THE FLUOROMETRIC DETERMINATION OF ALUMINUM
AND BORON IN METALS

By

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INTRODUCTION

Within the past six or eight years, there has occurred a greatly intensified application of physical principles to the solution of problems in analytical chemistry. Much of the impetus was due to peak wartime production, which demanded rapid control analyses in such fields as aviation fuel, metals, synthetic rubber, and medicinals. For many of these, classical gravimetric-style chemistry was altogether incapable of providing the necessary information.

Brief mention may be given to a few of the physicist's major recent contributions to the tools of chemistry. The mass spectrometer (95) is used for the analysis of complex hydrocarbon mixtures such as the lighter petroleum fractions. Ultraviolet and infrared spectroscopy (2, 92) are used for the elucidation of molecular structure and the determination of many types of organic compounds. The electron microscope (7) makes possible the study of catalysts and high polymers at magnifications up to 100,000. Identification and estimation of crystalline components of complex mixtures, such as paint pigments and welding rod coatings, by means of X-ray diffraction is reduced almost to the level of routine by a new Geiger-counter X-ray spectrometer (25). Spectrographic installations on a scale unheard of six years ago maintain accurate control of alloy content in the steel and aluminum industries (10, 40, 44).

Of all these physico-chemical methods, fluorescence

analysis can hardly claim to be the most important. Nevertheless, interest has grown rapidly in the applications to analytical chemistry of the characteristic light emitted by many liquids and solids under ultreviolet irradiation (15, 18, 27, 32, 38, 43, 58, 68, 71, 77). Most of the early work was concerned with qualitative identification of materials, based on empirical examination of complex organic substances. Quantitative fluorometry has been used most widely for determination in foods and tissues of vitamin B_1, thiamine, by alkaline ferrocyanide oxidation to the fluorescent "thiochrome" (35, 51), and of vitamin B_2, riboflavin, by virtue of its intrinsic fluorescence (11, 94).

Fluorescence analysis has found increasing use in the inorganic field also (28, 97, 101, 102). The number of fluorescence methods available for quantitative analysis is not large (23, 53, 78, 79, 99). Beryllium may be determined by morin or 1,4-dihydroxyanthraquinone, aluminum by morin, and gallium or zinc by 8-hydroxyquinoline. For the most part, these reactions are not highly specific and are subject to interferences; however, they are characterized by extreme sensitivity. The causes of error are analogous to those found in colorimetric analysis, and the realization is becoming more widespread that the recognition and control of experimental conditions is prerequisite to the acceptance of a fluorescence procedure as a trustworthy analytical method (29).

The purpose of the present research was to evolve

quantitative fluorometric procedures, after thorough investigation of the effects of experimental variables, for the analyses of small quantities of aluminum and of boron in metals. It was believed that such procedures would constitute a distinct improvement in sensitivity, specificity, and speed over existing conventional methods for these determinations.

THE NATURE OF FLUORESCENCE

Fluorescence is the emission of visible light by substances which are exposed to electromagnetic radiation; it ceases when the excitation ceases (71, p. 3, 4). Stokes Law states that the emitted light is of longer wavelength than the exciting rays (which are usually ultraviolet), but a few instances are known of the anti-Stokes effect.

A complete theoretical explanation for the fluorescence of liquids and solids has not yet been published, in spite of the stimulation afforded by the large growth of the fluorescent lighting industry (18, 36). Nevertheless, some understanding of the process may be obtained by considering first the simplest case, a monatomic gas.

In order to explain the observed spectrum, such an atom must be considered as capable of existing only in discrete energy states, $E = -2\pi^2 z^2 m e^4 / n^2 h^2$, where z is the atomic number, m the reduced mass, e the electronic charge, h Planck's constant, and n the quantum integer 1, 2, 3 which determines the energy level of the atom (20, 65). This restriction to discontinuous energy states was an arbitrary fundamental assumption made by Bohr, in disregard of the laws of classical electrodynamics; however, in the new quantum mechanics, this same limitation arises as a natural consequence of the very general fundamental postulates.

The atom normally exists in the state of lowest energy,

the ground level. However, it may be excited into a state
of higher quantum number and higher energy, corresponding to
a larger orbit of the valence electron, by some such energy
input as heat or electrical discharge. Then when the atom
falls back into a lower level, it emits light of frequency
N, where $N = E_2 - E_1 / h$. Light is emitted only during the
transition from a higher to a lower level, each different
stationary state being in itself non-radiating.

This furnishes a satisfactory explanation for the main
features of bright-line emission spectra of monatomic gases
(105). The reverse phenomenon of line absorption spectra,
which was first observed as the Fraunhofer lines in the solar
spectrum, may be readily demonstrated by passing light from
an incandescent solid through the gas at room temperature.
Inasmuch as the absorption lines observed coincide with the
emission lines of the gas, the interpretation is that ab-
sorption consists of the raising of the atom from a lower to
a higher energy level. The excess energy may be dissipated
as kinetic energy (heat) in collisions with other atoms.

Both absorption and emission are involved in the phe-
nomenon (48, 105) known as "resonance radiation." If sodium
vapor at very low pressure is illuminated by a strong beam
of sodium D light, the vapor is observed to emit a yellow
glow, of the same wavelengths as the illuminating beam.
Lithium and mercury vapors behave in a similar manner. Reso-
nance radiation, then, consists of absorption of a quantum
of light, which raises the atom from a lower to a higher

energy state, followed by a falling back to the lower state through the emission of a quantum of light of the same wavelength as the light absorbed.

Fluorescence of gases such as thallium vapor (55) is very closely related to resonance radiation; the difference is that the term fluorescence usually implies that the light emitted is of longer wavelength, and therefore lower energy, than the light absorbed. This may occur when absorption of a photon raises the atom from the ground state to a higher level, but the atom falls back to a metastable level which is not quite as low as the ground state. Since the fall is not as far as the rise, the energy emitted is less than that absorbed, and the light emitted is of lower frequency than that absorbed. Such metastable states exist because selection rules forbid electron transitions from certain multiplet states (found in polyvalent atoms) to lower levels such as the ground state.

Phosphorescence, which denotes light emission that persists after absorption has ceased, has been recently shown to be due to the metastable triplet state of the molecule (47).

Thus, an atom or molecule which is in an excited state due to absorption of a photon may return to the normal state (22, 74) by such paths as either emission of resonance radiation or fluorescence, or by a collision of the second kind in which the excess energy is converted into kinetic energy of the colliding molecules. It may also retain some of the energy, to be emitted later as phosphorescence, or else enter

into a chemical reaction with another molecule, or dissociate into smaller particles.

The discussion so far has been concerned with the line spectra of monatomic gases. However, for gas molecules made up of several atoms, the spectra observed consist of many bands, made up of individual lines bunched closely together. This complex structure is due to the fact that the energies of rotation of the molecule, and of vibration of the atoms within the molecule, are also quantized; but the difference in energy between one vibrational or rotational level and another is usually much less than the difference between electronic levels. Inasmuch as changes in electronic, rotational, and vibrational quantum numbers may occur simultaneously, each electronic level will now consist of a number of sub-levels, which differ among each other by the quantized energies of rotation and vibration. Instead of sharp-line spectra, therefore, transitions between quantum states result in bands (in the visible and ultraviolet) which contain lines of frequency $N = \Delta E_e + \Delta E_v + \Delta E_r / h = N_e + N_v + N_r$.

This furnishes another mechanism, probably even more important than that of metastable levels, which explains why the fluorescence band lies on the long wavelength side of the absorption band (6). All the vibrational energy associated with the excited state is lost by collision before the molecule returns to the lower level; this degradation of the superfluous vibrational energy into thermal or other energy means that less energy change occurs in emission than in ab-

sorption.

It is well known that the emission spectra of incandescent liquids and solids are structureless continua, in which the energy distribution follows the Planck black-body radiation law. Similarly, the fluorescent light emitted by most liquids and solids consists of one or more continuous bands which show no evidence of discrete lines. In such materials, the energy levels of the outer valence electrons are greatly modified by the nearness of the other molecules, by virtue of the mutual polarization and other binding forces between the molecules (38). In the case of solutions, interactions between solvent and solute molecules cause a similar effect. As a result, the sharp energy levels broaden out into quasi-continuous bands; although each band is made up of discrete states, these are so close together that the band can be considered as continuous (84). Fermi-Dirac statistics also leads to the conclusion that in condensed systems, the electronic energy levels form a continuous distribution rather than discrete states (85).

In spite of all these fairly satisfying considerations, exact predictions concerning fluorescence based on molecular structure are not yet possible. Light emission is favored if the energy gap between two bands is bridged in places by other permitted energies, such as by activating impurities in phosphors, but the quantitative application of this principle is empirical.

Among pure inorganic compounds, these fluoresce: salts

of the rare earths and uranium, platinocyanides, siloxenes, and thallous salts in solution (68, p. 71-78). Of the organic compounds, the following fluorescent types are notable: condensed polynuclear aromatic hydrocarbons, closed ring heterocyclics, and dyes which consist of perfectly closed rings. Amino and phenolic groups in the molecule tend to increase luminescence, while nitro and halogen groups decrease it (42). In the fluorescence resulting from the reaction between an inorganic ion and an organic reagent, such as was studied in this work, the fluorescence appears to depend on the formation of an additional ring in the organic molecule, by chelation of the ion with a functional grouping such as

$$- \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - \overset{\overset{\displaystyle OH}{\displaystyle |}}{C} - .$$

This grouping is characteristic of the beryllium-quinizarin, the aluminum-morin, and the boric acid-benzoin systems. But no theoretical basis has thus far been elucidated for the observed specificity for certain metallic ions in these fluorescence reactions.

MEASUREMENTS IN FLUOROMETRIC ANALYSIS

In fluorometric analysis, one determines the unknown concentration of a substance in solution by comparing the intensity of fluorescence with that of suitable standards, either visually or preferably with the aid of a photoelectric instrument. For many cases the intensity is a linear function of concentration in very dilute solution, but levels off and often decreases as the concentration increases further. However, linearity is not essential: a method is suitable for quantitative determinations, if only the standard curve be reproducible.

Variation of intensity with time is usual, rather than exceptional. Instrument readings may increase soon after mixing because the reaction which yields the fluorescent substance takes a considerable time to attain equilibrium. On the other hand, bright sunlight or the ultraviolet irradiation, sometimes aided by atmospheric oxygen, may cause photochemical destruction of the fluorescing molecules. Both of these antagonistic influences may operate simultaneously, as in the case of the boric acid-benzoin system; it then becomes necessary to take the readings at a definite time after mixing.

For making quantitative measurements in this work, the Lumetron fluorescence meter Model 402EF was used. The external appearance of this instrument is shown in Figure 27. In addition to the high voltage transformer, multiple-

reflection galvanometer, and instrument proper, a voltage
stabilizer was used between the line and the transformer.

A schematic diagram of the apparatus, also in Figure 27,
makes it easy to follow the manufacturer's explanation (67)
of the principle of operation.

> The light of the lamp is condensed by an optical
> system to form a parallel beam. This beam passes
> through a narrow-band filter which isolates the
> exciting light of the proper wave length. The
> exciting beam is then split into two parts. One
> part enters the sample holder which is provided
> with a thin front window of low ultraviolet ab-
> sorption. The fluorescence of the liquid is
> registered by two large barrier-layer photocells
> which are arranged laterally on both sides of the
> sample holder and are connected in parallel. Fil-
> ters between sample holder and photocells serve
> to isolate the specific fluorescence band and to
> eliminate the influence of primary light which
> may be scattered by particles suspended in the
> liquid.
>
> The other part of the beam is deflected by a front
> surface mirror and acts upon the balance cell
> which is mounted so that it can be turned through
> an angle of 90°. The two measuring photocells
> and the balance photocell are connected in a
> bridge circuit with slide wire and with a galva-
> nometer as the zero indicator.

Measurements were taken in the following way. First,
the galvanometer rest point was adjusted to the precise cen-
ter of the scale. Then a standard solution (containing, for
example, 0.020 mg. of aluminum) having the maximum fluores-
cence to be encountered was poured into the 25 ml. cell, and
placed inside the instrument. (The cell was always filled
to the same height, about one-quarter inch from the top.)
The slide-wire dial was set at 100.0, or some other con-
venient number, and the balance cell controls manipulated

until the galvanometer light-spot returned to zero. Reduction plate #4 or #5 was required in the aluminum, and #7 in the boron work, as the coarse adjustment necessary for balance.

Then the cell was emptied, rinsed, and refilled with the blank solution. The dial was set at 0.0, and the zero suppressor knob adjusted until the galvanometer spot returned to the center point. Thus the instrument was set so that scale readings from 0 to 100 represented aluminum concentrations from 0 up to 0.020 mg., in the example given.

Finally, the cell was filled with the unknown solution. Zero suppressor and balance-cell controls were left untouched, but now the slide wire dial was turned until the galvanometer spot returned to zero. This reading was used to calculate the aluminum concentration, either by direct ratio to the nearest standard, or else (for more precise work) by reference to a calibration curve prepared from the several standards of different concentrations. In the aluminum work, readings were taken as soon as possible after placing the cell inside the instrument, because it was noticed that readings tended to drift upwards when the solution fluoresced strongly, and to drift downwards when the fluorescence was rather weak.

It may be emphasized that the intensity scale is set in a quite arbitrary way. This is different from colorimetric analysis, where the scale usually expresses a definite physical quantity, the fraction of the light absorbed by the

colored solution. Here, however, the scale is set for any de-
sired range of fluorescence intensity, simply by using a solu-
tion of convenient standard fluorescence.

The reason for this difference, and also for the linear
dependence of intensity upon concentration, may be illuminated
by a derivation of the mathematical relationships involved
(27, 43, 77), which are analogous to Beer's law in colorime-
try. Some simplifying assumptions are made: the various
quantities are considered small in magnitude, and reabsorption
and scattering of the emitted light are neglected. Since only
light that is absorbed can cause fluorescence, we assume that
the fluorescence emitted is proportional to the absorption,
at low intensities. Thus $F = k (I_0 - I)$, where F is the fluo-
rescence intensity, k is the proportionality factor (involv-
ing the particular substance, solvent, etc.), I_0 is the initial
intensity of irradiating light, and I is the light remaining
after absorption.

Now, by Beer's law, $I = I_0 e^{-AcL}$, where A is the spe-
cific absorption, c is the concentration of the absorbing (and
fluorescing) molecules, and L is the length of optical path.
Substituting this into the previous equation gives $F = k I_0 (1 - e^{-AcL})$. A mathematical property of the expression
in parentheses is that when the exponent is small, the ex-
pression equals the positive value of the exponent, or
$F = k I_0 A c L$.

For a given reaction in a particular instrument, the
factors k, I_0, A, and L are all constants. The width of the

cell must also be considered, because the fluorescence is measured at right angles to the irradiating beam, but this too is a constant. Therefore, subject to the restrictions of small magnitude mentioned, the fluorescence intensity is proportional to the concentration of the substance: $F = K c$. In addition, the concentration of an unknown solution may be determined by comparing its fluorescence with that of a known solution: $c_1 / F_1 = c_2 / F_2$. This is a fundamental equation in quantitative fluorometric analysis.

FLUOROMETRIC DETERMINATION OF ALUMINUM

Origin of the Problem

The absence of specific sensitive reagents for the determination of aluminum is a notable handicap to the analytical chemist. This difficulty is reflected in the laborious procedures required for an accurate gravimetric analysis of small percentages of aluminum in steel (1, 49, 93) and in the fact that rock analysts usually calculate alumina by difference from the R_2O_3 precipitate (37).

Most frequently, aluminum is precipitated as the hydroxide by ammonia at pH about 6 or 7 (1); this requires the removal of practically all other heavy metals, which are similarly precipitated. Controlled hydrolytic precipitation of aluminum hydroxide by boiling in phenylhydrezine-thiosulfate solution (21) is a variation which possesses the advantage that complete removal of ferrous ion is not required. A third method, precipitation as the phosphate, does however require extensive preliminary separations (33).

Other weighing forms which have been recommended are the double sodium fluoride, cryolite (90) and the 8-hydroxyquinoline salt (88). The latter has also been used for the polarographic determination of aluminum, in either ammoniacal or acetic acid solution (107), and for the colorimetric determination by measuring the optical density of the salt in chloroform solution at 395 mμ (56).

A volumetric method for aluminum consists of adding potassium fluoride to the carefully neutralized tartrate solution, and titrating the alkali liberated according to the reaction $Al(OH)_3 + 6 KF = K_3AlF_6 + 3 KOH$. Many ions interfere, especially if present in high concentrations (86).

Several colorimetric reagents for aluminum have been proposed. Among these are Eriochromcyanin-R (72, 73) and hematoxylin (45), both of which yield violet lakes in slightly acid solution, and alizarin red S (9, 59).

The colorimetric reagent which has found widest use is "aluminon," ammonium aurintricarboxylate (34, 64, 106). In spite of interference by chromium, iron, beryllium, vanadium, titanium, and gallium, it has been used for colorimetrically determining from 0.04% to 1.5% of aluminum in steel (14), and for low percentages in non-ferrous alloys (81). Ether extraction and mercury cathode electrolysis were used, respectively, as separations in these two procedures. It may be noted that the experimental conditions such as pH must be carefully controlled, and that the reagent is barely sensitive to 0.001 mg. of aluminum per ml., so that the reported lower limit of application to steel is 0.04%.

Therefore the need was still felt for a method, other than spectrographic (67), suitable for determining down to less than 0.01% of aluminum in such materials as steels, bronzes, and minerals. In 1937, White and Lowe announced a new qualitative test (100) for aluminum, the red fluorescence given under ultraviolet by a solution of the dyestuff

Pontachrome Blue Black R, which is the sodium or zinc salt of 4-sulfo-2-hydroxy-α-naphthalene-azo-β-naphthol. Major advantages of the new test were its great sensitivity and the non-interference of beryllium, in contrast to the colorimetric reagents aluminon and alizarin red S, and to the fluorescence reagent morin. However, interference by iron, copper, chromium, nickel, cobalt, and fluoride was noted. The following ions were found not to interfere: silver, mercury, lead, bismuth, cadmium, arsenic, antimony, tin, zinc, manganese, indium, thallium, calcium, strontium, barium, magnesium, sodium, potassium, ammonium, lithium, rare earths, chloride, nitrate, sulfate, phosphate, and tartrate.

Three years later the same authors published a fluorometric method for quantitative determination of aluminum in pure solution by morin (99), but noted several interferences, and reported that they had not yet been able to use the more specific Pontachrome B.B.R. reagent for quantitative work.

