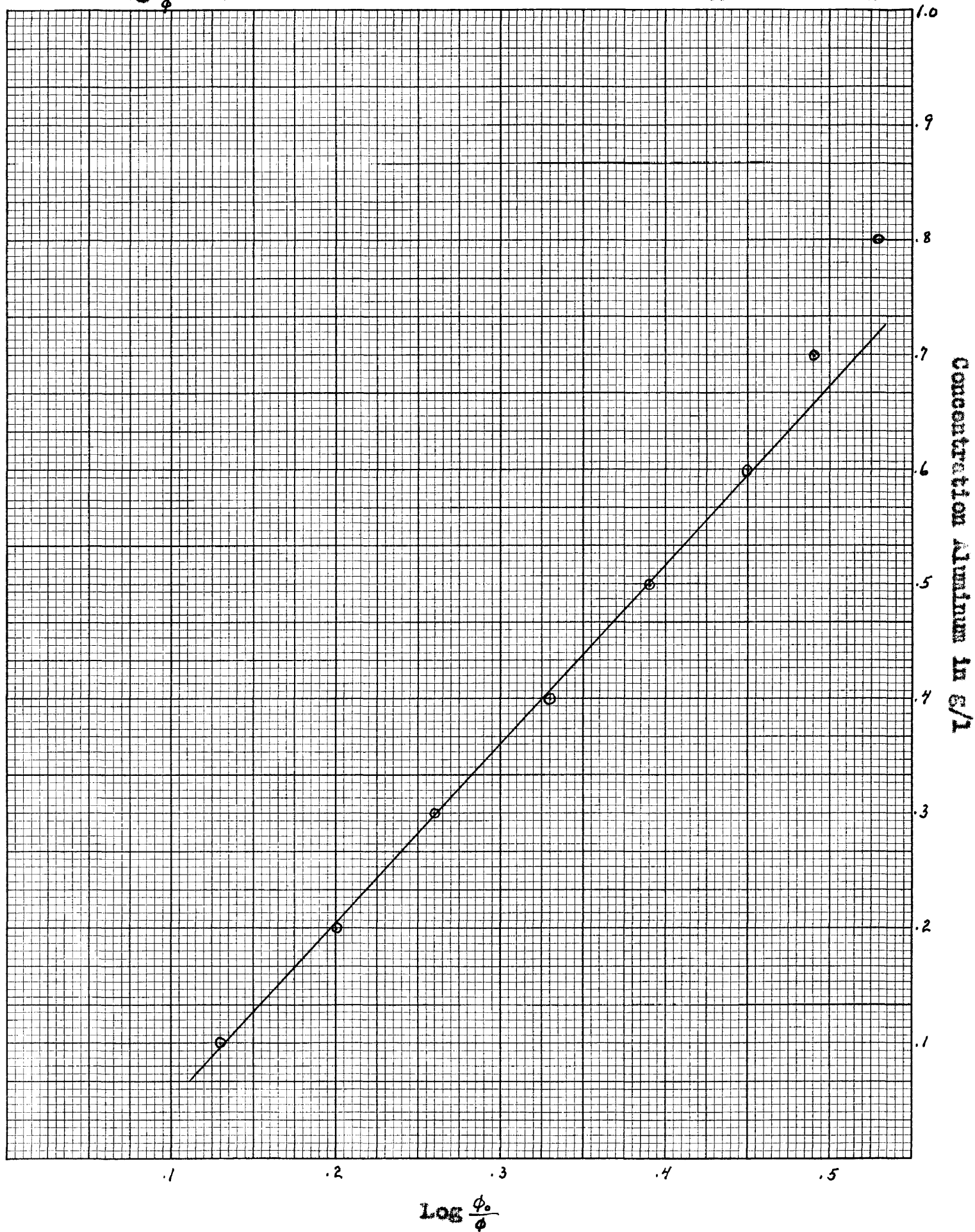
Graph No. 2
% Fluorescence vs. Aluminum Concs. from 0.01 g/l to 0.10 g/l