Shortly afterwards, Davydov and Devekki confirmed these results with the determination of small amounts of aluminum in pure solution with fair accuracy, using the fluorescence reagent quercetin, an isomer of morin (16). They also investigated qualitatively several interferences in both the quercetin and B.B.R. tests; for the latter, they added the information that an approximately tenfold excess of vanadium, titanium, or molybdenum would destroy the fluorescence, and

a similar amount of manganese or tungsten would increase the
intensity.

The remainder of this section is an account of the first
successful use of the sensitive specific reagent Pontachrome
Blue Back R for the determination of small amounts of alumi-
num, not only in pure solution but also in such industrially
important materials such as steels, bronzes, and minerals.

Apparatus and Reagents

Quantitative measurements were made with a Lumetron Fluo-
rescence Meter, Model 402EF, the construction and operation
of which were described in the previous section. The trans-
missions of the primary (Corning #5874) and secondary filters
used are shown in Figure 26. The Beckman spectrophotometer
and pH meter were used for transmission and pH measurements,
respectively.

All chemicals used were of C.P. quality or better.

Standard solution of aluminum, 1.00 ml. = 0.0100 mg.,
was made by dissolving 0.1760 gram of $K_2Al_2(SO_4)_2$. 24 H_2O
in water and diluting to one liter.

Weaker standard solution of aluminum, 1.00 ml. =
0.00100 mg., was made by pipetting out 100 ml. of the above
solution and diluting to one liter.

Ammonium acetate solution, 10%, was made by dissolving
50 grams of the salt in water and diluting to 500 ml.

Pontachrome Blue Back R (Color Index 202), 0.1% solution,
was made by dissolving 0.50 gram of dye in 500 ml. of 95%

ethyl alcohol, and allowing to stand a few days before use.
This dye may also be purchased under the name Superchrome
Blue Black, from the National Aniline Division of Allied
Chemical and Dye Corp.

Pontachrome Violet SW (Color Index 169), 0.1% solution,
was made exactly like the B.B.R. solution.

Sodium hydroxide solution, 10%, was prepared by dissolv-
ing 25 grams in 250 ml. of water in a large platinum dish,
using a platinum stirring rod; this solution was kept in a
ceresin bottle. These precautions were necessary, in order
to avoid aluminum contamination from glassware.

Dilute sulfuric acid, 1:9, was made by pipetting 100 ml.
of concentrated acid into a few hundred ml. of water in a
1000 ml. volumetric flask, cooling, and diluting to the mark.

Dilute sulfuric acid, 1:19, was prepared by pipetting
out 50 ml. of the 1:9 acid into a 100 ml. volumetric flask,
and diluting to mark.

Experimental Work

Effect of Variation of Conditions.

In order to provide a foundation for the quantitative
work, it was necessary first to study the effect of various
conditions such as pH, temperature, amount of dye added, and
time of standing.

Effect of pH. The effect of varying pH on the inten-
sity of fluorescence emitted by the aluminum-B.B.R. complex
under ultraviolet irradiation was studied by preparing a

series of 20 solutions in 50 ml. volumetric flasks. To each
flask were added 5.0 ml. of aluminum solution (equal to 0.050
mg.), 5.0 ml. of 10% ammonium acetate solution as a buffer,
1.0 ml. of 0.1% B.B.R. solution, and quantities of acetic
acid or ammonium hydroxide sufficient to give a range of pH
from 2.4 to 9.8. Measurements of pH were made with the Beck-
man pH Meter, Laboratory Model. The solutions were diluted
to the mark, shaken vigorously, and allowed to stand for two
hours before measurements were taken. Under these conditions,
the optimum pH is about 4.8 or 4.9, as shown in Table 1 and
Figure 1; the peak is a rather broad one.

Studies of the effect of pH under somewhat different
conditions were also made; one of these may be mentioned in
detail. The aluminum content was cut down to 0.010 mg., to
which were added 5.0 ml. of 10% ammonium acetate, 1.5 ml. of
0.1% B.B.R., and varying amounts of acetic acid. In this
case the maximum intensity of fluorescence was found at about
pH 4.7 (Table 2 and Figure 2) and small variations of pH had
a greater effect than at the higher aluminum level.

Amount of dye. Next studied was the effect of the con-
centration of Pontachrome Blue Black R on the intensity of
fluorescence. A series of 15 solutions of 50 ml. volume was
made up, each containing 0.050 mg. aluminum, 0.50 gram am-
monium acetate, 0.10 ml. of glacial acetic acid to give a pH
close to the optimum, and amounts of 0.1% alcoholic dye solu-
tion varying from none to 5.0 ml. The solutions were allowed
to stand 50 minutes before readings were taken. It is

evident from Table 3 and Figure 3 that the maximum intensity results when 1.5 ml. are used. Solutions containing more than this amount showed a rapid decrease in fluorescence in those portions furthest from the ultraviolet source, indicating a progressive absorption of the energizing radiation.

Acetic acid blank. It was considered desirable to investigate possible variations of intensity resulting from the use of differing amounts of acetic acid, and to discover whether significant amounts of aluminum were present in the acid. Solutions were prepared which contained 0.5 gram ammonium acetate, 1.5 ml. of dye, and acetic acid varying from none to 2.0 ml.; but no aluminum was added. Measurements after 1½ hours (recorded in Table 4 and Figure 4) indicate only small variations. In particular, no variation from a perfect blank reading existed at all throughout the entire range of acetic acid used in the remainder of this work, 0.05 to 0.12 ml. The slight increase observed may be due to pH rather than to aluminum present in the acid.

Time of standing. Since it was known that the fluorescence did not attain its maximum intensity immediately after mixing, the change of intensity with time was investigated. To 0.100 mg. aluminum were added 10 ml. of 10% ammonium acetate, 0.06 ml. of acetic acid, and 2.0 ml. of 0.1% B.B.R., followed by immediate dilution to 50 ml. The temperature was 23° C. Readings of intensity were taken starting one minute after mixing, for a period of 170 minutes; the solutions remained under constant irradiation during this time.

The next day, after about 1000 minutes, another measurement was made on this same solution. It may be observed from Table 5 and Figure 5 that the intensity increases rapidly during the first 20 minutes, but practically attains constancy after about an hour. Later experience showed that the increase during the 24 hours after the first two hours was often greater (up to an average of $\frac{1}{2}\%$ per hour) than found in this run.

The time effect was also investigated at a much lower aluminum level. A solution was prepared which contained 0.010 mg. of aluminum, 5.0 ml. of 10% ammonium acetate, 1.0 ml. of 1:24 sulfuric acid, and 1.5 ml. of 0.1% B.B.R. in a volume of 50 ml. The temperature was 24° C. Measurements were made over a period of one hour, under constant irradiation, and another measurement was made after three hours. Results similar to the preceding--equilibrium after one hour-- were obtained, as is evidenced in Table 6 and Figure 6.

Temperature. In order to determine whether maximum intensity could be obtained in a shorter time by heating the solution, the following experiment was performed. A solution containing 0.010 mg. of aluminum, 5 ml. of 10% ammonium acetate, and 0.05 ml. of acetic acid was diluted to 48 ml. and heated to 70° C., and then 1.5 ml. of 0.1% B.B.R. was added. Readings of fluorescence were taken during the next hour and a half. As may be seen from Table 7 and Figure 7, the intensity increases much more slowly than--and even after 90 minutes is far from equalling--that of a solution mixed at

room temperature and allowed to stand two hours.

A similar experiment, using 0.020 mg. and a mixing temperature of 80° C., gave a slightly worse rate of fluorescence development, as shown in Table 8 and Figure 8. It is apparent that heating the solution yields no benefit in hastening attainment of equilibrium.

The effect of cooling was studied next. A 50 ml. solution containing 0.020 mg. of aluminum, 0.5 gram of ammonium acetate, 0.05 ml. of acetic acid, and 1.5 ml. of 0.1% B.B.R. was allowed to stand several hours, and its fluorescence measured at room temperature, 25° C. Then it was cooled in ice, and the intensity measured at 10, 15, and 20 degrees. The slight increase noted at these low temperatures (Table 9 and Figure 9) may be due partly to the thermal contraction of the solution. This same solution was then heated to incipient boiling and allowed to cool, readings being taken during the cooling. The intensity dropped sharply as a result of heating, and even after cooling back to room temperature had recovered only a little more than half of its original value.

A similar experiment was performed, using 0.030 mg. of aluminum. Again, cooling down to 10° C. caused an intensity increase of a few percent; and after heating to 60° and cooling back to room temperature, the fluorescence was only about two-thirds as great as originally. A third trial gave similar results. Therefore, far from increasing or accelerating the development of fluorescence, heating such a solution causes

disadvantageous irreversible decrease of intensity.

In most of the following work, the conditions employed
to obtain maximum fluorescence, as determined above, were:
1.5 ml. of 0.1% B.B.R., a pH about 4.8 (resulting from 0.50
gram of ammonium acetate plus about 0.05 ml. of acetic or
sulfuric acid), mixing at room temperature, and letting stand
1 or 1½ hours before measuring.

Dependence of Fluorescence on Concentration of Aluminum.

A considerable number of experiments were performed to
determine how nearly the fluorescence intensity is a linear
function of aluminum concentration. In a typical series, 20
solutions were made up to contain 0.5 gram of ammonium ace-
tate, 1.5 ml. of B.B.R., 0.06 ml. of acetic acid, and aluminum
varying from none up to 0.100 mg., in a volume of 50 ml., and
let stand for two hours before reading. As can be seen from
Table 10 and Figure 10, the fluorescence increases in a fairly
linear manner until a saturation point is reached at about
0.050 mg. of aluminum, beyond which the intensity remains
almost perfectly constant. Figure 18 shows the appearance
of such solutions containing 0, 5, and 20 micrograms of
aluminum, when irradiated by ultraviolet.

The question arose whether higher-energy ultra-violet
radiation might not extend the useful range beyond 0.050 mg.
Accordingly, a 2.92 mm. thickness of Corning filter #9863
(which transmits from 2300 to 4000 A) was substituted for the
usual ultraviolet filter, a 3.85 mm. thickness of #5874
(which transmits only from 3200 to 4000 A). However, a

series of solutions almost identical with the previous set
showed a saturation plateau at about the same concentration,
in spite of the shorter wavelengths; although the lower half
of the curve did become more nearly linear, as may be seen
in Table 11 and Figure 11.

It was found that the point of flattening depended on
the amount of B.B.R. used. When only 1.0 ml. of dye was
present, the plateau began at about 0.030 mg. of aluminum
(Table 12 and Figure 12).

Two more sets, each consisting of 20 solutions, were
prepared; one covered the range from 0 up to 0.020 mg., the
other from 0 to 0.040 mg. All solutions contained 1.5 ml.
of B.B.R., 0.5 gram of ammonium acetate, and 0.07 ml. of
acetic acid. Table 13 and Figure 13 show that the concentra-
tion-intensity relation is nearly linear up to 0.020 mg., but
Table 14 and Figure 14 demonstrate a considerable deviation
above 0.025 mg.

All of the above work was done at a room temperature
about 24° C. Another series going up to 0.020 mg. was pre-
pared during the summer, when room temperature was 33° C.
Each solution contained 1.0 ml. of 1:19 sulfuric acid, 1.5
ml. of B.B.R., and 0.5 gram of ammonium acetate. A slightly
greater deviation from strict linearity is observed at the
higher temperature, in Table 15 and Figure 15.

To investigate the lower limit of sensitivity, a series
covering the range zero to 0.001 mg. was prepared, each
solution containing 0.5 gram of ammonium acetate, 0.12 ml.

of acetic acid, and 1.5 ml. of B.B.R. Although Table 16 and
Figure 16 show a fairly linear relation, this is not com-
pletely reliable because of the rapid decrease of the weak
fluorescence during the period of irradiation. However, it
was easy even visually to distinguish definitely among solu-
tions containing none, 0.0004, and 0.0008 mg. of aluminum in
the 50 ml. volume. This corresponds to a sensitivity of 1
part in 125,000,000.

By this demonstration of the reproducible, nearly-
linear dependence of fluorescence intensity on concentration,
there was established a convenient means of quantitatively
determining very small amounts of aluminum in pure solution.

Nature of the Fluorescent substance.

To determine if possible the formula of the fluorescent
complex, a solution of 5 grams of B.B.R. dyestuff and 25
grams of potassium aluminum sulfate crystals in 300 ml. of
water was adjusted to pH about 5.0, by the addition of solid
ammonium acetate, and allowed to stand a few hours. It was
then extracted with successive 100 ml. portions of n-amyl
alcohol, although troublesome emulsions were encountered, and
the strongly fluorescent extracts were carefully evaporated
to dryness. Analysis of the dried residue indicated that
two dye molecules were combined with each aluminum hydroxide
molecule. Calculated for $AlOHO_2$ $(C_{20}H_{11}N_2SO_3Na)_2$: C, 56.74%;
H, 2.74%; Al, 3.19%. Found: C, 56.64%, 58.13%; H, 4.30%,
4.58%; Al, 3.19%, 3.21%. The experiment was repeated, using
dye:alum ratios of 1:2 and 1:10, and the aluminum percentages

found in the dried residues were about the same as the above.

Absorption spectra of fluorescing and non-fluorescing dye solutions.

Two solutions were prepared which each contained 0.5 gram of ammonium acetate, 1.0 ml. of 1:19 sulfuric acid, and 1.5 ml. of B.B.R. solution in 50 ml. volume; but one contained 0.020 mg. of aluminum and the other contained no aluminum. The transmission of each solution was measured against distilled water over the entire visual range, using the Beckman spectrophotometer. An interesting verification of Stokes' Law is shown in Table 17 and Figure 17: the fluorescing solution has a much stronger absorption band, just on the short wavelength side of the fluorescence band.

Separations of aluminum from interferences.

It still remained to apply this method to the analysis of actual industrial materials, such as steel. Inasmuch as even small amounts of ferric ion quench the fluorescence, a prime necessity was seen to be either separating the iron or rendering it innocuous.

First, it was found that ferrous ion plus a little sulfurous acid did not sensibly diminish the fluorescence. So it was hoped that the iron could be left in the fluorescing solution, but kept in the reduced state. However, every attempt at adjusting the pH to 4.8, by adding ammonia to a ferrous sulphate solution buffered with ammonium acetate, resulted in the precipitation of ferric hydroxide, even in the presence of much sulfurous acid. No fluorescence was ever

observed in a solution containing aluminum and B.B.R., in which such precipitation had taken place. Attempts to reduce and so redissolve the ferric hydroxide, using metallic zinc, lead, or copper, were also unavailing. (It may be remembered that ferric hydroxide precipitates at about pH 4, while ferrous hydroxide comes out at pH 6.)

Complex formation. Next investigated was the masking of ferric iron through complex formation. A solution was made up in the usual way, using 0.100 mg. of aluminum and 2.0 ml. of B.B.R., except that 1.00 gram of ammonium citrate was used as the buffer instead of ammonium acetate. The solution showed very little fluorescence, and even this disappeared upon addition of 100 mg. of iron as ferric nitrate. In another experiment, 0.50 grams of ammonium tartrate added to a fluorescing solution reduced the intensity slightly, but it failed to prevent complete quenching upon addition of 50 mg. of iron as ferric nitrate. Similar results were obtained with ammonium oxalate. It is apparent that neither citrate, oxalate, nor tartrate avails for eliminating interference due to iron. Therefore the conclusion was reached that it would be necessary to separate the iron from the aluminum.

Extraction by amyl alcohol. It was known that this fluorescent complex could be extracted from aqueous solution by butyl alcohol; n-amyl alcohol was preferred here, because of its lower solubility in water. When 50 ml. of n-amyl alcohol was shaken up with 50 ml. of a water solution containing 0.010 mg. of aluminum, 0.5 gram of ammonium acetate, and 0.07 ml. of

acetic acid, the fluorescence of the alcohol layer was three
times as intense as that of the original solution had been.
However if 10 drops of sulfuric acid were added to a similar
aqueous solution before extraction, practically no fluores-
cence was observed in the alcohol. Moreover, adding a dilute
acid solution of 20 mg. of iron as either ferrous sulfate or
ferric chloride likewise prevented any fluorescence in the
extracting alcohol. It was seen that this procedure was not
suitable, because of the necessity for adjusting the pH be-
fore extraction.

Cupferron. Another separation tried was the precipita-
tion of iron by cupferron, the ammonium salt of nitroso-β-
phenylhydroxylamine. A solution of 50 mg. of iron and 0.050
mg. of aluminum in 10 ml. of 1:24 sulfuric acid was cooled
in ice, and treated with 10 ml. of cold 6% aqueous solution
of cupferron and a little macerated paper pulp. The red-brown
iron precipitate was filtered off, washed with 1:4 acetic
acid, and discarded. The filtrate and washings were adjusted
to pH 5.0 with ammonium hydroxide, and 1.5 ml. of 0.1% B.B.R.
added. But no fluorescence at all was observed, probably due
to the nitroso group in the excess cupferron present, or its
oxidation by air to a nitro compound. Nitro compounds such
as nitrobenzene are known to interfere with fluorescence, by
absorbing the ultraviolet.

Another attempt was then made, with provision for destroy-
ing the excess cupferron in the filtrate. To several cold
solutions containing 50 mg. of iron plus aluminum varying

from none to 0.010 mg. in 1:9 sulfuric acid, was added 5 ml. of cold 6% cupferron solution with vigorous stirring. The filtrate and washings of 5:95 hydrochloric acid were collected in a 250 ml. beaker, 10 ml. of concentrated nitric acid added, and evaporated down to copious fumes of sulfuric acid. Such a treatment with nitric and sulfuric acids usually suffices to destroy any organic matter in solution. However, less than one-tenth of the normal fluorescence was observed when the solutions were diluted, adjusted to pH 5.0, and treated with 1.5 ml. of B.B.R. It therefore seemed that the nitro compounds resulting from the cupferron were resistant to destruction, and this line of work was dropped.

Sodium hydroxide. Another reagent often used to separate iron from aluminum is sodium hydroxide. To 10 ml. portions of 1:24 sulfuric acid containing 20 mg. of iron, were added respectively zero, 0.005, and 0.010 mg. of aluminum. Each solution was warmed and poured with stirring into 20 ml. of hot 10% sodium hydroxide solution in a platinum dish. The mixture was heated several minutes until the ferric hydroxide coagulated, then it was filtered through double Whatman #40 9 cm. papers into another platinum dish. The solution was adjusted to pH 5.0 with acetic acid and 1.5 ml. of B.B.R. added, diluted to 50 ml., and let stand one hour. The fluorescence of the blank was fairly high, corresponding to 0.005 mg., but the other two samples showed low recoveries: 0.003 mg. found for 0.005 added, and 0.002 found for 0.010 added. It was evident that this method also was not satisfactory, as might

have been predicted from the well-known extraction of aluminum from glassware (such as the funnel) by hot alkali, and the strongly adsorptive properties of ferric hydroxide precipitate.

Mercury cathode electrolysis. Electrolysis of a weak sulfuric acid solution, in a cell whose cathode is a layer of mercury at the bottom, is frequently used as an effective means for the separation of large amounts of iron from small amounts of aluminum. The Melaven type of cell (52) was used in these investigations; usually, twelve volts were applied, resulting in a current of about 0.4 ampere.

An iron solution for use in these experiments was prepared by dissolving 1.00 gram of National Bureau of Standards iron #55a (which contains 0.001% of acid-soluble aluminum) in 25.0 ml. of 1:9 sulfuric acid, and diluting to 500 ml. Aliquots of 10 ml. of this solution plus varying amounts of aluminum were electrolyzed for one hour, the spray being washed down at intervals, and then drawn off into a 50 ml. volumetric flask containing 5.0 ml. of 10% ammonium acetate and 1.5 ml. of 0.1% B.B.R. After standing at least one hour, the fluorescence was measured and compared with standards of 0.010, 0.020, and 0.030 mg. made up simultaneously. (These standards also contained 5 ml. of 10% ammonium acetate and 1.5 ml. of B.B.R., and in addition 1.0 ml. of 1:19 sulfuric acid, the same amount as was present in a 10 ml. aliquot of the iron solution. These amounts of acid and buffer were found to give a pH about 4.8, close to the optimum.)

For highly precise work, the aluminum concentration of the unknown should be read off a calibration curve (prepared from the standards) which is not perfectly linear. In most cases, however, it suffices merely to calculate the concentration from the nearest standard by simple proportion, assuming linearity.

After several trials in which difficulties were eliminated, quite accurate results were obtained for synthetic standard low aluminum steels, as shown in Table 18.

Analysis of National Bureau of Standards Steels.

Determinations of acid-soluble aluminum content (which is of greater metallurgical interest than total aluminum) were made on several National Bureau of Standards analyzed steels, using the following method. For aluminum percentages up to 0.10%, a 1.000 gram sample was dissolved in 25.0 ml. of 1:9 sulfuric acid, and diluted without filtration to 500 ml.; a 0.1000 gram sample was used for higher percentages, up to about 1.0%. A 10 ml. aliquot was electrolyzed in a mercury cathode cell for about an hour; the solution and rinsings were drawn off into a 50 ml. volumetric flask which contained 5.0 ml. of 10% ammonium acetate plus 1.50 ml. of 0.1% B.B.R., and diluted to the mark. After standing at least one hour, the fluorescence intensity was measured and compared with standards prepared simultaneously and similarly, including electrolysis, and containing the same amounts of acid, buffer, and dye as the unknown. The results obtained were quite good, as shown in Table 19, especially in the case of steel 14c,

which is most typical of the low aluminum class. Even at the 1% level good results were obtained, but the fluorescence method offers little advantage over the gravimetric, for such large amounts.

If a determination of the acid-insoluble aluminum oxide in the steel is required also, the following method is used. The insoluble residue remaining after dissolving a 1.000 gram sample in 1:9 sulfuric acid was filtered off on a retentive paper, and washed thoroughly with 5:95 hydrochloric acid and then water. After ignition in a platinum crucible until all carbon had disappeared, 1 ml. of 1:1 sulfuric acid and 5 ml. of hydrofluoric acid were added. The mixture was evaporated down to heavy fumes of sulfuric acid, and allowed to cool. The sides of the crucible were washed down with 6 or 8 ml. of water, and the mixture evaporated and fumed strongly again. When cool, it was transferred to a large platinum dish with 50 ml. of water, and heated until the salts dissolved completely. The solution was barely neutralized to methyl-red with aluminum-free 10% sodium hydroxide solution, and then 25.0 ml. of 1:9 sulfuric acid were added. The resulting solution was transferred to a 500 ml. volumetric flask, diluted to the mark, and shaken well. A 10 ml. aliquot was pipetted out for mercury cathode electrolysis, and the remainder of the analysis carried out as described in the preceding paragraph. Excellent results were obtained on an NBS steel, as indicated in Table 20.

<u>Possible interferences not removed by mercury cathode elec-</u>
<u>trolysis.</u>

The mercury cathode treatment quantitatively removes
iron, chromium, molybdenum, cobalt, nickel, copper, zinc,
gallium, germanium, arsenic, selenium, tellurium, platinum
metals, rhenium, silver, cadmium, indium, tin, gold, mercury,
thallium, lead, and bismuth, and manganese only partially;
but aluminum, beryllium, boron, titanium, zirconium, vanadium,
alkalis, alkaline earths, rare earths, earth acids, tungsten,
and uranium remain completely in the solution.

As already noted, beryllium does not interfere in the
B.B.R. determination of aluminum. It was of interest to in-
vestigate possible interference by titanium, vanadium, and
zirconium, since they were about all that might be left as-
sociated with aluminum after mercury-cathode electrolysis of
an ordinary steel. Solutions were made up to contain 0.010
mg. of aluminum, 5.0 ml. of 10% ammonium acetate, 1.0 ml. of
1:19 sulfuric acid, 1.5 ml. of 0.1% B.B.R., and up to 50 mg.
of titanium, vanadium, or zirconium. Table 21 and Figures
19 and 20 show that interference is nil by zirconium, slight
by titanium, and moderate by vanadium. However, it must be
remembered that these elements will normally be present in a
steel mostly as carbides which are insoluble in 1:9 sulfuric
acid, and therefore only a small fraction will be found as-
sociated with the solution containing the aluminum. Thus,
very good results (Table 21) were obtained by B.B.R. analysis
of a 0.085% titanium and a 0.11% vanadium steel which had

previously been carefully analyzed by the lengthy gravimetric
method (sodium bicarbonate preliminary separation, then mer-
cury cathode, then cupferron to remove titanium or vanadium,
and finally ammonia precipitation and ignition to aluminum
oxide.)

It was also found that 100 mg. of calcium chloride in
50 ml. of fluorescing solution causes a slight increase in
fluorescence; 100 mg. of magnesium sulfate is practically
without effect; and 100 mg. of sodium sulfate causes a slight
decrease.

Analysis of National Bureau of Standards bronzes.

Phosphor bronze, ounce metal, and manganese bronze were
among the alloys analyzed. Certain changes in the procedure
were necessary: for example, nitric acid had to be used to
obtain complete solution of the sample, yet even small quan-
tities of nitric acid vitiate the mercury cathode electrolysis
and destroy the desired fluorescence.

The procedure finally adopted was as follows. A 1.000
gram sample (or 0.1000 gram, if the aluminum content was
greater than 0.10%) was dissolved in 10 ml. of 1:1 nitric
acid in a 250 ml. beaker, 20 ml. of 1:1 sulfuric acid added,
and the mixture evaporated down to copious fumes of sulfuric
acid. After cooling, the sides were washed down with about
15 ml. of water, and the contents again evaporated to heavy
fumes. Each evaporation was accomplished in a few minutes
by heating the beaker over a free flame, while swirling the
contents vigorously. The cooled mixture was diluted with

about 100 ml. of water and barely neutralized to methyl red
with 10% sodium hydroxide solution, and 25.0 ml. of 1:9 sul-
furic acid were added. After dilution to 500 ml., a 10 ml.
aliquot was pipetted out for mercury cathode electrolysis.
The remainder of the analysis was completed in the manner
already described for steels.

Very good results were obtained for five alloys, as
shown in Table 25. Deviations from the true value were
less than in the results given by the several standardizing
laboratories on the certificates issued by the National
Bureau of Standards. Here again, the fluorescence method
offers the greatest advantages over the conventional gravi-
metric method in the analysis of low aluminum alloys, con-
taining a few hundredths of a percent.

Analysis of National Bureau of Standards Minerals.

In this case also, changes were required in the method
of getting the sample into solution. For materials consist-
ing largely of silica, the following direct method was found
suitable. A 0.1000 or 0.5000 gram sample (depending on
aluminum content) was weighed into a 20 ml. platinum cru-
cible and treated with 2 ml. of 1:1 sulfuric acid and 10 ml.
of 48% hydrofluoric acid. The mixture was evaporated down
to copious fumes, cooled, diluted with about 10 ml. of water,
and again evaporated to heavy fumes. It was then added to
100 ml. of water, heated until all salts dissolved, and made
barely neutral to methyl red with 10% sodium hydroxide. After
addition of 25.0 ml. of 1:9 sulfuric acid and dilution to 500

ml., a 10 ml. aliquot was electrolyzed in the mercury cathode cell for about an hour. The determination was completed in the manner described for steel, and the results were calculated to percent aluminum oxide. Table 24 shows that the accuracy obtained for glass sand #51 and silica brick #102 was very good, with smaller deviations from the true values than reported by the standardizing laboratories. The blank on the entire procedure was quite small, about 0.0001 mg. of aluminum oxide on the 10 ml. aliquot.

For other types of minerals, it was more convenient to proceed with the ordinary scheme of analysis, and then apply the fluorescence method to the determination of alumina in the R_2O_3 ammonia precipitate. This may be illustrated in the case of NBS dolomite #88. A 1.000 gram sample was heated at 1100° C. for thirty minutes, then boiled with 40 ml. of 1:1 hydrochloric acid. The small insoluble residue (which contained much of the aluminum, in the form of silicates) was filtered off, washed, ignited in a platinum crucible, treated with 5 drops of 1:4 sulfuric acid and 5 ml. of 48% hydrofluoric acid, and evaporated to dryness. Then it was fused with 0.5 gram of potassium pyrosulfate, the cooled melt dissolved in water, and this solution added to the original filtrate and washings. About 10 grams of ammonium chloride were added, and the R_2O_3 precipitated as usual by ammonia, using methyl red indicator. The hydroxides were filtered on 12.5 cm. #41 paper, washed a few times, transferred to a beaker by a jet of water, and dissolved by the addition of 25.0 ml. of 1:9

sulfuric acid. Then the solution was diluted to 500 ml., a
10 ml. aliquot pipetted out for electrolysis, and the deter-
mination completed in the usual manner. The results obtained
were quite satisfactory, as shown in Table 24.

At first, a different method was tried for getting the
minerals into solution: fusion of the sample with 5 grams
of anhydrous sodium carbonate plus one gram of fused boric
acid. However, this gave a very high blank, about 0.020 mg.
of alumina on the 10 ml. aliquot; spectrographic examination
later disclosed the presence of a few hundredths of a percent
of alumina in the fused boric acid used. Besides, even after
subtracting the blank, eight determinations gave results of
about 0.12% alumina for #88 (certified value 0.067%); and
six determinations on #102 gave results that were ten percent
too high. This method was therefore discarded and not further
investigated.

Comparison of Pontachrome Blue Black R with Pontachrome Vio-
let SW.

Pontachrome Violet SW, the sodium salt of 5-sulpho-2-
hydroxybenzene-azo-β-naphthol has also been recommended as
a fluorescence reagent for aluminum (70). It gives an orange
fluorescence at 5850-6250 A, compared with the red fluores-
cence of B.B.R. at 6365-6975 A. Measurements of the intensity
of this orange fluorescence were made using a double thickness
of amber cellophane substituted for the red plastic secondary
filter used in the B.B.R. experiments.

First studied was the effect of the amount of dye present.

A series of solutions was made up, each containing 0.010 mg. of aluminum, 0.5 gram of ammonium acetate, 1.0 ml. of 1:19 sulfuric acid, and amounts of 0.1% V.S.W. solution ranging up to 5.0 ml. After dilution to 50 ml., the solutions were let stand one hour, and then measured. The intensity remained constant over a wider range of dye concentration (Table 25 and Figure 21) than in the case of B.B.R.

Next, the effect of variations in pH was investigated. A series of solutions was made up, each containing 0.010 mg. of aluminum, 0.5 gram of ammonium acetate, 1.0 ml. of 0.1% V.S.W. solution, and varying amounts of 1:19 sulfuric acid or 10% sodium hydroxide, in a volume of 50 ml. The pH was measured and, after 1½ hours, the fluorescence was read. It is apparent from Table 26 and Figure 22 that small deviations from the optimum pH of 5.0 cause an even greater change of intensity than in the case of B.B.R. This necessity for more precise control of pH represents a disadvantage.

However, an almost perfectly linear relation was found between aluminum concentration and fluorescence intensity (Table 27 and Figure 23) in the range zero to 0.020 mg.; the solutions contained 1.0 ml. of 0.1% V.S.W., 0.5 gram of ammonium acetate, and 0.8 ml. of 1:19 sulfuric acid. A saturation plateau appeared at higher concentrations--about 0.060 mg. in 50 ml.--as is shown in Table 28 and Figure 24. Rather good results were obtained in the very low range 0 to 0.001 mg. (Table 29 and Figure 25), but the readings decreased too rapidly to be completely reliable.

NBS steel #14c was analyzed by a method similar to that described for B.B.R., except that the 1.000 gram sample was dissolved in 20.0 ml. of 1:9 sulfuric acid, 1.0 ml. of 0.1% V.S.W. was used, and the standards were prepared with 0.80 ml. of 1:19 sulfuric acid. The result obtained, 0.022% acid-soluble aluminum, agreed perfectly with the certified value (Table 30). Also, a synthetic standard steel containing 0.101% gave 0.101%, and a synthetic standard 0.026% gave 0.025% and 0.027%.

Nevertheless, it was observed that in several cases the V.S.W. fluorescence was destroyed partially or completely by traces of iron which remained on glassware in spite of ordinary cleaning operations. Because of this and the narrower pH range of V.S.W., it was decided to concentrate the work on B.B.R., as the more useful reagent of the two. But it has been shown that V.S.W. is capable of giving excellent results-- the choice is largely a matter of personal preference.

Summary

A rapid fluorometric method has been developed and tested, for the quantitative determination of from 0.001% to somewhat over 1% of aluminum in steels, bronzes, and minerals. This represents a range of 0.0002 to 0.025 mg. of aluminum in a volume of 50 ml. The necessity for special micro-technique is avoided by the use of aliquots of a macro sample; the sensitivity is better than 1 part in 100,000,000. For small percentages of aluminum, this method surpasses other

procedures in speed, sensitivity, accuracy, and freedom from interference.

The preferred reagent is the dyestuff Pontachrome Blue Black R, which is used at a pH of 4.6 in buffered solution. Excellent results may also be obtained with Pontachrome Violet SW. Electrolysis in a mercury cathode cell serves to eliminate interfering ions.

Studies have been conducted on the changes in intensity of fluorescence under variation of experimental conditions such as temperature, time of standing, pH, dye concentration, and aluminum concentration. The probable composition of the fluorescent substance has been established by analysis, after amyl alcohol extraction from aqueous solution.

FLUOROMETRIC DETERMINATION OF BORON

Origin of the problem

Very small amounts of boron have been found significant in soils and plant nutrition, and a few thousandths of a percent is of importance in steel manufacture (12, 17). The search for highly sensitive analytical procedures for boron has been stimulated by the fact that conventional methods are not suited for the determination of microgram quantities of boron.

Widely used for moderate amounts is the Chapin distillation method (6), which has been applied to steels (31) and waters and plant materials (104). The boron is first isolated by a very specific separation, distillation of methyl borate from a nearly anhydrous mixture of sample, methyl alcohol, and a little sulfuric acid. The distillate is made alkaline, evaporated to a small volume, acidified, and the carbon dioxide is boiled out. Using dilute sodium hydroxide, the solution is made exactly neutral to methyl red, and then a large excess of mannitol or glycerol is added. The polyhydric alcohol causes boric acid to change its behavior from that of a very weak acid to that of a fairly strong monobasic acid. Therefore the amount of sodium hydroxide required to bring the solution back to neutrality (to phenolphthalein) is a measure of the boric acid present. Among the sources of difficulty are: volatility of boric acid with steam, the

introduction of boron from glassware and reagents, and the presence of carbon dioxide which makes endpoints less sharp and causes a plus error.

Instead of using visual indicators, the mannitol titration has been accomplished by a null-point potentiometric method (76). It has been determined that as many as 27 moles of mannitol per mole of boric acid are required for accurate results (39).

Gravimetric procedures are least suitable for the determination of microgram quantities of boron, but two of these may be given brief mention. In Gooch's method (82) methyl borate is distilled out of the sample and passed through a weighed absorber containing lime, which is converted to calcium borate with attendent increase in weight. In the other scheme (49, p. 390-6) continuous ether extraction for 20 hours completely removes boron from aqueous solution; a little diammonium hydrogen phosphate is added, the ether evaporated off, and the residue heated and weighed as BPO_4.

Spectrographic techniques (26, 50) have yielded fairly accurate analyses of boron in steel, through the use of electrodes impregnated with a solution of drillings of the steel. However, the strongest boron lines 2496.8 Å and 2497.7 Å are very close to iron lines, so better results are obtained in the second order spectrum with its greater dispersion (13). A carefully standardized procedure makes it possible to use massive steel specimens and the point-to-plane technique.

A variety of colorimetric reagents have been proposed
for the determination of small amounts of boron. Many of
these are polyhydroxy aromatics, which form chelation com-
pounds with boric acid in concentrated sulfuric acid solution.
Perhaps the most widely used of these is quinalizarin, which
is 1, 2, 5, 8-tetrahydroxyanthraquinone. It has been used
for the analysis of soils (4, 80), steels (57, 75), and
stainless steels (96), after such separations as sodium hydrox-
ide or mercury cathode electrolysis (41), which are much less
specific than the distillation of methyl borate. Disadvan-
tages of the quinalizarin method are: difficulty in visual
matching of the precise shade in the pink-to-blue transition;
and unpleasantness of working in concentrated sulfuric acid
solution which absorbs moisture from the air and thereby suf-
fers changes in color, and also causes the precipitation of
salts which cloud the solution. However, an absolute accuracy
of 0.0005% is claimed. It may be noted that the acid-soluble
and acid-insoluble portions of a steel must each be analyzed
separately for their boron content.

Another sensitive reagent is turmeric, or the coloring
matter extracted from it, curcumin, which gives a red color
with boric acid. This has been called the most sensitive
test for boron. It has been used for water (24), plants (30),
steels (41), and soils (83). The sensitivity of curcumin has
been increased by the addition of trichloroacetic acid (66),
oxalic acid (60), and salicylic acid (54).

Many other color reactions for identification of boron

have been proposed. Solway Purple (Color Index 1073) in con-
centrated sulfuric acid gives a deep blue color (69). An
olive-green color results from 4,4'-diamino-1,1'-dianthra-
quinonylamine in concentrated sulfuric acid (3). Pentamethyl-
quercetin gives a yellow color (61), which however does not
obey Beer's Law. A concentrated sulfuric acid solution of
Chromotrop 2B (p-nitrobenzeneazo-1, 8-dihydroxy-naphthalene-
3, 6-disulfonic acid) causes a change from blue to green (46,
69). Alizarin S in concentrated sulfuric acid gives an orange
color, more readily matched than that of quinalizarin (19).
Carmine red in concentrated sulfuric acid is changed from red
to blue (108). Cochineal in concentrated sulfuric acid is
changed from red to violet (5).