Graph No. 3
% Fluorescence vs. Aluminum Concs. from 1 mg/l to 10 mg/l



Graph No. 4
Log $\frac{\phi_0}{\phi}$ vs. Aluminum Concentrations from 0.1 g/l to 1.0 g/l



to the light absorbed

$$D = \log \frac{F_k}{F_k - F}$$

where F_k is the fluorescent intensity accompanying complete absorption I_0 . Where intensities are measured in per cent, as for the Pulfrich photometer

$$D = \log F_k - \log (F_k - F)$$

$$\text{or} \quad D = 2 - \log (100 - F)$$

Knowing the values of D for various concentrations, ϵ may be calculated from Beer's law

$$\epsilon = \frac{D}{c \cdot d}$$

where c = concentration in mols/l

d = cell thickness in cm.

An average value of 29 as the molecular extinction coefficient for this fluorescent solution was obtained. (Table No. 7) The fair constancy of ϵ at all dilutions gives further evidence of adherence to Beer's law.

Table No. 6

The Region of Direct Proportionality between Fluorescent Intensity and Aluminum Concentration together with Specific Fluorescence Factors and Perrin's Constant. 1 g Al/l used as Standard for Comparison.

c (g/l)	F	$\phi = F/c$	$\log \frac{\phi_0}{\phi}$	K
1.000	100.0	100	0.58	58
.900	99.6	111	.53	59
.800	98.3	123	.49	61
.700	96.1	136	.45	64
.600	93.4	155	.39	65
.500	87.7	175	.33	66
.400	82.9	206	.26	65
.300	72.2	241	.20	66
.200	55.0	275	.13	65
.100	36.3	363	Region of Direct Proportionality	
.0900	32.3	359		
.0800	29.7	364		
.0700	27.1	387		
.0600	23.1	385		
.0500	19.8	396		
.0400	15.8	395		
.0300	11.7	390		
.0200	7.8	390		
.0100	3.6	360		

379 = Avg. = ϕ_0

Table No. 7

Values of Functions Obtained in Calculation of Molecular
Extinction Coefficients for Aluminum Morin Solutions

c (g/l)	c' (mol/l) $\times 10^{-2}$	F	$(F_k - F)$	$\log (F_k - F)$	$2 - \log(F_k - F)$	ξ
1.000	3.7	100	0.0	- - -	- - -	--
.900	3.3	99.6	0.4	- - -	- - -	--
.800	3.0	98.3	1.7	.23	1.77	33
.700	2.6	96.1	3.9	.59	1.41	30
.600	2.2	93.4	6.6	.82	1.18	29
.500	2.0	87.7	12.3	1.09	.91	25
.400	1.5	82.9	17.1	1.23	.77	29
.300	1.1	72.2	27.8	1.44	.56	28
.200	.74	55.0	45.0	1.65	.35	26
.100	.37	36.3	63.7	1.80	.20	28
.0900	.33	32.3	67.7	1.83	.17	29
.0800	.30	29.7	70.2	1.85	.15	28
.0700	.26	27.1	72.9	1.86	.14	30
.0600	.22	23.1	76.8	1.89	.11	28
.0500	.20	19.3	80.2	1.90	.10	28
.0400	.15	15.8	84.2	1.92	.08	30
.0300	.11	11.7	88.2	1.95	.05	25
.0200	.074	7.8	92.2	1.96	.04	30
.0100	.037	3.6	96.4	1.98	.02	<u>30</u>

Avg. = 29

 $d = 1.8$ cm.

Having determined the value of ϵ it is possible to calculate the theoretical intensity which should be observed for a given concentration from the relationship

$$\log \frac{I_0}{I} = \epsilon \cdot c \cdot d$$

where all values are known except that of I . Table No. 8 shows a comparison between values measured and those calculated assuming a value of 29 for ϵ .

Assuming the validity of the Beer-Lambert law, it is also possible to calculate the concentration of an unknown solution if its intensity is measured and if the D value is known for any other concentration. Table No. 9 shows a comparison between actual concentrations and those calculated.

$$\frac{D_1}{D_2} = \frac{c_1}{c_2} = \frac{2 - \log (100 - F_1)}{2 - \log (100 - F_2)}$$

Table No. 8

Comparison between Fluorescent Intensity Values Measured and Those Calculated Assuming a Molecular Extinction Coefficient Value of 29.

c (g/l)	c' (mol/l) $\times 10^{-2}$	D	I(%)	I _{abs.} (I ₀ - I)%	F (found %)
1.000	3.7	1.93	1.1	98.9	100.0
.9000	3.3	1.72	1.9	98.1	99.6
.800	3.0	1.57	2.7	97.3	98.3
.700	2.6	1.38	4.4	95.6	96.1
.600	2.2	1.15	7.1	92.9	93.4
.500	2.0	1.04	9.1	90.9	87.7
.400	1.5	.78	16.7	83.3	82.9
.300	1.1	.57	26.9	73.1	72.2
.200	.74	.39	40.1	59.9	55.0
.100	.37	.19	64.1	35.9	36.3
.0900	.33	.17	67.6	32.4	32.3
.0800	.30	.15	70.8	29.2	29.7
.0700	.26	.136	73.1	26.9	27.1
.0600	.22	.115	76.7	23.3	23.1
.0500	.20	.104	78.7	21.3	19.8
.0400	.15	.078	83.6	16.4	15.8
.0300	.11	.057	87.7	13.3	11.7
.0200	.074	.039	91.4	8.6	7.8
.0100	.037	.019	95.7	4.3	5.6

Table No. 9

Comparison between Actual Aluminum Concentrations and Those Calculated from Fluorescent Intensity Values and the Beer-Lambert Law

c (g/l)	c' (mol/l) $\times 10^{-2}$	$2 - \log (F_k - F)$	Conc. calc.
1.000	3.7	1.93	---
.900	3.3	1.72	0.89
.800	3.0	1.57	.81
.700	2.6	1.36	.71
.600	2.2	1.15	.60
.500	2.0	1.04	.54
.400	1.5	.78	.40
.300	1.1	.57	.30
.200	.74	.39	.20
.100	.37	.19	.10
.0900	.33	.17	.088
.0800	.30	.15	.078
.0700	.26	.136	.070
.0500	.20	.115	.060
.0400	.15	.104	.054
.0300	.11	.078	.040
.0200	.074	.039	.020
.0100	.037	.019	.010

In order to check on the accuracy of the method, "unknown" alum solutions of aluminum content up to 1 g/l were examined by this method. Where the concentrations were calculated by formula from the measured intensities the error ranged from 2% to 15%; as determined graphically the error ranged from 2% to 6%. The results are given in Table No. 10.

Table No. 10

Results of Analysis of Three Solutions of Unknown Al Content

Mark	Conc. Al in g/l actually present	F	Calc. Conc.	Conc. shown by graph
1	0.10	35.2	0.098	0.098
2	.50	87.0	.46	.47
3	.75	97.8	.86	.77

INTERFERING ELEMENTS

Iron and chromium form black precipitates with morin and consequently will interfere with quantitative determinations of aluminum by this method. In the presence of both aluminum and iron or of aluminum and chromium the precipitates may be filtered off through a clay filtering medium and aluminum detected qualitatively in the filtrate by the green fluorescence of the morin compound. Highly colored ions such as copper, nickel, and cobalt will produce slight variations in the color shade observed but may be compensated for by addition of approximately a like

amount to the standard aluminum solution used for comparison. Silver destroys the fluorescence probably through its oxidative action. It has been reported in the literature⁽²³⁾ that lead, zinc, and molybdenum in neutral solutions will produce fluorescence effects with alcoholic morin solutions similar to that obtained with aluminum. This has been confirmed but holds only for neutral solutions. In the presence of a small amount of acetic acid these elements show no fluorescence with morin whereas the presence of acetic acid exerts a favorable influence on the aluminum reaction. Beck⁽⁵⁶⁾ has reported the fluorescence of morin with scandium, gallium, and indium in solutions containing mineral acid.