A few fluorescence reactions have been described for the
detection of boron, but not for its quantitative determination.
Neelakantam and Row found that adding boric acid to solutions
of ortho-hydroxy-carbonyl compounds in concentrated sulfuric
acid caused intensification or color change of their fluores-
cence in nearly all cases (62). In particular, resacetophenone
in sirupy phosphoric acid gave a blue fluorescence with 1 p.p.m.
of boric acid, in the absence of such interfering ions as chro-
mate, chlorate, nitrite, and fluoride (63). A very dilute solu-
tion of 1-amino-4-hydroxyanthraquinone in concentrated sulfuric
acid gives an intense orange-brown fluorescence (69). Evapo-
rating an acetone solution of flavonols, boric acid, and
oxalic acid to dryness gives an intense yellow dye, which
fluoresces strongly in the yellow-green region (91).

In describing benzoin, $C_6H_5-CO-CHOH-C_6H_5$, as a fluorescence reagent for the detection of zinc, White and Neustadt stated that boric acid also gives an intense fluorescence with benzoin, in slightly alkaline solution (102). White and Busker found very few metals which interfered in the benzoin-boric acid reaction, among them antimony, beryllium, zinc, and metals which are precipitated by sodium hydroxide (98), and found that better results were obtained in alcohol than in water solution.

It appeared worthwhile to attempt to develop the benzoin reaction into a procedure for quantitative fluorometric determination of microgram quantities of boron.

The desired goal was achieved as described in the balance of this section. First, the effects of various conditions on the fluorescence intensity were investigated quantitatively. Next it was shown that the intensity was a linear function of boron concentration, under carefully specified conditions. Finally, through the use of the methyl borate distillation, it was found possible to successfully analyze by the new method samples of an industrial material, steel, of known boron content.

Apparatus and Reagents

Measurements of fluorescence intensity were made with the Lumetron fluorescence meter model 402EF, using a 4.77 mm. thickness of Corning Violet Ultra #5860 as the primary filter, and sheets of Wratten 2A gelatin as the secondary filters. The relation of the transmissions of these filters to the boron-

benzoin greenish-white fluorescence band at 4400-6300 A is shown in Figure 30. It may be noted that turbidity of the solution would cause no error, because no light which is passed by the primary filter can get through the secondary filters to affect the photocells.

An all-silica distilling apparatus was used in the analysis of steels. It consisted of a 100 ml. distilling flask, closed at the top by a ground joint, and connected by another ground joint to a condenser tube about 50 cm. long and 10 mm. diameter, which was cooled by a water jacket.

In order to avoid boron contamination from glassware, vessels of platinum or quartz were used wherever possible. However, the 50 ml. glass-stoppered volumetric flasks used for the final solutions were of Pyrex glass.

Benzoin solution, 0.50%, was prepared by dissolving 2.50 grams of benzoin (recrystallized twice from alcohol) in 500 ml. of redistilled ethyl alcohol.

Ordinary 95% ethyl alcohol was found to possess considerable fluorescence, so it was always redistilled from an all-glass apparatus, and stored in a glass-stoppered bottle made of boron-free glass. After such treatment, the alcohol gave only a slight fluorescence.

Absolute methyl alcohol, C. P. analyzed, and isopropyl alcohol were used without further purification.

Standard boron solution A, 1.00 ml. = 0.100 mg. of boron, was prepared by dissolving 0.5715 gram of analytical reagent grade boric acid in water and diluting to one liter. A weaker

solution B, containing 0.010 mg. of boron per ml., was pre-
pared by tenfold dilution of A. By fivefold dilution of B,
a still weaker solution C was prepared, having 2.0 micrograms
of boron per ml.

Sodium hydroxide solution, 0.6 N, was prepared by dis-
solving 24 grams of C. P. sodium hydroxide in water in a plati-
num dish, transferring to a quartz flask, and diluting to one
liter.

Distilled water only was used in these experiments.

Experimental Work

Effect of variation of conditions.

Preliminary investigations showed that in approximately
65% alcohol solution containing about 0.02% of benzoin and
a little sodium hydroxide, the intensity of fluorescence in-
creased when the boric acid concentration was increased. But
the intensity was also greatly affected by time of standing,
concentration of benzoin and of alkali, and the order in
which the reagents were added. Therefore it was necessary
first to study the influence of each variable individually,
holding the others constant. The temperature was $25^{\circ} \pm 2^{\circ}$
in all these experiments.

Time of standing. In a 50 ml. volumetric flask, 1.0 ml.
of standard solution B (containing 0.010 mg. of boron) was
mixed with 1.0 ml. of 0.6 N sodium hydroxide, and diluted im-
mediately to about 45 ml. with ethyl alcohol. Then as rapidly
as possible 4.0 ml. of 0.5% benzoin solution were added, a

stop-watch was started, the mixture diluted to the mark with alcohol and shaken vigorously, and half of it poured into the 25 ml. cell and placed in the instrument. Readings of fluorescence intensity were taken at one minute intervals, under continuous irradiation. After ten minutes, the solution in the cell was discarded and replaced by the other half of the original mixture. Readings were again taken at one minute intervals. As shown in Table 31 and Figure 31, the fluorescence increases at first, reaches a maximum after about 4 minutes, and then drops off smoothly. The portion of the same solution which was not exposed to ultraviolet radiation for ten minutes after mixing shows a relatively high intensity at first, but this drops rapidly to a value comparable with what would have been observed if irradiation had been continuous from the moment of mixing.

The experiment was repeated, except that 1.0 ml. of solution A was used, containing 0.100 mg. of boron. Very similar results were obtained, in Table 32 and Figure 32. These graphs suggest that two antagonistic influences are at work here. One, which tends to increase the intensity, is the probably far-from-instantaneous reaction which produces the fluorescent compound; the other, which tends to decrease the intensity, is the oxidation or photochemical destruction of the fluorescent compound. Relative to the hypothesis of oxidation, it was found that the readings remained more nearly constant in a covered than in an uncovered cell.

It was thought that adding an anti-oxidant might help

keep the readings constant. However, addition of 0.1 gram
of sodium dithionite, $Na_2S_2O_4$, resulted in a much weaker
fluorescence, precipitation in the solution, and just as
great a variation with time. Similarly, the addition of 0.2
gram of resorcinol to a solution made up with 0.100 mg. of
boron failed to give constancy of readings (Table 33 and
Figure 33) although the initial intensity of the portion not
irradiated for the first ten minutes was relatively greater.
It may be emphasized here that the scale of the instrument
was readjusted arbitrarily for each of the experiments on the
effect of variation of conditions.

Because of the possible usefulness of the methyl borate
separation, methyl alcohol was tried as a solvent instead of
ethyl alcohol. In other respects, conditions were similar;
1.0 ml. of sodium hydroxide, 1.0 ml. of solution B containing
0.010 mg. of boron, and 4.0 ml. of benzoin were mixed and
diluted in the usual manner, and the time measured and read-
ings taken as before. The general features of the curve re-
mained the same, except that both the rise and decay of fluo-
rescence were more gradual, as may be seen in Table 34 and
Figure 34. But the intensity was very much less than in
ethyl alcohol solution.

The experiment was repeated at the higher level of 0.100
mg. of boron in methanol solution. The readings became quite
constant in this case, as evidenced in Table 35 and Figure 35.
However, most of the later work was done at lower boron con-
centrations, so it was decided to return to using ethanol,

and thus avoid sacrificing sensitivity.

Concentration of sodium hydroxide. A series of ten solutions was prepared and mixed in the manner previously described; each contained 4.0 ml. of benzoin, varying amounts of NaOH solution up to 4.0 ml., enough water to make the sum of water and NaOH equal 4.0 ml., and 5.0 ml. of solution C equivalent to 0.010 mg. of boron. It was found in this and subsequent experiments that satisfactory and reproducible readings could be obtained two minutes after mixing, but the interval must be timed accurately and the technique carefully standardized.

Maximum fluorescence was obtained by the use of about 0.25 ml. of 0.6 N sodium hydroxide in the 50 ml. volume, according to Table 36 and Figure 36. The shape of the curve indicates two opposing influences: the fluorescence reaction requires a small but definite amount of alkali for greatest intensity, but excess alkali seems to cause more rapid destruction of the desired compound.

The experiment was repeated at the higher concentration of 0.100 mg. of boron. A curve of the same general shape was obtained, with the maximum again at about 0.25 ml. of NaOH.

Concentration of benzoin. A series of solutions was prepared in the usual manner, each containing 0.50 ml. of 0.6 N sodium hydroxide, 0.010 mg. of boron added as 5.0 ml. of solution C, and various amounts of 0.5% benzoin solution up to 7.0 ml. Readings taken two minutes after mixing gave the results in Table 37 and Figure 37. The curve is approximately

parabolic, which shows that the intensity is proportional to the square root of the concentration of benzoin. This indicates either that two molecules of benzoin are required to produce each molecule of fluorescent compound, or else that benzoin exists in alcohol solution as a dimer.

Concentration of water. Inasmuch as the reaction is carried out in alcohol solution, it was not surprising to find that the amount of water present affected the intensity. Ten solutions were prepared as usual, each containing 1.0 ml. of solution A equal to 0.100 mg. of boron, 1.0 ml. of 0.6 N sodium hydroxide, 4.0 ml. of 0.5% benzoin, and various amounts of water up to 10 ml. Table 38 and Figure 38 show that the intensity measured five minutes after mixing decreased considerably as the water content increased, so it was necessary to control closely the amount of water, as well as of NaOH and benzoin, in the later quantitative determinations. The abscissas of the graph, entitled "total ml. of water," include the 2 ml. of water present in the NaOH and boric acid solutions, as well as the excess water added.

Dependence of fluorescence on concentration of boron.

If the relation between fluorescence intensity and boron concentration should prove to be linear, the application of this reaction to quantitative analysis would be greatly facilitated. Accordingly, this phase was investigated next.

A set of solutions was prepared, in the customary fashion, containing various quantities of standard solution A, plus sufficient water to make the sum equal 5.0 ml. As seen in Table

39 and Figure 39, the intensity increased in a fairly uniform manner up to about 0.350 mg. of boron, and then leveled off.

Next, a smaller range of concentrations was investigated more intensively, from zero up to 0.050 mg. of boron in the 50 ml. volume. In this region, the graph was found to be quite nearly a straight line, as shown by Table 40 and Figure 40.

An even more nearly perfectly linear relation was obtained when the region zero to 0.010 mg. of boron was studied more thoroughly; this is shown in Table 41 and Figure 41. Consequently, all of the analyses performed later were within this lowest range of concentrations. An additional advantage was the smaller sample weight of steel required.

Other alcohols than ethyl were tried as solvents. Isopropyl alcohol gave a quite linear relation up to about 0.050 mg. of boron (Table 42 and Figure 42), but methyl alcohol under the given conditions showed a rather irregular increase of intensity with boron concentration up to 0.100 mg. (Table 43 and Figure 43). The fluorescence was strongest by far in ethanol, however.

In all these experiments, the solutions had to be shielded from exposure to bright sunlight, which caused the fluorescence to decrease greatly.

Determination of boron in pure solution.

The above findings were applied to the determination of boron by fluorometry. Known amounts of boron (as boric acid) dissolved in 5.0 ml. of water were mixed with 0.50 ml. of

0.6 N sodium hydroxide in a 50 ml. volumetric flask, and diluted to about 45 ml. with ethyl alcohol. Then 4.0 ml. of 0.50% benzoin were added, a stopwatch started simultaneously, and the solution diluted to the mark with ethanol. It was shaken vigorously, the requisite amount was poured into the cell, and the fluorescence intensity measured at exactly two minutes after the addition of the benzoin. The amount of boron present was determined by reference to a standardization graph, constructed by drawing a straight line through the two points given by standard solution containing 0.000 and 0.010 mg. of boron, respectively. The standard solutions were prepared in the same manner and at the same time as the "unknowns."

Excellent results were obtained by the above procedure, the average error for these microgram quantities of boron being only 1.5%, as shown in Table 44.

Determination of boron in steels.

Finally, it was desired to apply these results to the analysis of the industrially important material steel, in which the presence of two or three thousandths of a percent of boron causes great improvement in the mechanical properties.

Preliminary experiments showed that mercury cathode electrolysis was not a suitable separation, because of the alcohol insoluble salts produced by neutralization of the acid electrolyzate. Accordingly, separation of boron by distillation as methyl borate was decided upon.

The method finally evolved for the determination of

acid-soluble and acid-insoluble boron in steel was as follows.
A 0.100 gram sample of steel was transferred to the 100 ml.
flask of the all-silica distilling apparatus, 5 ml. of 1:4
sulfuric acid were added, and the apparatus connected up as
for a distillation, the receiver being a 300 ml. platinum
dish containing 0.50 ml. of 0.6 N sodium hydroxide. The flask
was warmed until the steel dissolved completely; usually a
drop or two of liquid distilled over. Then a silica boiling
chip and 40 ml. of methanol were added to the flask, and the
contents distilled down to a few ml., where salts started to
separate out. The flask was cooled in ice-water, and an
additional 30 ml. of methanol and another boiling chip added,
and the contents distilled down to the separation of salts
again, the distillate being collected in the same receiver.
The well-mixed distillate was evaporated to dryness, and the
residue dissolved in 5.50 ml. of water. Then about 20 ml.
of ethanol were added, and the slightly turbid mixture trans-
ferred to a 50 ml. volumetric flask and diluted to about 45
ml. with alcohol. Simultaneously with the starting of a
stopwatch, 4.0 ml. of 0.50% benzoin were added, and the solu-
tion diluted to the mark with ethanol and shaken well. The
requisite amount was poured into the cell, and the fluores-
cence measured at exactly two minutes after the addition of
the benzoin. Standards prepared similarly, except for dis-
tillation, were used to construct a standardization graph of
scale reading against boron concentration, from which the
percentage of boron present could be determined. This gave

the amount of acid-soluble boron in the steel.

In order to determine the acid-insoluble boron, the residue remaining in the flask after the second distillation was dissolved in 15 ml. of hot water, and filtered through a retentive 12.5 cm #42 Whatman paper. The filtrate and washings were discarded, and the filter paper sprinkled with about 100 mg. of anhydrous sodium carbonate and ignited in a platinum crucible until the carbon had mostly disappeared. The residue was fused for a minute or two, allowed to cool, dissolved in 5 ml. of 1:4 sulfuric acid, and transferred to the silica distilling flask with 40 ml. of ethanol. From this point on, the procedure was exactly the same as for the acid-soluble portion: double methanol distillation into 0.50 ml. of alkali, evaporation of the distillate to dryness, solution in 5.5 ml. of water, and addition of reagents and measurement of fluorescence in the usual manner. The blank was determined by running a boron-free steel through the entire procedure; it amounted to about 0.0015% of boron.

Analyses of some Bureau of Standards steels by the above method are listed in Table 45. The sums of the acid-soluble and acid-insoluble boron contents found, minus the blank, were quite close to the certified values. However, low results were obtained on steels of higher boron content, presumably because of losses during the distillation or evaporation. It was nevertheless felt that the new method is fundamentally sound, because the distillation is a standard method and the validity of the fluorometric determination in pure solution was proven beyond question.

Summary

A new, highly sensitive method for the quantitative determination of boron has been developed, based on the intensity of greenish-white fluorescence obtained upon addition of benzoin, in slightly alkaline 85% ethanol solution. Studies have been made of the effects of such variables as time of standing, type of alcohol, and concentrations of benzoin, alkali, and water.

Intensity of fluorescence has been shown to be a linear function of boron concentration in the range from 0 to 10 micrograms, in a volume of 50 ml. Excellent results were obtained in the determination of such amounts of boron in pure solution, the accuracy being 1 or 2 parts per hundred.

This method has been applied successfully to the determination of a few thousandths of one percent of boron in steel, a problem of current industrial interest. The highly specific separation by distillation of methyl borate, a standard procedure, serves as a preliminary removal of interfering elements.

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Table 1

EFFECT OF pH ON FLUORESCENCE INTENSITY, 0.050 MG.

Sample	Acetic Acid Added, ml.	NH$_4$OH Added, ml.	pH	Scale Reading
1	0.00	-	6.0	69.4
2	0.01	-	5.7	71.7
3	0.02	-	5.55	75.3
4	0.03	-	5.45	73.8
5	0.05	-	5.30	75.5
6	0.10	-	5.15	75.4
7	0.20	-	4.7	75.0
8	0.50	-	4.25	72.3
9	1.00	-	3.95	68.2
10	2.0	-	3.65	63.2
11	3.0	-	3.45	59.3
12	4.0	-	3.35	58.3
13	5.0	-	3.25	51.8
14	10.0	-	2.90	50.8
15	20.0	-	2.40	47.0
16	-	0.02	7.90	10.3
17	-	0.10	8.50	1.5
18	-	0.20	8.95	0.7
19	-	0.50	9.45	0.2
20	-	1.00	9.80	0.1

Table 2

EFFECT OF pH ON FLUORESCENCE INTENSITY, 0.010 MC.

Sample	Acetic Acid Added, ml.	pH	Scale Reading
1	0.00 ml.	6.5	13.0
2	0.02 ml.	5.7	29.0
3	0.05	5.45	51.3
4	0.08	5.25	63.5
5	0.10	5.1	72.6
6	0.13	5.0	76.0
7	0.20	4.9	82.0
8	0.40	4.6	86.0
9	0.60	4.45	79.0
10	0.80	4.32	64.5
11	1.00	4.2	59.0
12	2.00	3.8	50.0
13	4.00	3.5	24.0
14	6.00	3.4	16.4
15	8.00	3.2	14.0
16	10.00	3.1	11.5

Table 3

EFFECT OF B.B.R. CONCENTRATION ON FLUORESCENCE INTENSITY

Sample	B.B.R. Added, ml.	Scale Reading
1	0.00 ml.	0.0
2	0.20	32.1
3	0.40	59.7
4	0.60	77.4
5	0.80	87.4
6	1.00	93.0
7	1.20	98.0
8	1.50	100.0
9	2.00	83.6
10	2.50	60.7
11	3.00	45.6
12	3.50	33.0
13	4.00	28.9
14	4.50	19.2
15	5.00	13.4

Table 4

BLANK DUE TO ACETIC ACID

Sample	Acetic Acid Added, ml.	Scale Reading	Resulting Error
1	0.00 ml.	1.5	0.30 γ Al
2	0.05 ml.	0.0	0.00
3	0.10	0.0	0.00
4	0.20	0.1	0.02
5	0.40	0.5	0.10
6	1.00	1.0	0.20
7	2.00	1.5	0.30

Table 5

TIME REQUIRED TO ATTAIN FULL INTENSITY OF FLUORESCENCE, 0.100 MD.