The following ions were found to have no effect on the fluorescence: Hg^+ , Hg^{++} , Bi^{+++} , Cd^{++} , As^{+++++} , As^{+++} , Sb^{+++} , Sn^{++++} , Sn^{++} , Mn^{++} , Tl^{+++} , Ca^{++} , Ba^{++} , Sr^{++} , Mg^{++} , Na^+ , K^+ , NH_4^+ , Li^+ and common anions except fluorides.

(B) Studies Carried Out in an Effort to Develop New Specific Fluorescent Tests for the Cations.

Inasmuch as no theory has been suggested or developed which might predict what combinations of metals and types of organic radicals would give characteristic fluorescence, it was proposed to prepare solutions of a number of metals and examine them for fluorescence on addition of small amounts of solutions of dyestuffs and other organic compounds readily available. It was hoped in this way to obtain some clue as to the nature of the organic radicals which would most likely give the desired effect and at the same time to discover some new fluorescent tests.

Approximately 0.01 M solutions of the following ions were used: Al^{+++} , In^{++} , Mg^{++} , Pb^{++} , Be^{++} , Th^{++++} , Zr^{++++} , Ni^{++} , Co^{++} , Ag^+ , As^{+++} , Cu^{++} , Fe^{+++} , Ba^{++} , Mn^{++} , Hg^{++} , Ce^{+++} , Cr^{+++} , Sn^{++++} . One ml. of a 0.1% aqueous or alcoholic solution of the dyestuff or organic material was added to 10 ml. of the cation solutions contained in soft glass test tubes. Solutions were tested under acid and alkaline conditions and were allowed to stand over night before making a final observation. In addition tests for fluorescence were made by placing a few drops of the solution on a filter paper and examining under ultraviolet light. A Hanovia analytical quartz mercury vapor lamp, described above under light sources, was used as a source of ultraviolet light.

A list of the organic materials used is given in Table No. 11. A number of dyestuffs are listed for which the

structural formula was not readily available but could be obtained from the manufacturer or by analysis should the results warrant.

Table No. 11

Organic Materials Studied for Fluorescence in Combination with
Cations

Material	Color Index Number	Structural Formula
Acid Anthracene Red G	443	Appear only on origin
Acid Black BE Conc.	246	
Acid Violet 4 BNS	695	
Alizarin	1027	
Alizarin Astrole B	1075	
Alizarin Saphirole B	1054	
Alizarin Yellow BW	40	
Alphazurine 2 G	712	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Aluminon		Shown only on original
Amidine Develop Bordeaux 2 C	375	
Amidine Fast Brown 3 R	601	
Amidine Fast Scarlet 4 BA Conc.	450	
Aniline Azo Betanaphthol		
Anthranilic Acid		
Anthraquinone Violet Base	1080	
Aurine	724	
Auramine Base	655	
Azo Rubin Conc.	179	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Bark Crystals	1233	Shown only on original
Benzidine		
Benzoin oxime		
Benzoflavine	791	
Benzopurpurin 4 B	448	
Benzyl Green B	667	
Blue for Cotton	707	
Boiling Bromine	768	
Bronze Blue RWA Extra	1268	
Brom Cresol Purple		

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Brom Phenol Blue		Shown only on original
Brom Thymol Blue		
Chinoline Yellow	801	
O-chlor-m-toluidine		
Chlorantine Fast Orange T4RL	821	
Chrysoidine	20	
Chrysomine	410	
Cibacete Orange 4 R Powder	1230	
Cibacete Red 3 B	1210	
Cibacete Scarlet G Powder	1228	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with
Cations

Material	Color Index Number	Structural Formula
Cibacete Yellow GGN Powder	1197	Shown only on original
Cloth Fast Black 2 BN	307	
Cloth Fast Blue R	289	
Congo Red	370	
Coriphosphine OX	787	
Cresolphthalein		
Cresol Red		
Crystal Violet	681	
Cyanol FF	715	
Diamine Fast Red FC New	419	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with
Cations

Material	Color Index Number	Structural Formula
Diphenyl Red 55	436	Shown only on original
Diphenyl yellow 6GS	814	
Diphenyl amine		
Direct Black 61R	581	
Direct Brill Violet Conc. 2R	387	
Direct Brown 5 G Mk. Conc.	596	
Direct Yellow 19 Conc.	620	
Dithionamide		
Dithione		
Erythrosine	772	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with
Cations

Material	Color Index Number	Structural Formula
Fast Crinson GRA	51	Shown only on original
Fast Light Yellow E 2GA	333	
Fast Red B (Bordeaux B)		
Formyl Violet Conc.	698	
"G" Salt		
Rematin Crystals	1343	
8-Hydroxy quinoline		
Indian Yellow G	146	
Induline	660	
Iodeosine	773	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Inositol		Shown only on original
Riton Fast Green	735	
Riton Fast Violet 10 B	696	
Riton Fast Orange	27	
Malachite Green	657	
Metanil Yellow	138	
Methyl Red	211	
Methyl Violet B Conc.	680	
Methylene Blue		
Metol		

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Milling Violet	758	Shown only on original
Naphthol Yellow S		
Nat'l Alizarine Blue GRL	1066	
Nat'l Niagara Blue RW	512	
Alphanitrosobetanaphthol		
Orange for Cotton	21	
Orange G	151	
Orange I	150	
Phenol Red		
Phloroglucin		

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Phosphine	793	Shown only on original
Pontacyl Green Sn Extra	737	
Primuline		
Quinazarine Green Base	1078	
Resorcin Brown	234	
Rhodamine B	749	
Rocceline	176	
Rosaniline Base	677	
Safranine Y Extra Conc.	841	
Salicylaldoxime		

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material	Color Index Number	Structural Formula
Setacyl Direct Violet R Conc.	394	Shown only on original
Succo Fuchsine S	692	
Succo Soluble Blue D-400 Conc.	706	
Tartrazine	640	
Thiocarbamide		
Thioflavine T	815	
Thymol Blue	765	
Turmeric	1238	
Xylidene Orange	78	

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with
Cations

Material	Material
Acid Blue RN	Diphenyl Fast Orange SE
Brown for Cotton	Diphenyl Fast Orange WS
Chlorantine Fast Brown ERL	Direct Brill Green CEM
Chlorantine Fast Brown SRL	Direct Fast Orange SE
Chlorantine Fast Green BL	Eclipse Bronze
Chlorantine Fast Grey	Eriochrome Geranol R
Chlorantine Fast Grey BLN	Erio Fast Brill. Violet R. Conc.
Chlorantine Fast Red 6ALL	Erio Fast Red G Conc.
Chlorantine Fast Violet	Erio Flavine SX Extra
Chlorantine Fast Violet 4BL	Formol Fast Black G Conc.
Chlorantine Fast Yellow 4GL	Helio Red Fast Pink
Chrysophenine Y Extra Conc.	Hypernic Crystals
Cibacete Black DGN Powder	Inocyl Brilliant Blue
Cibacete Navy Blue EN	Inocyl Orange
Cibacete Sapphire Blue	Kiton Fast Red 4BL
Cloth Fast Green B	Kiton Fast Yellow
Cloth Fast Orange R	Kiton Pure Blue
Cloth Fast Red GRG	Lanasol Blue B
Cloth Fast Violet B	Logwood Crystals
Cotton Red 5B	Madder Lake
Diazophenyl Brown 3RW	Nat'l Erie Yellow Y
Diphenyl Blue G	Neolan Black 2 G
Diphenyl Fast Bordeaux BL	Neolan Black WA Ex

Table No. 11 (cont'd)

Organic Materials Studied for Fluorescence in Combination with Cations

Material

Neolan Green BL Conc.