Minutes After Mixing	Scale Reading
1	20.4
2	31.0
3	39.7
4	46.0
5	50.1
6	53.0
7	56.0
8	58.5
9	60.3
10	62.0
12	63.9
14	66.1
16	67.5
18	68.5
20	69.3
25	70.3
27	70.6
30	71.2
35	71.7
40	72.0
45	72.2
50	72.4
55	72.5
60	72.7
70	73.0
80	73.2
90	73.4
100	73.5
110	73.6
120	73.6
130	73.7
140	73.8
150	74.0
160	74.1
170	74.2
1000 (next day)	76.0

Table 6

TIME REQUIRED TO ATTAIN FULL INTENSITY OF FLUORESCENCE, 0.010
MG.

Minutes After Mixing	Scale Reading
1	10.5
2	18.5
3	25.8
4	31.9
5	37.0
6	40.5
7	41.8
8	43.5
9	44.5
10	48.0
11	49.5
12	50.7
13	51.3
14	52.0
15	53.1
16	54.0
18	54.5
20	55.0
25	57.2
30	58.0
35	59.2
40	60.0
45	60.0
50	60.0
55	60.1
60	60.2
180	59.3

Table 7

TIME CHANGE OF FLUORESCENCE AFTER HEATING TO 70° C.

Minutes After Mixing	Scale Reading	Temperature
2	10.6	60° C
3	10.6	
4	10.6	53°
5	10.5	
6	10.8	50°
7	11.3	
8	11.5	
9	11.7	
10	12.4	43°
12	13.5	
14	13.7	
16	15.6	38°
18	16.1	
20	17.0	35°
25	18.2	
30	19.4	31°
35	21.2	
40	22.3	28°
45	23.2	
50	23.7	27°
55	24.1	
60	25.5	26°
65	28.0	
70	29.1	
75	30.0	
80	30.5	
85	31.3	25°
90	32.2	

A solution of the same composition, but mixed at room temperature (24° C) and let stand 2 hours, gave a reading of 50.0.

Table 8

TIME CHANGE OF FLUORESCENCE AFTER HEATING TO 60° C.

Minutes After Mixing	Scale Reading	Temperature
1	4.0	
2	4.8	
3	5.0	59° C
4	5.9	
5	6.2	53°
6	6.6	
7	6.7	
8	7.2	48°
9	7.8	
10	8.2	45°
12	8.7	
14	9.1	42°
16	9.3	39°
18	9.9	36°
20	10.5	
22	10.8	34°
24	11.2	
26	11.6	32°
28	12.1	
30	12.5	30.5°
32	12.9	
34	13.2	29.5°
36	13.4	
38	13.7	
40	14.0	28°
45	14.5	27.5°
50	15.1	27°
55	15.5	26.5°
60	16.0	

A solution of the same composition, but mixed at room temperature (25° C) and let stand 2 hours, gave a reading of 50.0.

Table 9

EFFECT OF TEMPERATURE ON FLUORESCENCE

Temperature	Scale Reading
25° C	52.0
Cooled in ice, then	
at 10° C	53.5
15° C	53.2
20° C	51.5
Heated, then allowed to cool	
60° C	16.0
55° C	18.5
50°	20.1
45°	21.8
40°	23.5
35°	25.5
30°	27.9
25°	30.2

Table 10

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, A

Sample	Al Added, Micrograms	Scale Reading
1	0.0	0.0
2	2	2.1
3	5	6.5
4	10	13.7
5	15	21.2
6	20	28.8
7	25	35.8
8	30	46.0
9	35	58.3
10	40	68.1
11	45	78.0
12	50	83.7
13	55	85.2
14	60	86.2
15	65	86.6
16	70	86.9
17	75	86.0
18	80	88.3
19	90	86.0
20	100	87.5

Table 11

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, B

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	2	2.4
3	5	6.8
4	10	13.7
5	15	21.5
6	20	30.0
7	25	37.9
8	30	48.1
9	35	56.1
10	40	65.3
11	45	74.4
12	50	81.1
13	55	84.1
14	60	86.5
15	65	88.0
16	70	88.5
17	75	89.0
18	80	89.4
19	90	89.0
20	100	90.0

Table 12

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, C

Sample	Al Added, Micrograms	Scale Reading
1	0.0	0.0
2	5.0	11.8
3	10	28.2
4	15	43.3
5	20	58.4
6	25	76.5
7	30	86.6
8	35	90.7
9	40	92.0
10	45	90.4
11	50	90.0

Table 13

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, D

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	1	4.6
3	2	8.9
4	3	13.5
5	4	18.1
6	5	22.6
7	6	25.7
8	7	31.6
9	8	36.1
10	9	41.2
11	10	44.5
12	11	48.5
13	12	51.8
14	13	56.1
15	14	60.8
16	15	65.4
17	16	72.3
18	17	75.5
19	18.5	82.0
20	20	90.0

Table 14

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, E

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	2	4.1
3	4	8.5
4	6	12.2
5	8	18.0
6	10	22.5
7	12	26.0
8	14	29.5
9	16	37.0
10	18	41.4
11	20	45.0
12	22	50.4
13	24	55.0
14	26	60.5
15	28	65.8
16	30	72.1
17	32	79.0
18	34	86.1
19	36	93.1
20	40	101.0

Table 15

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, F

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	2	8.0
3	4	16.5
4	6	26.0
5	8	35.5
6	10	44.6
7	12	54.0
8	14	64.0
9	16	74.0
10	18	85.0
11	20	97.0

Table 16

DEPENDENCE OF B.B.R. FLUORESCENCE ON ALUMINUM CONCENTRATION, G

Sample	Al Added, Micrograms	Scale Reading
1	0.00	10.0
2	0.20	34.0
3	0.40	52.5
4	0.60	64.0
5	0.80	83.0
6	1.00	100.0

Note: These readings decreased rapidly while the solutions were in the instrument.

Table 17

ABSORPTION SPECTRA OF BUFFERED B.B.R. SOLUTIONS

Wavelength, Millimicrons	Blank, no Al, % Transmission	Fluorescing Solution, % Transmission
400	60.8	65.8
420	60.5	66.5
440	59.0	65.8
460	53.5	59.2
480	45.6	48.0
500	39.0	37.0
520	35.8	30.0
540	37.5	27.0
560	41.3	29.0
580	49.0	39.0
600	59.0	60.5
620	66.3	76.5
640	72.5	84.2
660	80.0	89.0
680	89.0	93.0
700	92.3	94.3
720	94.7	96.1
740	95.0	96.2
760	97.7	98.3

Table 18

ANALYSIS OF SYNTHETIC STANDARD STEELS

Al Present %	Scale Reading	Al Found %
0.000 Standard	0.0	
0.050 Standard	50.0	
0.001	1.0	0.001
0.026	24.8	0.025
	26.0	0.026
0.051	51.4	0.051
	49.6	0.050
0.078	78.7	0.079

Table 19

ANALYSIS OF BUREAU OF STANDARDS STEELS FOR ACID-SOLUBLE ALUMINUM

Steel	Certified Value, %	Found, %
55a	0.001	0.001
		0.001
		0.001
		0.001
14c	0.022	0.021
		0.021
		0.024
		0.022
		0.022
		0.021
		0.021
		0.022
106a	1.07	1.05
		1.05
		1.12
		1.13
106	1.06 (total)	1.09
		1.09
		1.05
		1.05

Table 20

ANALYSIS OF BUREAU OF STANDARDS STEEL FOR
ACID-INSOLUBLE ALUMINA

Steel	Certified Value, %	Value Found, %
14c	0.011	0.011
		0.011
		0.011
		0.012

Table 21

INTERFERENCE BY TITANIUM, VANADIUM, AND ZIRCONIUM

Metal Added, Micrograms	Scale Reading	Error, Micrograms Al in 10 Micrograms
Titanium:		
0.0	50.0	0.0
10	47.5	-0.5
20	45.0	-1.0
30	43.0	-1.4
40	40.5	-1.9
50	38.5	-2.3
Vanadium:		
0	48.0	0.0
20	46.0	-0.4
30	44.3	-0.7
40	37.0	-2.2
50	20.0	-5.8
Zirconium:		
0	46.0	0.0
10	45.5	-0.1
20	45.5	-0.1
40	44.5	-0.3
50	44.0	-0.4

Table 22

DETERMINATION OF ALUMINUM IN TITANIUM AND VANADIUM STEELS

Steel	Gravimetric Analysis	Al Found, %
K	0.066% Al, 0.085% Ti	0.064
		0.066
		0.064
		0.063
	0.051% Al, 0.11% V	0.053
		0.053
		0.053
		0.054

Table 23

ANALYSIS OF BUREAU OF STANDARDS BRONZES

Alloy	Certified Value, %	Aluminum Found, %
62	1.13	1.09
		1.14
		1.11
62a	0.92	0.93
		0.93
		0.95
		0.96
62b	0.97	0.98
		0.95
		0.95
		0.97
63	0.05	0.044
		0.051
		0.052
		0.055
124a	0.006	0.006
		0.008

Table 24

ANALYSIS OF BUREAU OF STANDARDS MINERALS

Sample	Certified Value, %	Alumina Found, %
81	0.265	0.268
		0.279
		0.287
88	0.067	0.065
		0.067
		0.063
		0.062
102	1.96	1.98
		2.01
		2.03

Table 25

EFFECT OF V.S.W. CONCENTRATION ON FLUORESCENCE INTENSITY

Sample	V.S.W. Added, ml.	Scale Reading
1	0.5	48.8
2	1.0	51.0
3	2.0	50.0
4	2.5	50.0
5	3.0	45.2
6	4.5	28.0
7	5.0	24.5

Table 26

EFFECT OF pH ON V.S.W. FLUORESCENCE

Sample	10% NaOH Added, ml.	1:19 H_2SO_4 Added, ml.	pH	Scale Reading
1	0.40	–	8.7	6.1
2	0.10	–	7.6	1.5
3	–	–	6.1	13.4
4	–	0.30	5.4	63.0
5	–	0.70	5.0	83.5
6	–	1.00	4.8	61.0
7	–	1.50	4.5	50.0
8	–	2.00	4.3	20.5
9	–	3.00	2.7	2.5
10	–	5.00	1.6	3.7

Table 27

DEPENDENCE OF V.S.W. FLUORESCENCE ON ALUMINUM CONCENTRATION

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	1	4.9
3	2	9.3
4	3	14.0
5	4	20.6
6	5	24.8
7	6	30.4
8	7	35.9
9	8	41.8
10	9	46.8
11	10	51.5
12	11	56.9
13	12	61.8
14	13	66.4
15	14	72.4
16	15	77.0
17	16	82.0
18	17	86.3
19	18	91.9
20	20	101.6

Table 28

DEPENDENCE OF V.S.W. FLUORESCENCE ON ALUMINUM CONCENTRATION
(HIGH RANGE)

Sample	Al Added, Micrograms	Scale Reading
1	0	0.0
2	5	12.4
3	10	26.0
4	15	37.8
5	20	50.0
6	25	61.0
7	30	71.0
8	35	78.4
9	40	84.8
10	45	91.0
11	50	92.4
12	55	96.4
13	60	97.8
14	65	100.8
15	70	98.4
16	75	102
17	80	101.5
18	85	101.5
19	90	103
20	100	103.5

Table 29

DEPENDENCE OF V.S.W. FLUORESCENCE ON ALUMINUM CONCENTRATION
(LOWEST RANGE)

Sample	Al Added, Micrograms	Scale Reading
1	0.00	34.0
2	0.20	37.3
3	0.40	40.1
4	0.60	42.6
5	0.80	46.3
6	1.00	50.0

Table 30

ANALYSIS OF ALUMINUM STEELS BY V.S.W. FLUORESCENCE

Steel	Found, %
14a (0.022%)	.022
.026% synthetic standard	0.025
	0.027
.101% synthetic standard	0.101

Table 31

CHANGE OF FLUORESCENCE WITH TIME
0.010 MG. OF BORON IN ETHANOL

Minutes After Mixing	Scale Reading
2	31.5
3	37.5
4	40.5
5	40.8
6	39.5
7	37.0
8	33.8
9	30.0
10	26.0

Fresh portion of same solution

11	35.5
12	25.0
13	17.5
14	11.7
15	7.5

Table 32

CHANGE OF FLUORESCENCE WITH TIME
0.100 MG. OF BORON IN ETHANOL

Minutes After Mixing	Scale Reading
2	40.0
3	47.5
4	50.0
5	50.8
6	49.9
7	47.0
8	43.0
9	38.2
10	32.5

Fresh portion of same solution

10.7	51.0
11	46.5
12	37.0
13	27.0
14	17.5
15	10.0

Table 33

CHANGE OF FLUORESCENCE WITH TIME, USING RESORCINOL AS ANTI-OXIDANT

Minutes After Mixing	Scale Reading
1	22.0
2	39.5
3	47.0
4	48.0
5	46.5
6	44.3
7	41.3
8	39.0
9	33.8
10	31.0

Fresh portion of same solution

11	100.0
12	73.0
13	54.0
14	41.5
15	35.0
18	24.0

Table 34

CHANGE OF FLUORESCENCE WITH TIME
0.010 MG. OF BORON IN METHANOL

Minutes After Mixing	Scale Reading	Minutes After Mixing	Scale Reading
1	20.0	32	52.7
1½	22.3	33	52.8
2	24.4	34	52.7
3	28.3	35	52.5
4	31.2	36	52.4
5	33.3	37	52.2
6	35.4	39	52.4
8	39.0	40	52.1
9	40.9	42	52.3
10	42.4	44	52.1
11	43.3	46	51.9
12	44.3	48	50.6
13	45.1	50	49.8
14	45.5	52	49.4
15	46.0	54	49.4
16	46.4	56	49.3
17	47.0	58	48.5
18	47.7	60	48.1
19	48.5	Fresh portion of same solution	
20	49.4		
21	50.0	60-3/4	58.7
22	50.3	61-1/2	52.0
23	50.5	62	51.4
24	50.9	63	51.2
25	51.2	64	51.4
26	51.5	65	51.5
27	51.8	67	51.9
28	52.1	70	52.7
29	52.5	75	53.0
30	52.6	77	52.9
31	52.7		

Table 35

CHANGE OF FLUORESCENCE WITH TIME
0.100 MG. OF BORON IN METHANOL

Minutes After Mixing	Scale Reading	Minutes After Mixing	Scale Reading
1	12.5	14	24.2
2	15.5	15	24.4
3	18.4	17	24.4
4	20.5	20	24.2
5	22.0	22	24.0
6	22.6	Fresh portion of	
7	23.1	same solution	
8	23.6	23	37.0
9	24.0	24	30.0
10	24.2	25	25.8
11	24.3	26	23.3
12	24.4	27	22.0
13	24.4	29	20.6
		32	20.0

Table 36

EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON FLUORESCENCE

Sample	0.6N NaOH Added, ml.	Scale Reading
1	0.05	39.7
2	0.10	64.2
3	0.25	75.0
4	0.50	67.0
5	0.75	59.5
6	1.00	50.5
7	1.50	42.0
8	2.00	35.0
9	3.00	26.8
10	4.00	20.6

Table 37

EFFECT OF BENZOIN CONCENTRATION ON FLUORESCENCE

Sample	0.5% Benzoin Added, ml.	Scale Reading
1	0.50	21.5
2	1.25	44.0
3	2.0	56.0
4	3.0	74.0
5	3.5	76.4
6	4.0	81.5
7	4.5	86.0
8	5.0	92.0
9	6.0	97.3
10	7.0	97.0

Table 36

EFFECT OF WATER CONCENTRATION ON FLUORESCENCE

Sample	Total Water, ml.	Scale Reading
1	2.0	48.7
2	3.0	44.8
3	4.0	40.5
4	5.0	35.2
5	6.0	33.8
6	7.0	32.9
7	8.0	29.5
8	9.0	28.1
9	10.0	26.0
10	12.0	23.0

Table 39

RELATION OF FLUORESCENCE TO BORON CONCENTRATION, HIGH RANGE

Sample	Boron Added, Micrograms	Scale Reading
1	0	0.0
2	50	10.4
3	100	18.4
4	150	30.2
5	200	38.4
6	250	45.7
7	300	52.1
8	350	56.3
9	500	52.8

Table 40

RELATION OF FLUORESCENCE TO BORON CONCENTRATION, MIDDLE RANGE

Sample	Boron Added, Micrograms	Scale Reading
1	0	0.0
2	10	17.4
3	20	39.0
4	30	60.5
5	40	83.0
6	50	99.0

Table 41

RELATION OF FLUORESCENCE TO BORON CONCENTRATION, LOW RANGE

Sample	Boron Added, Micrograms	Scale Reading
1	0.0	0.0
2	2.0	19.2
3	4.0	36.7
4	6.0	58.9
5	8.0	74.5
6	10.0	95.5

Table 42

RELATION OF FLUORESCENCE TO BORON CONCENTRATION, IN ISOPROPYL ALCOHOL

Sample	Boron Added, Micrograms	Scale Reading
1	0	0.0
2	10	16.4
3	20	42.1
4	30	65.0
5	40	90.5
6	50	100.0

Table 43

RELATION OF FLUORESCENCE TO BORON CONCENTRATION,
IN METHYL ALCOHOL

Sample	Boron Added, Micrograms	Scale Reading
1	0	0.0
2	10	5.0
3	20	12.0
4	30	24.5
5	40	30.6
6	50	45.3
7	60	55.0
8	70	59.5
9	80	71.0
10	100	88.0

Table 44

DETERMINATION OF BORON IN PURE SOLUTION

Boron Added, Micrograms	Boron Found, Micrograms	Error, %
0.0	0.00	
	-0.02	
	0.05	
2.0	2.00	0.0
	2.06	3.0
	2.10	5.0
4.0	3.88	3.0
	3.94	1.5
	4.10	2.5
5.0	4.90	2.0
6.0	5.97	0.5
	5.99	0.2
	6.01	0.2
8.0	7.83	2.1
	7.88	1.5
	7.82	2.3
9.0	8.92	0.9
10.0	10.02	0.2
	9.98	0.2
	9.95	0.5

Average error = 1.5%

Table 45

DETERMINATION OF BORON IN BUREAU OF STANDARDS STEELS

Steel	Certified Value, %	Found, %
825	0.0006	.0007 .0005 .0005
826	0.0011	.0013 .0011 .0009 .0010
151	0.0027	.0028 .0028 .0025 .0027

EFFECT OF pH ON FLUORESCENCE INTENSITY,
0.050 MG
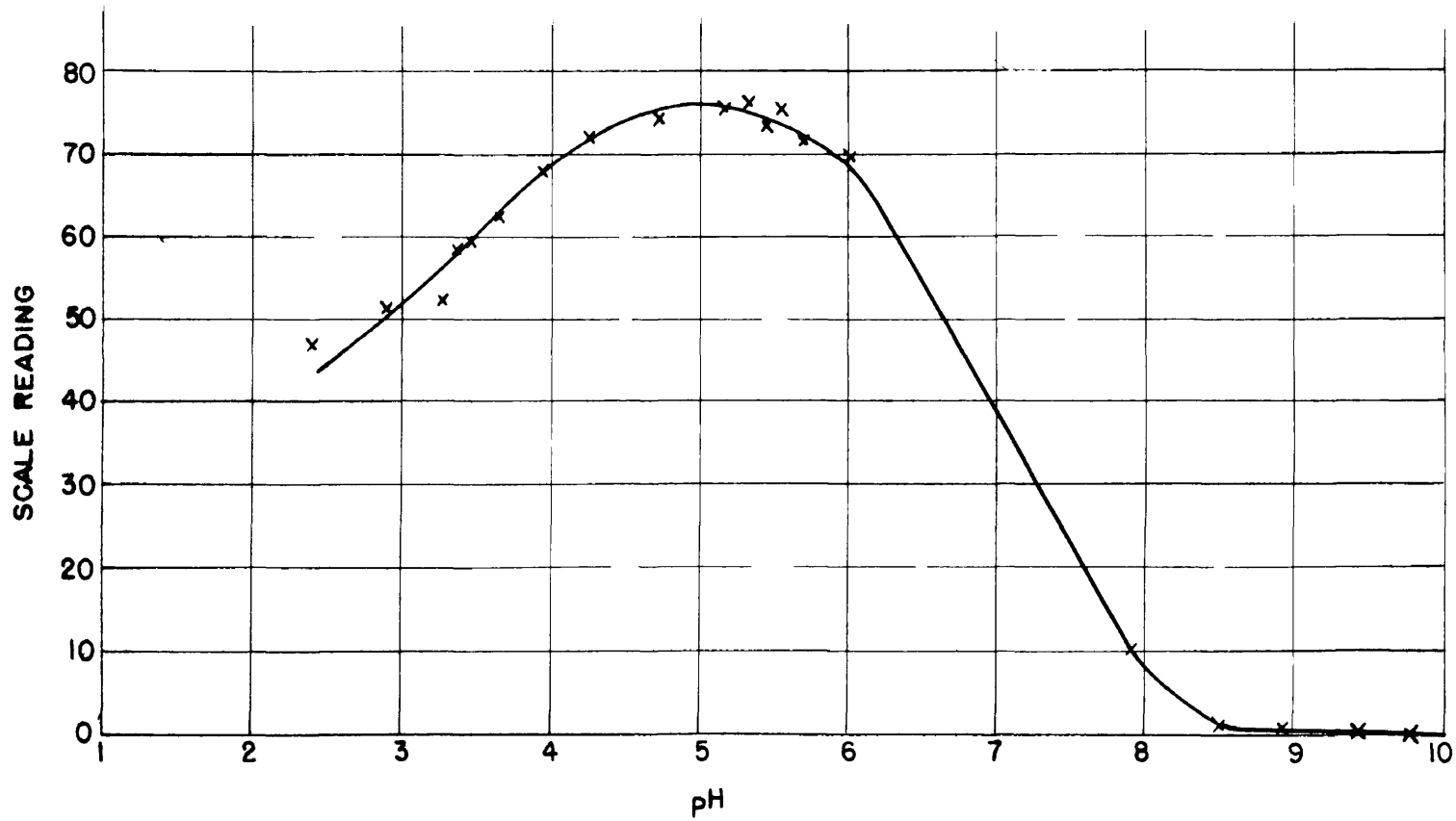
FIG. 1

EFFECT OF pH ON FLUORESCENCE INTENSITY, 0.010 MG.
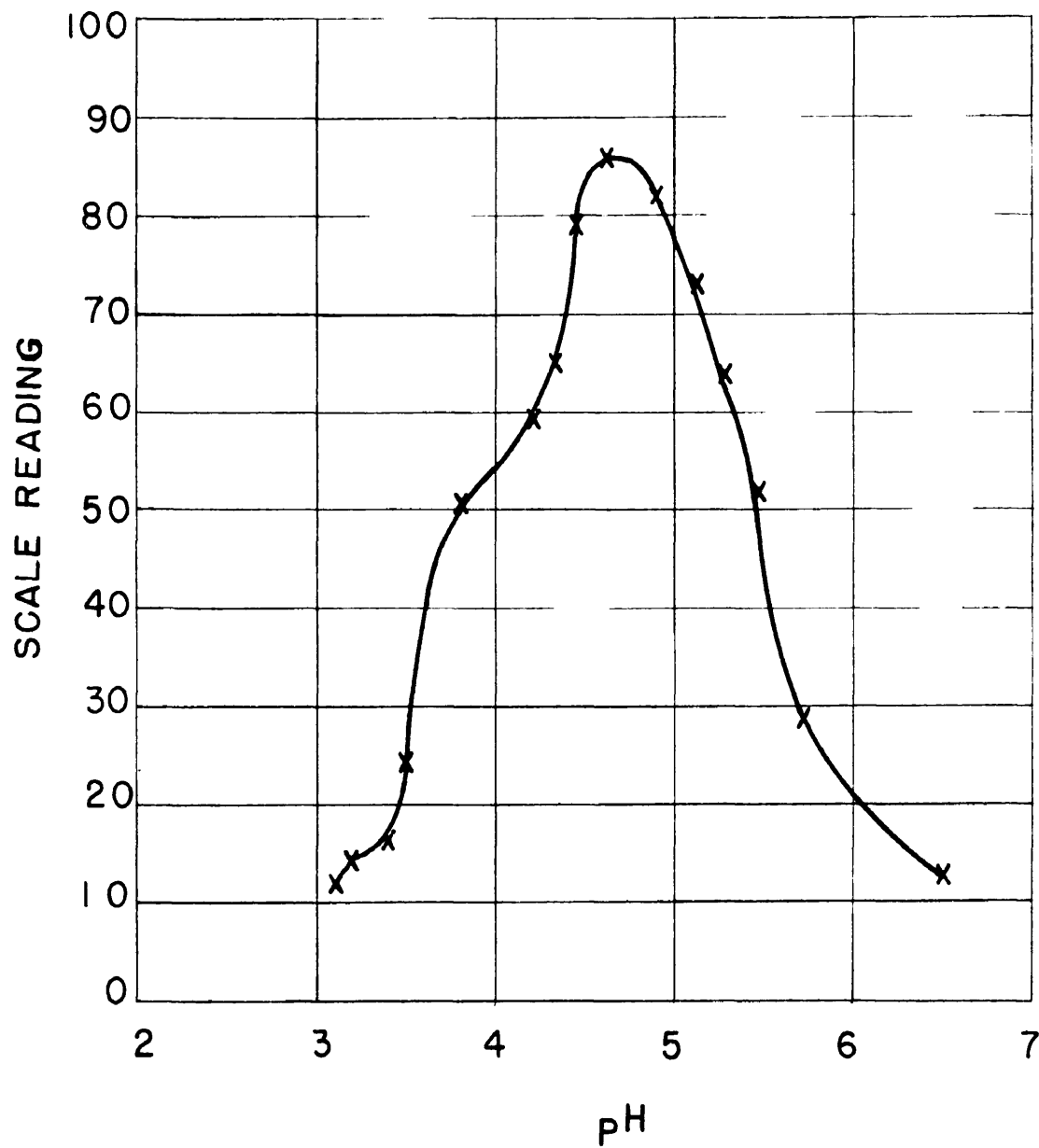
FIG. 2

EFFECT OF BBR CONCENTRATION ON FLUORESENCE INTENSITY

SCALE READING

ML OF 0.1% BBR
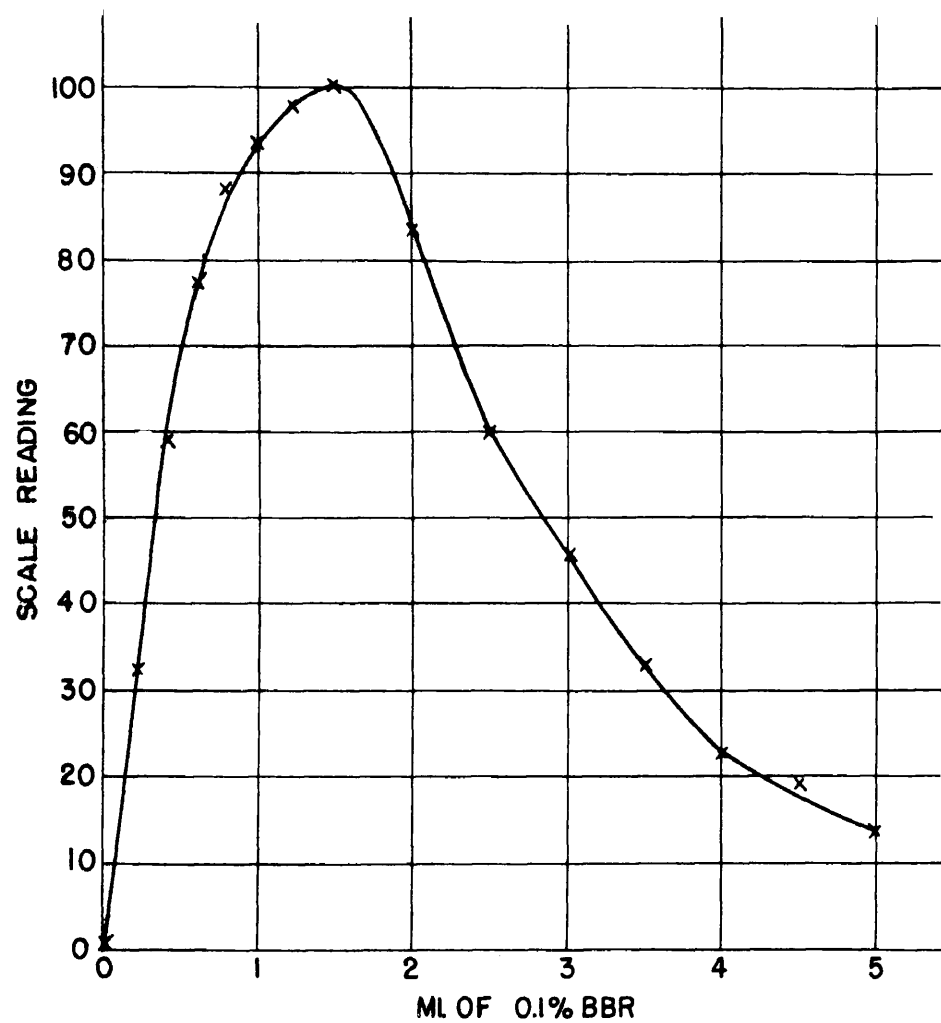
FIG. 3

BLANK DUE TO ACETIC ACID
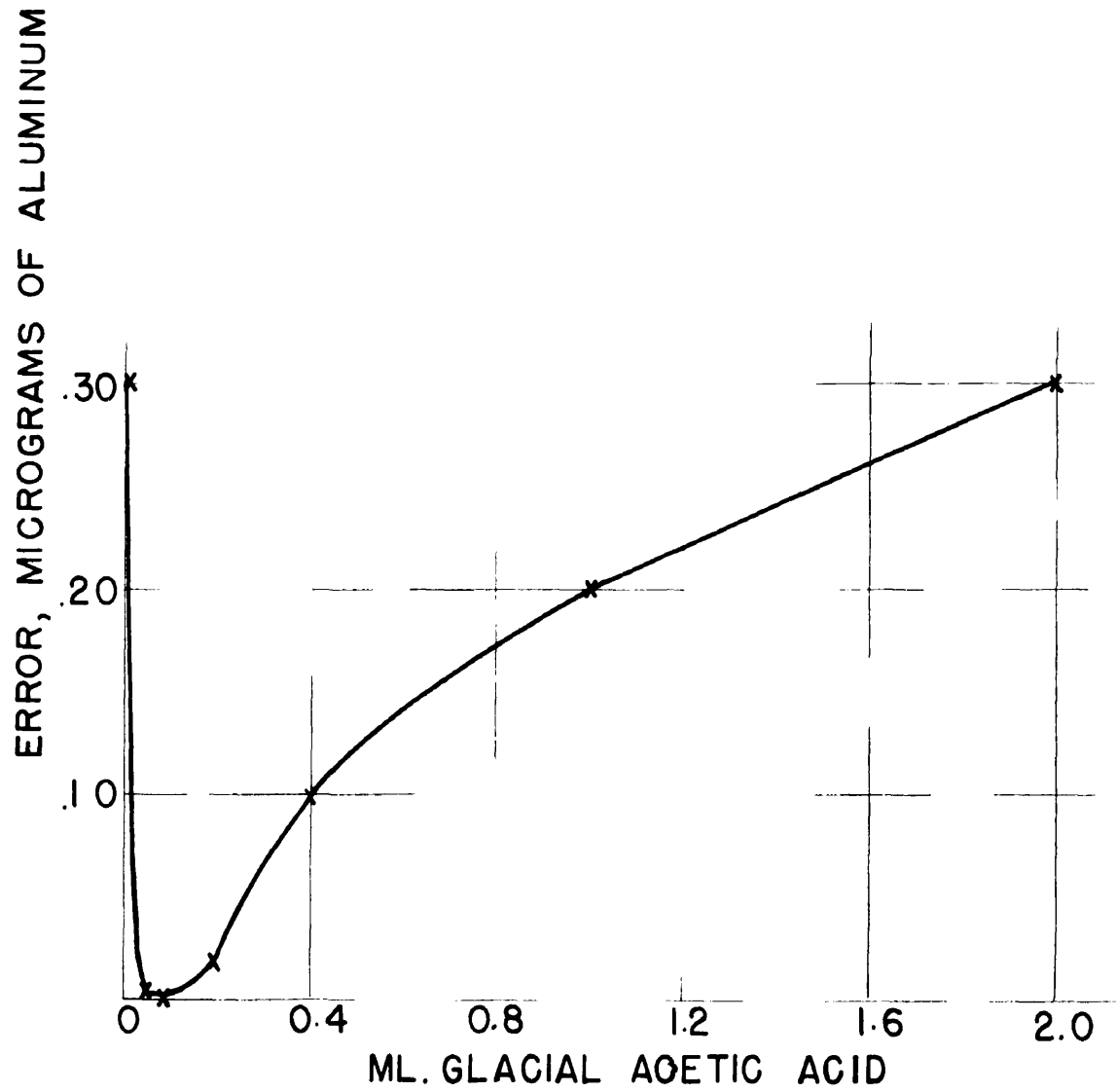
FIG 4

TIME REQUIRED TO ATTAIN FULL INTENSITY OF FLUORESCENCE, 0.100 MG.