Neolan Orange R

Neolan Red 3B

Neolan Violet Brown

Neolan Yellow GR Conc.

Neutral Brown RX

Novazol Acid Blue BL

Osage Orange Crystals

Phosphine G

Silk Black 4BF

Succ Soluble Acid Blue D-380 Conc.

Typhor Carmine

Union Jade Green

Violet for Cotton

New Fluorescent tests were discovered as follows:

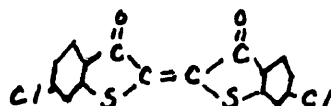
Thorium

A brilliant orange red fluorescence consisting of a band lying between wave lengths 6300 \AA^0 and 6800 \AA^0 was obtained with thorium solutions in the presence of an alcoholic solution of Cibacete Red 3 B. The alcoholic dye solution itself shows a faint fluorescence which is clearly distinguishable from that obtained in the presence of thorium. This fluorescence is apparently associated with a change in the red color of the dyestuff to purple brought about by thorium and visible in ordinary white light. The appearance of this purple color may be used as a colormetric test for thorium to dilutions of 1:20,000. By observing the fluorescence produced under ultraviolet light the test is more sensitive and 2.5 gamma may be detected at a dilution of 1:40,000. This seems to be the only colormetric test applicable to thorium which has been described in the literature to date.

The test is not sensitive to small changes in pH value but strong alkali will destroy the fluorescence. Best results are obtained with neutral or slightly acid solutions. Aluminum is the only other element of those studied which will respond to this test.

Cibacete Red 3 B, Color Index No. 1210, is listed as having a structural formula similar to that of the type

of the thioindigo vat dyes.

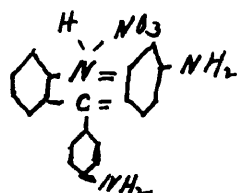


Inasmuch as this structure has not been confirmed by private communication with the manufacturers and determination of the structure is beyond the scope of this paper, it is impossible at the present time to make any assumptions regarding salt formation or other type of reaction which might be taking place between thorium and the dyestuff.

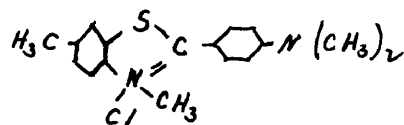
Zinc

Zinc solutions on standing over night with a small amount of Benzopurpurin 4B were found to deposit a copious amount of a brown flocculent precipitate and the supernatant liquid to show a blue fluorescence extending as a band from wave length 3745 Å° to 4210 Å°. This test is sensitive to zinc at dilutions of 1:10,000. Ba⁺⁺, Co⁺⁺, Cu⁺⁺, Pb⁺⁺, Mg⁺⁺, Mn⁺⁺, Ni⁺⁺ and Al⁺⁺⁺ give the same fluorescent phenomenon although with weakened intensity.

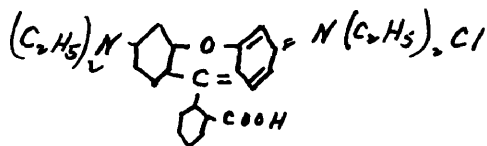
The structural formula of this dyestuff, Color Index No. 448, indicates the possibility of salt formation on the sulfonic groups present. Should one atom of zinc combine with the two sulfonic groups present a closed structure would be formed which is apparently conducive to fluorescence, as evidenced by the structure of fluorescent dyestuffs such as phosphine, thioflavine T and Rhodamine B



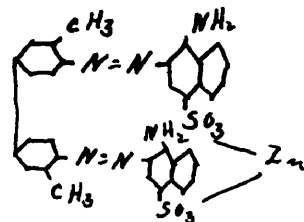
Phosphine



Thioflavin T



Rhodamine B



Zinc salt of Benzopurpurin 4B

Silver

The bright blue fluorescence of "G" salt in alcoholic solution is converted to a dull gray in the presence of silver nitrate solutions. This test is sensitive to 1 gamma at a dilution of 1:40,000. No other ions were found to interfere with the test. The reaction is best carried out in a slightly acid solution.