FIG 5

511
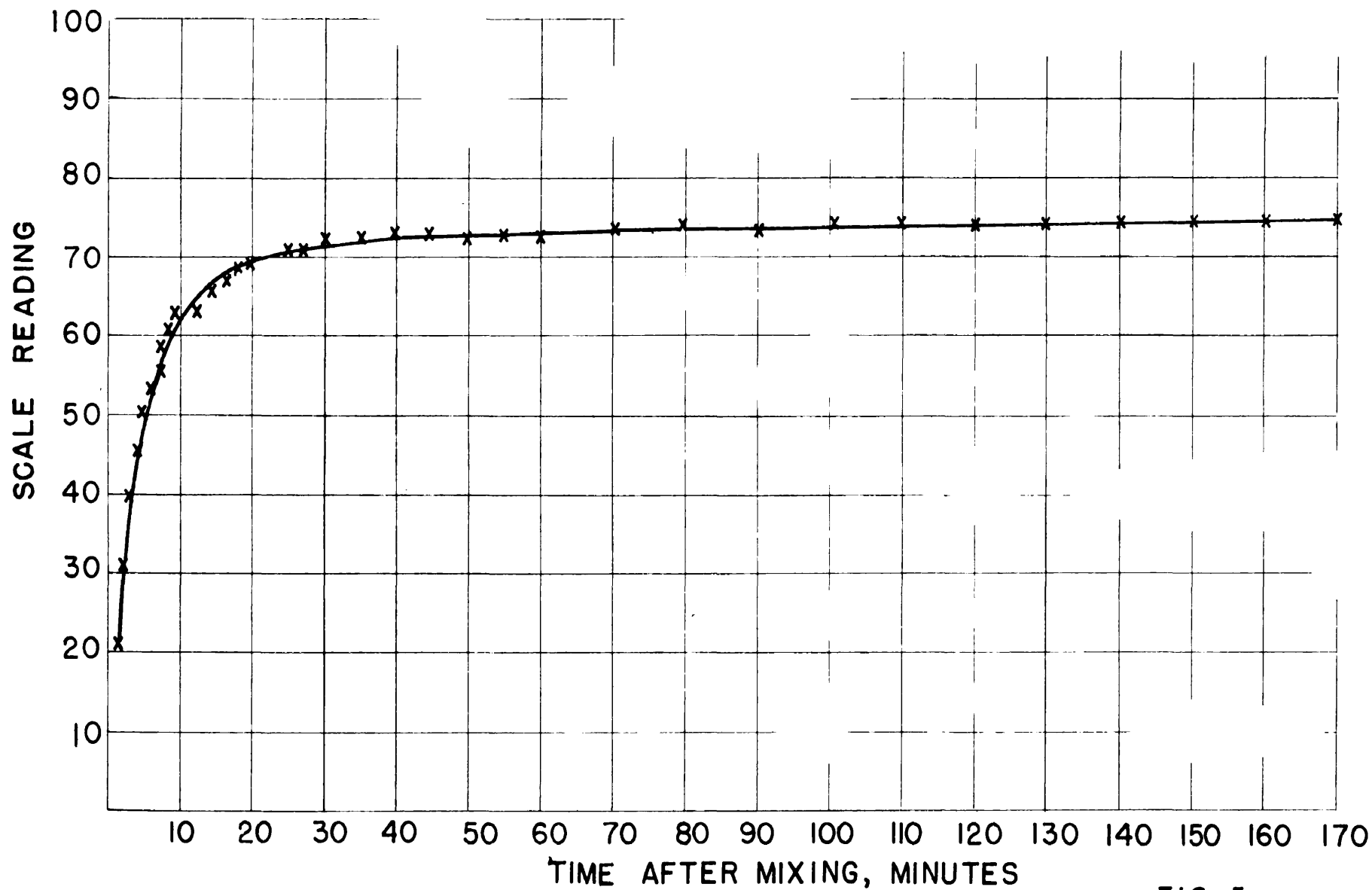
TIME REQUIRED TO ATTAIN FULL INTENSITY OF FLUORESCENCE,
0.010 MG
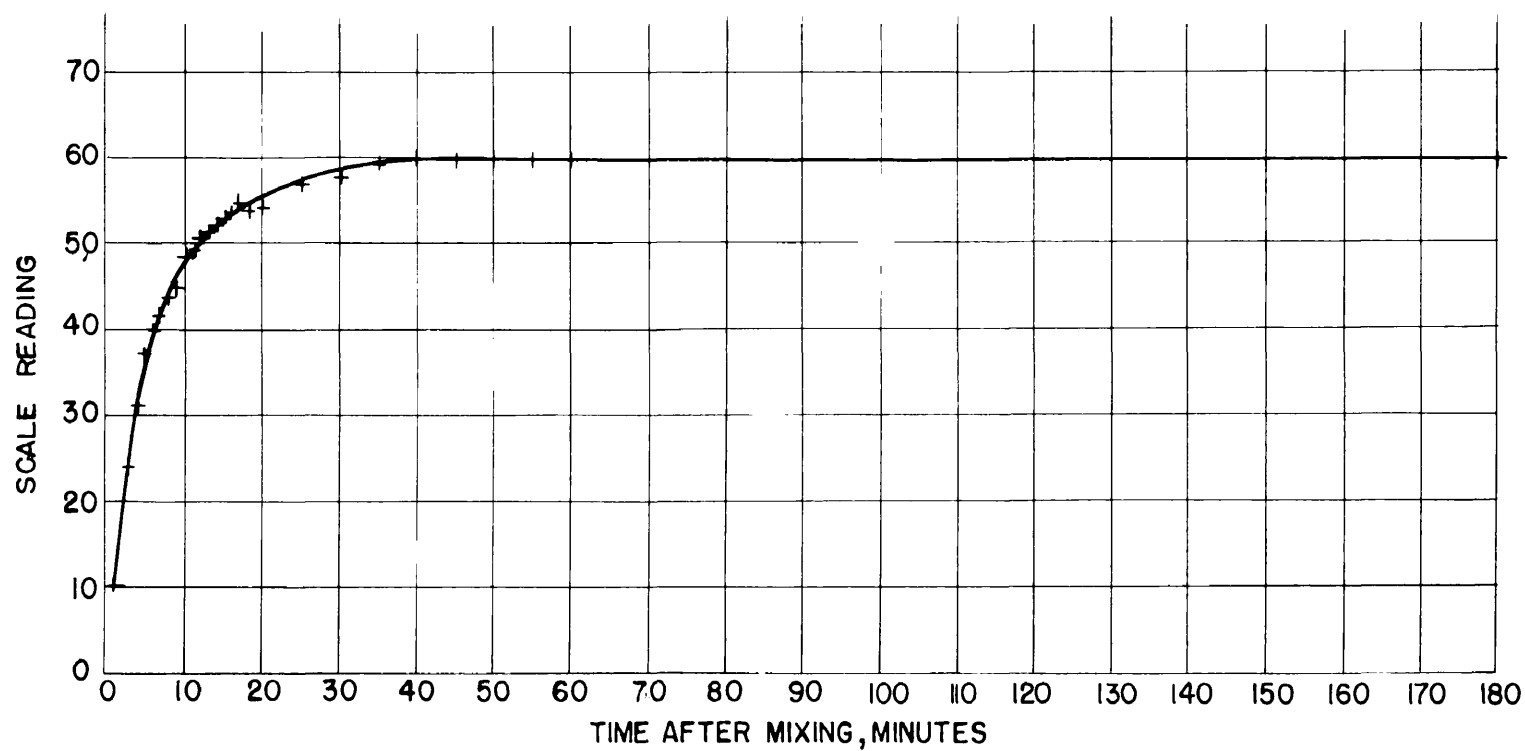
FIG 6

TIME CHANGE OF FLUORESCENCE AFTER HEATING TO 70°C
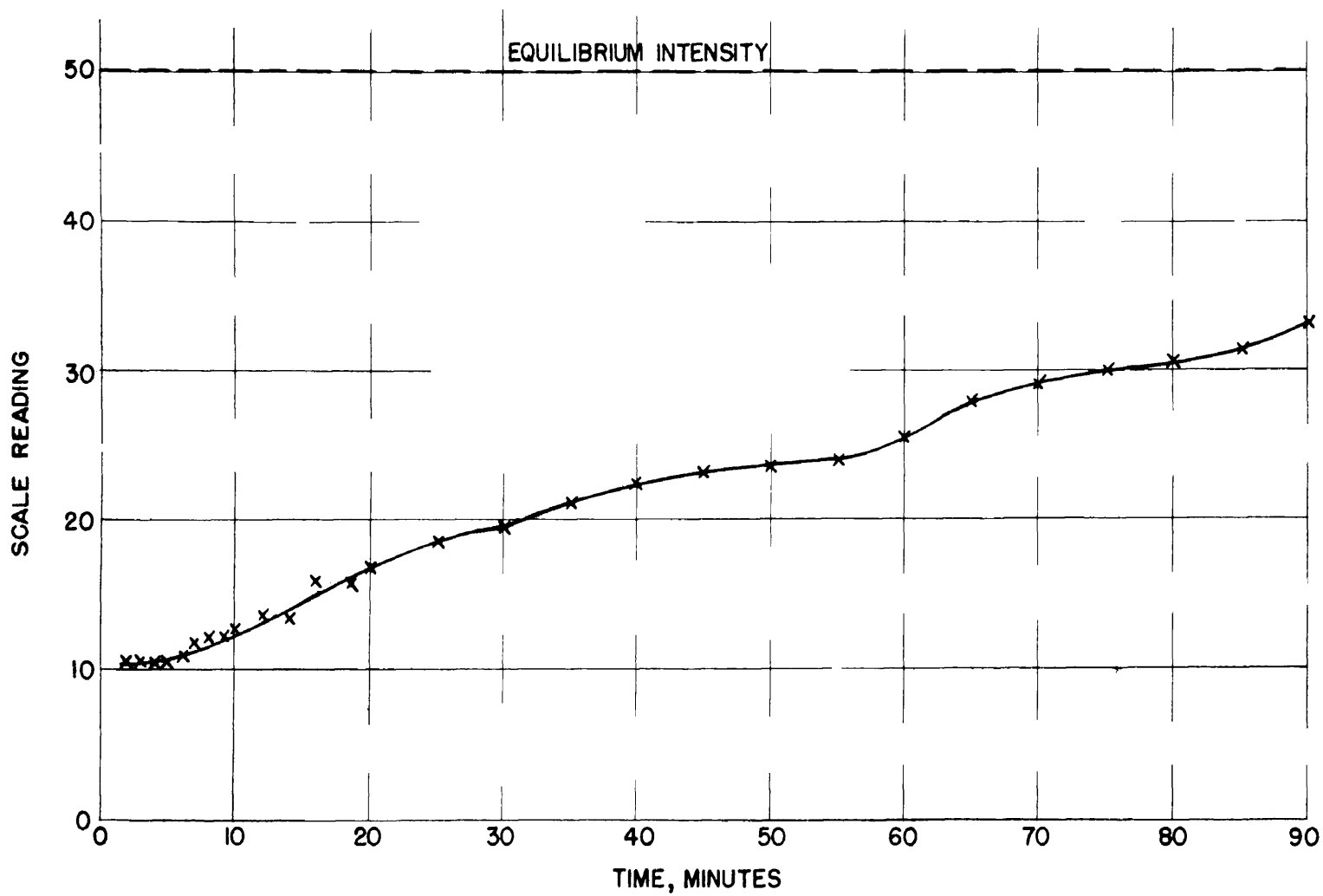
FIG. 7

TIME CHANGE OF FLUORESCENCE AFTER HEATING TO 80 °C.
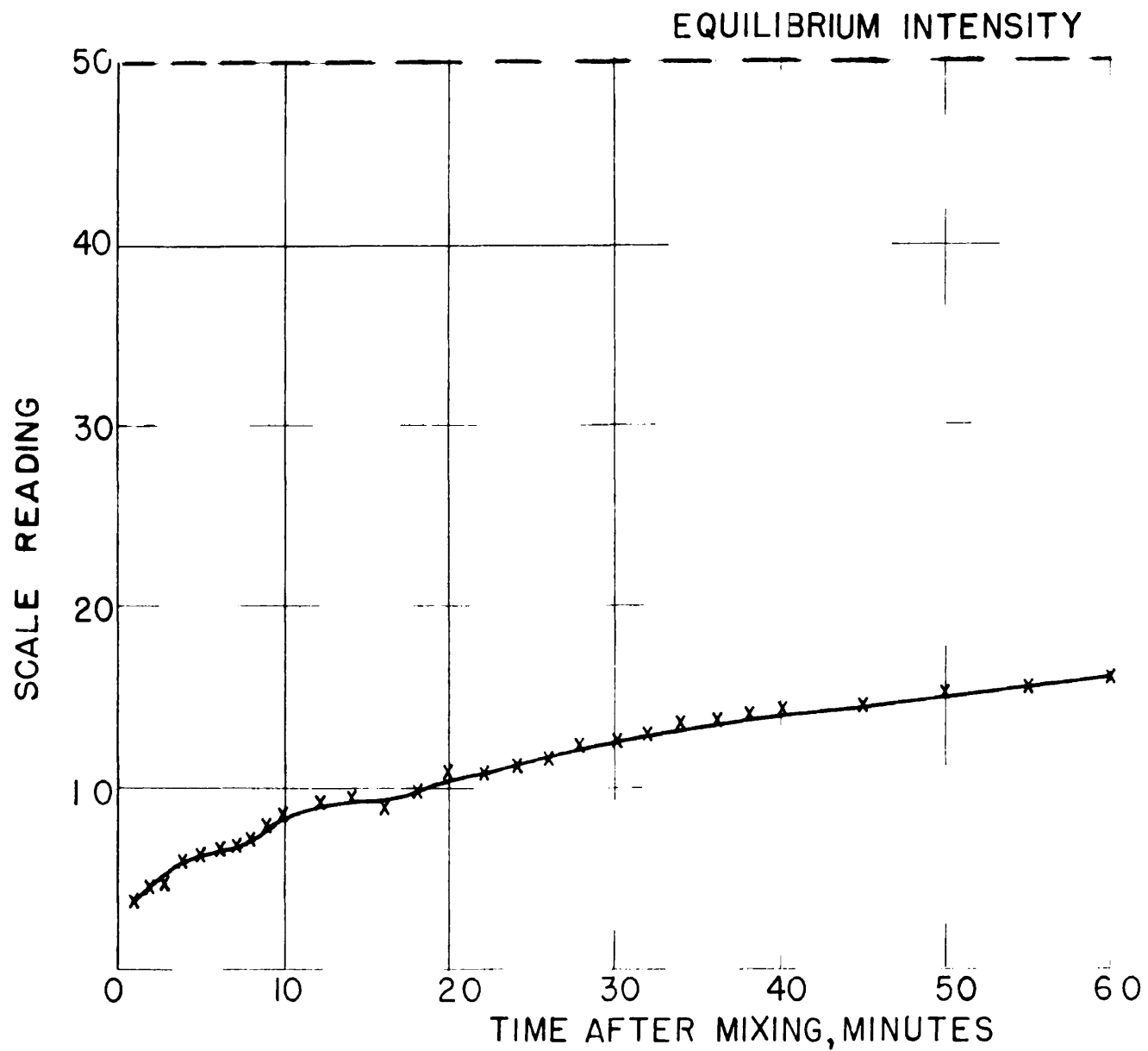
FIG 8

EFFECT OF TEMPERATURE ON FLUORESCENCE
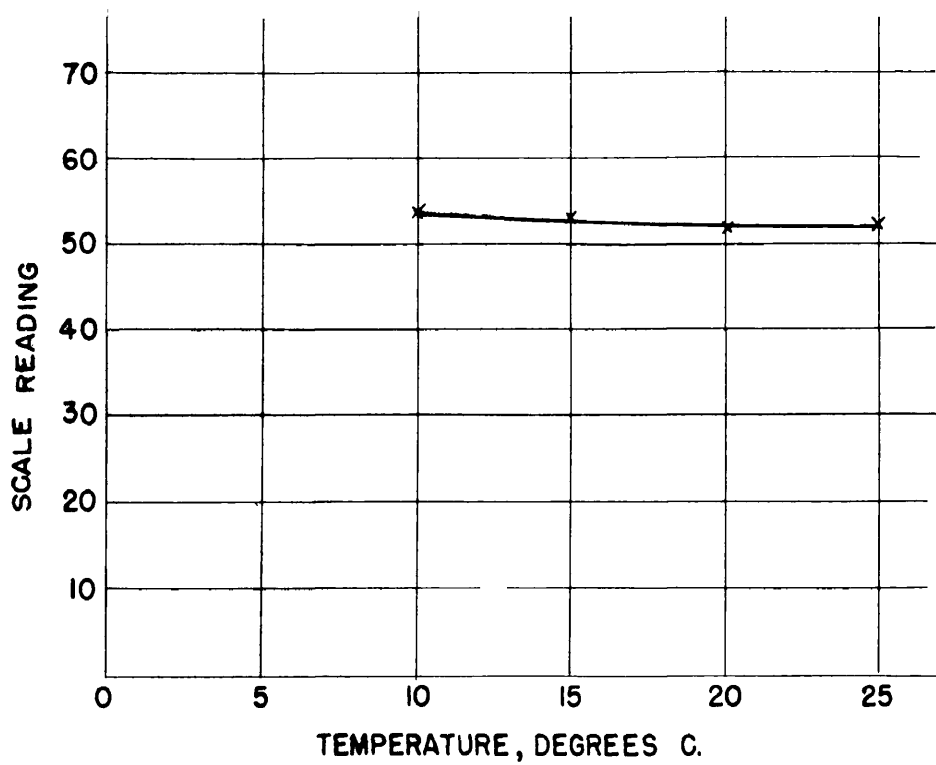
FIG. 9