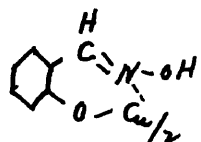
Copper

In working with salicylaldoxime, the well known analytical reagent for copper, it was found that the test was much improved if examined under ultraviolet light. Copper solutions destroy the pale green fluorescence of alcoholic solutions of salicylaldoxime. This reagent has been used to determine 0.5 gamma copper at a dilution of 1:75,000 by the formation of a yellow greenish precipitate or opalescence. By observing the disappearance of fluorescence of the salicylaldoxime as the copper solution

is added the sensitivity may be increased to 1:2,000,000. Unfortunately acids, even weak acids such as acetic, and all other cations tested except the alkali and alkaline earths destroyed the fluorescence also.

The reagent is prepared by dissolving the solid material in about 5 ml. of alcohol and pouring this solution slowly into 95 ml. of water. An oily suspension is formed that disappears on slight shaking.

The formula of the copper compound is represented as follows:



CONCLUSIONS

- (I) Aluminum may be determined quantitatively by photometric measurement of the intensity of fluorescent solutions produced by the aluminum-morin reaction. The variation of intensity with concentration was found to follow the Lambert-Beer law. In common with other fluorescent solutions at low concentrations the intensity was found to be directly proportional to the concentration, while at higher concentrations, above 0.1 g Al/l the intensity followed a relationship proposed by Perrin. The molecular extinction coefficient under the conditions studied was found to be 29.
- (II) In searching for characteristic fluorescent tests for metallic ions over 175 dyestuffs and organic materials have been added to solutions of 19 different cations and examined for fluorescence under ultraviolet light. New fluorescent tests were discovered as follows:
- (a) Thorium - produces a brilliant orange red fluorescence with Cibacete Red 3 B, C.I. 1210. Limit of recognition 2.5 gamma, dilution 1:40,000.
 - (b) Zinc - precipitates with Benzopurpurin 4 B giving a blue fluorescing supernatant liquid. Limit of recognition 1:10,000.
 - (c) Silver - destroys the fluorescence of "G" salt. Limit of recognition 1 gamma, dilution 1:40,000.
 - (d) Copper - the sensitivity of the salicylaldehyde reagent for copper was found to be greatly improved if the reaction is observed under ultraviolet light.

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ABSTRACT

Fluorescence methods are becoming more useful to the analyst as the fundamental principles become more fully understood. The effects of impurities and relatively high concentrations have been treated from a theoretical standpoint. Light sources, filters, and methods of examination applicable to inorganic analysis have been discussed. A compilation of a number of qualitative tests for metals and inorganic substances involving fluorescence has been prepared.

It has been found that aluminum may be determined quantitatively within 3% by measurement of the intensity of aluminum solutions fluorescing in the presence of the dyestuff morin. Below concentrations of 0.01 g Al/l intensity and concentration are directly proportional. Above this value intensity bears an exponential relationship to concentration.

$$\phi = \phi_0 e^{-\kappa c}$$

where ϕ_0 is the specific fluorescence constant (F/c) obtained from more dilute solutions. The fluorescing solutions were found to follow the Lambert-Beer law. The value of the molecular extinction coefficient under the conditions studied was found to be 29. Iron, chromium, silver and highly colored ions interfere with the determination. Lead, zinc, alkaline earth metals, and members of the sulfide group do not interfere if the solution is made slightly acid with acetic acid.

ABSTRACT (Cont'd)

Over 175 dyestuffs and organic materials have been studied in combination with 19 different cations in an attempt to develop new fluorescent tests for these elements. Tests were discovered for thorium, zinc, silver, and copper.

BIOGRAPHY

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