DEPENDENCE OF BBR FLUORESENCE ON ALUMINUM CONCENTRATION, A
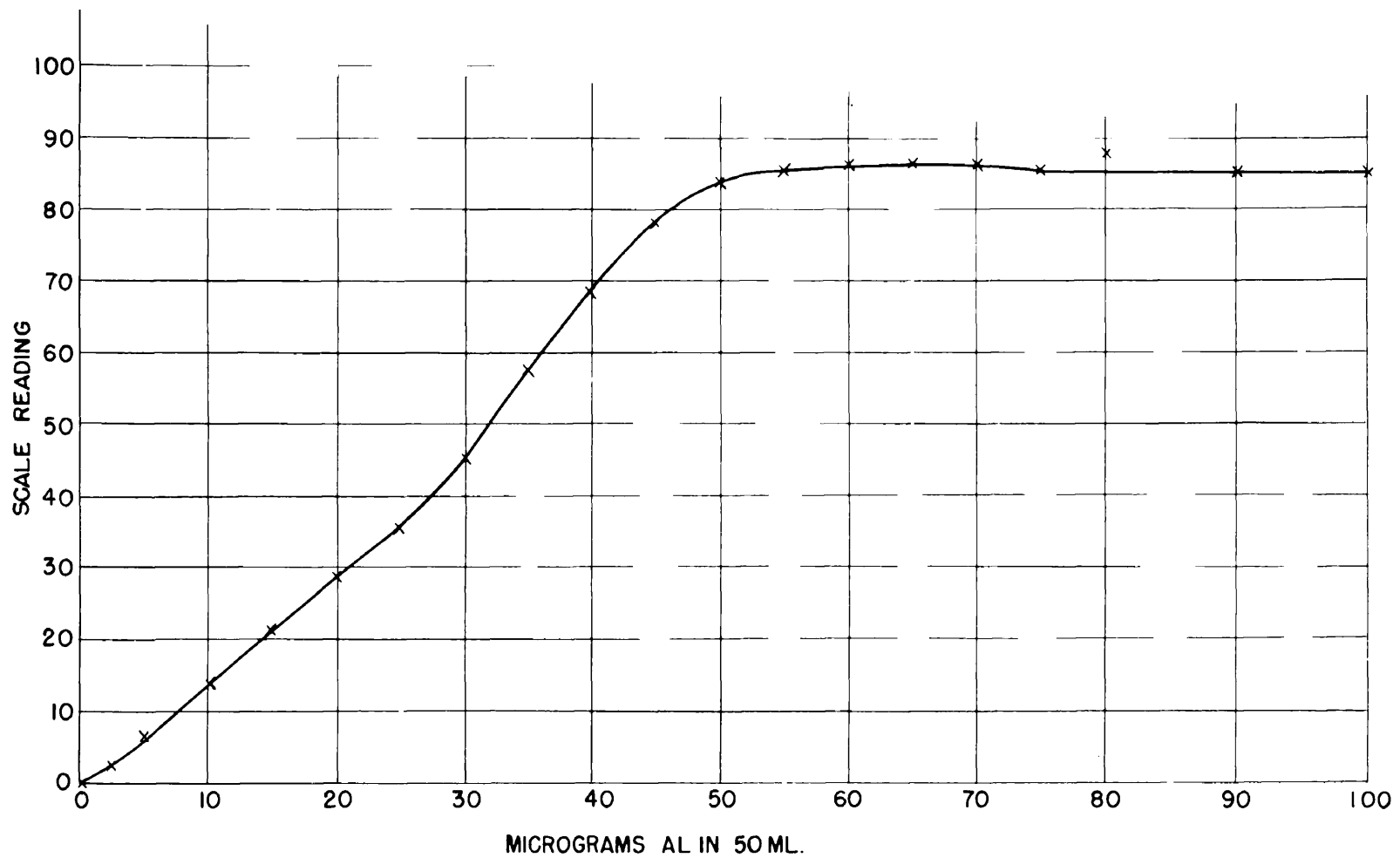
FIG. 10

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, B
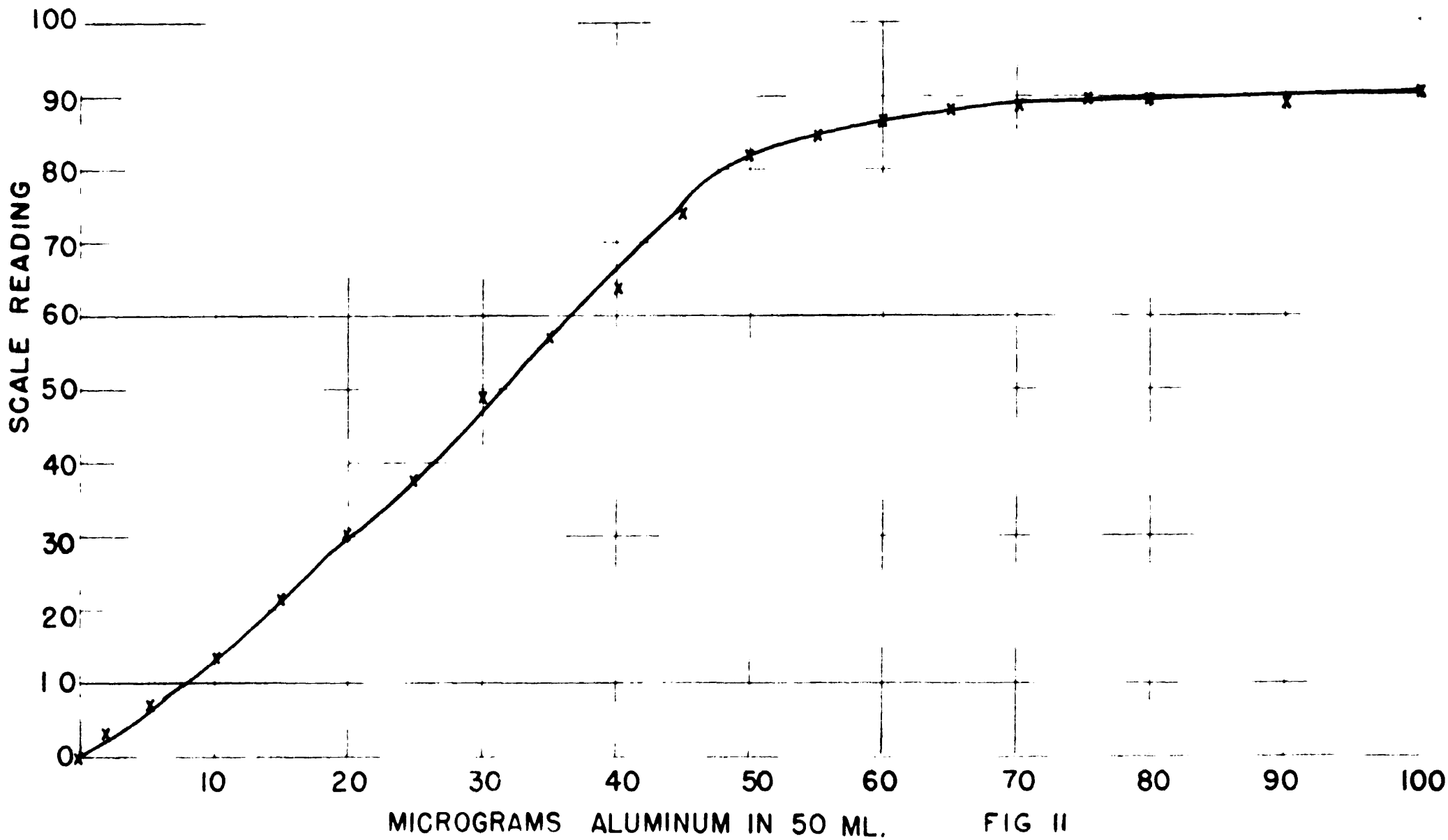
FIG II

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, C

FIG 12
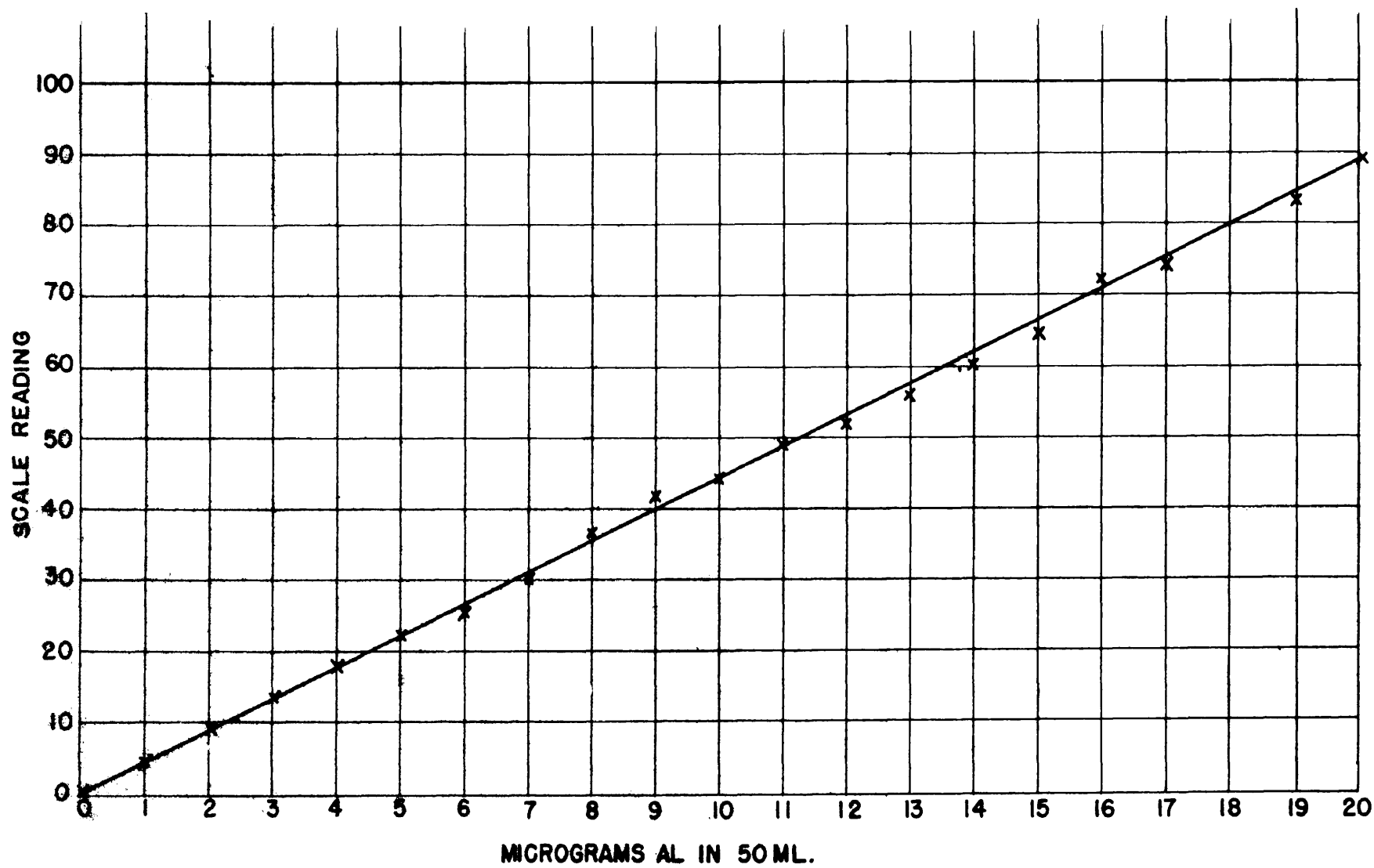
SCALE READING

MICROGRAMS AL. IN 50 ML.

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, D

FIG. 13

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, E

SCALE READING

MICROGRAMS AL. IN 50 ML.

FIG 14

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, F

SCALE READING

MICROGRAMS AL IN 50 ML.
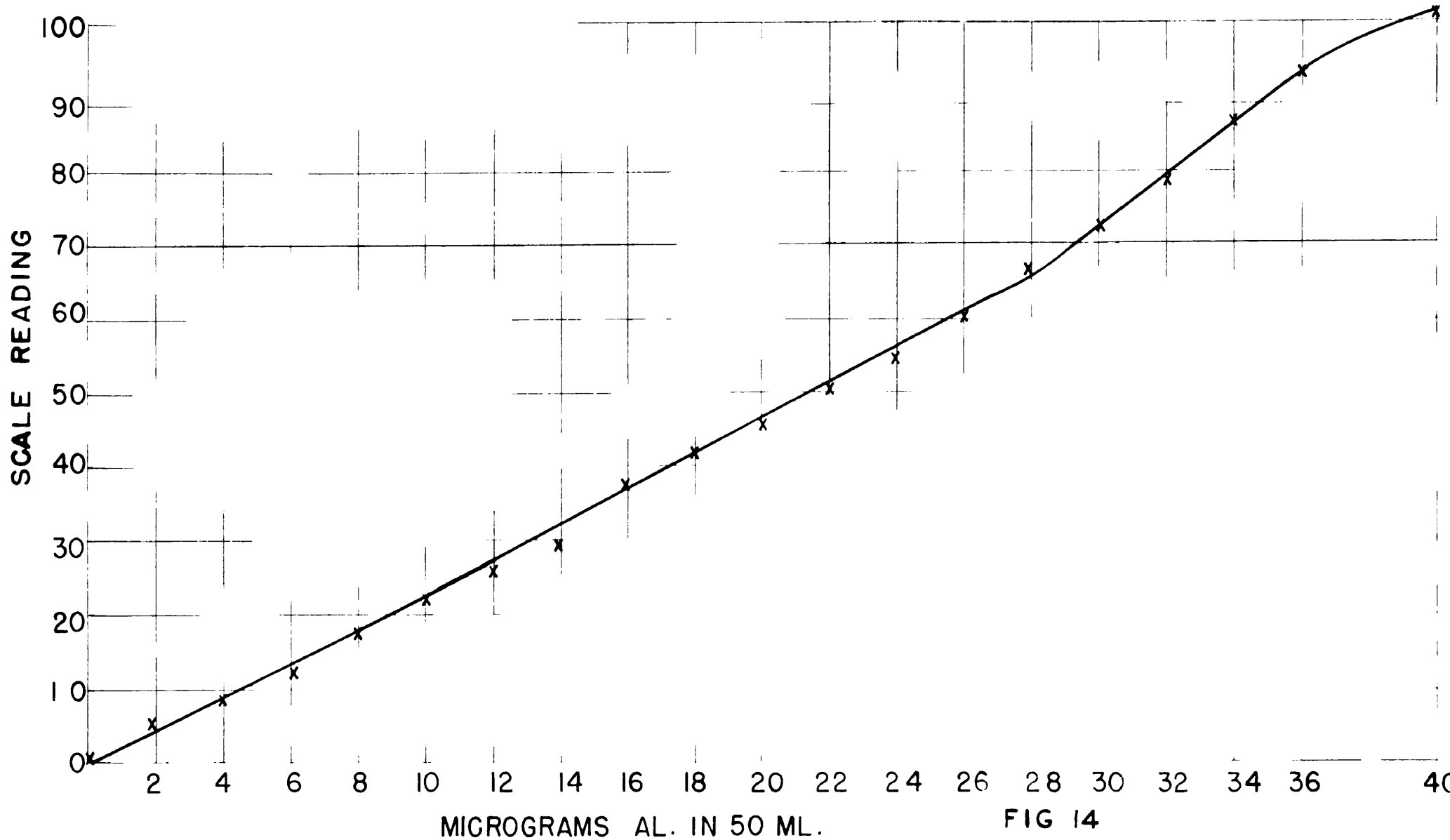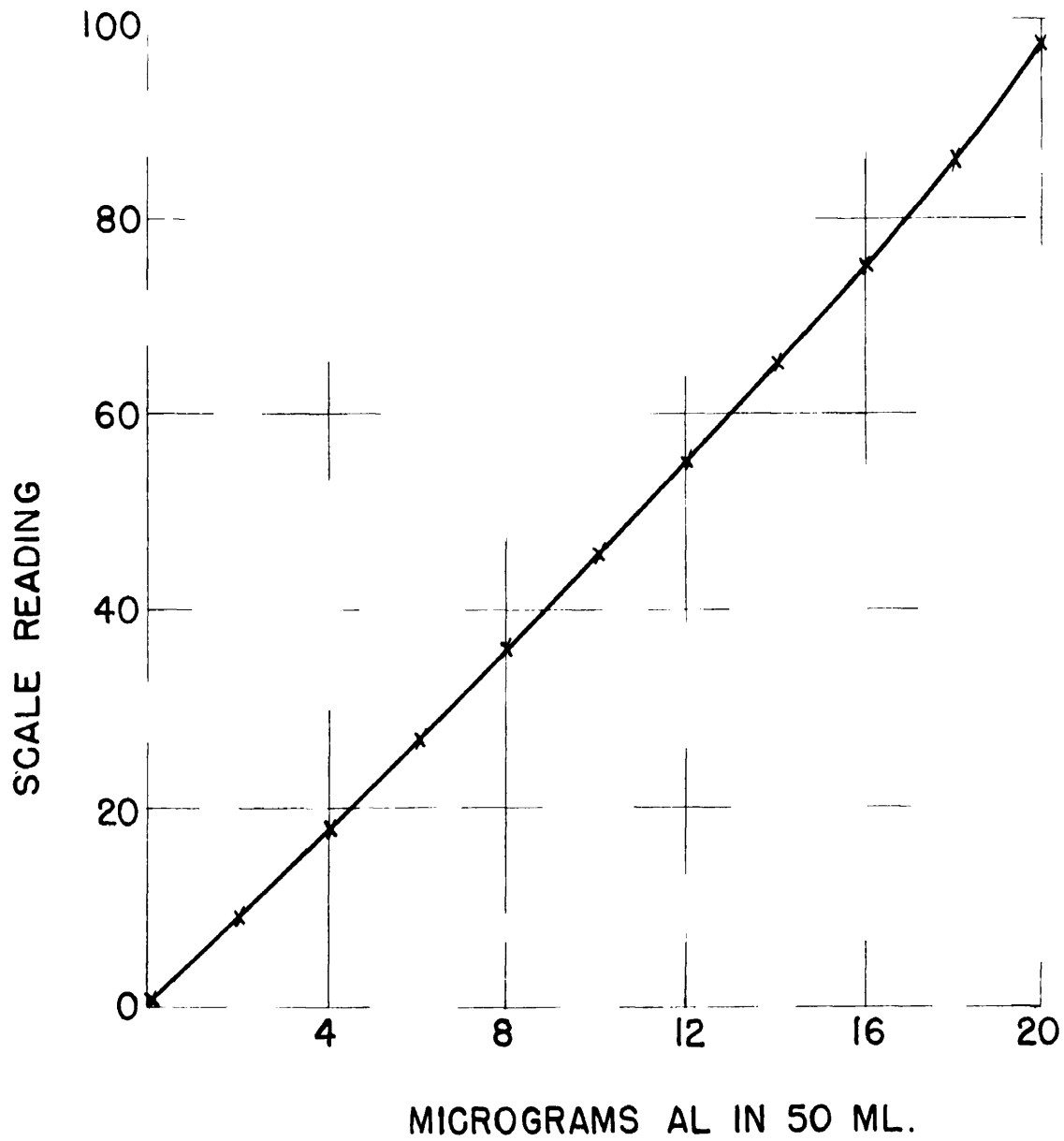
FIG 15

DEPENDENCE OF BBR FLUORESCENCE ON ALUMINUM CONCENTRATION, G
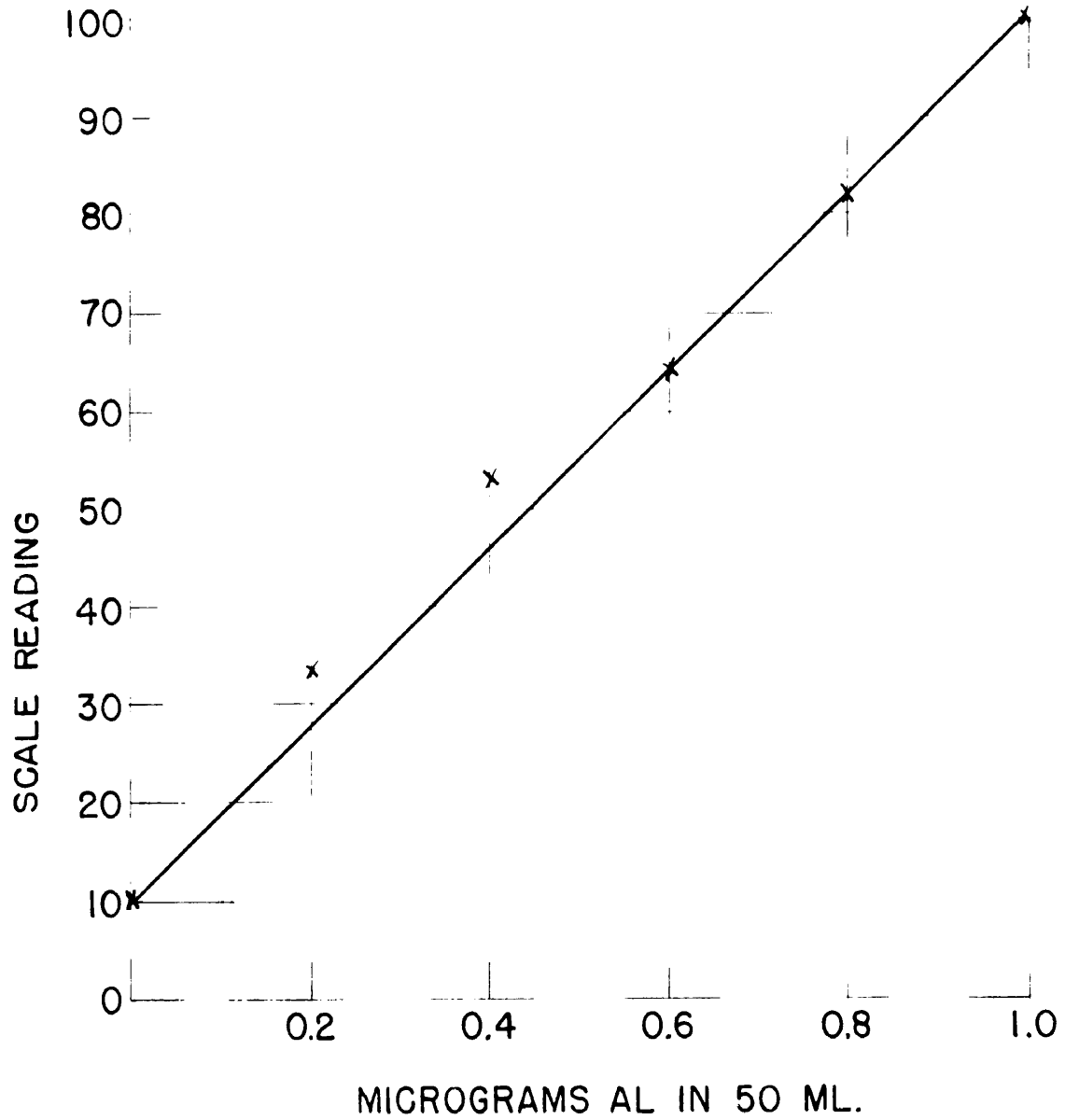
FIG 16

ABSORPTION SPECTRA OF BUFFERED BBR SOLUTIONS
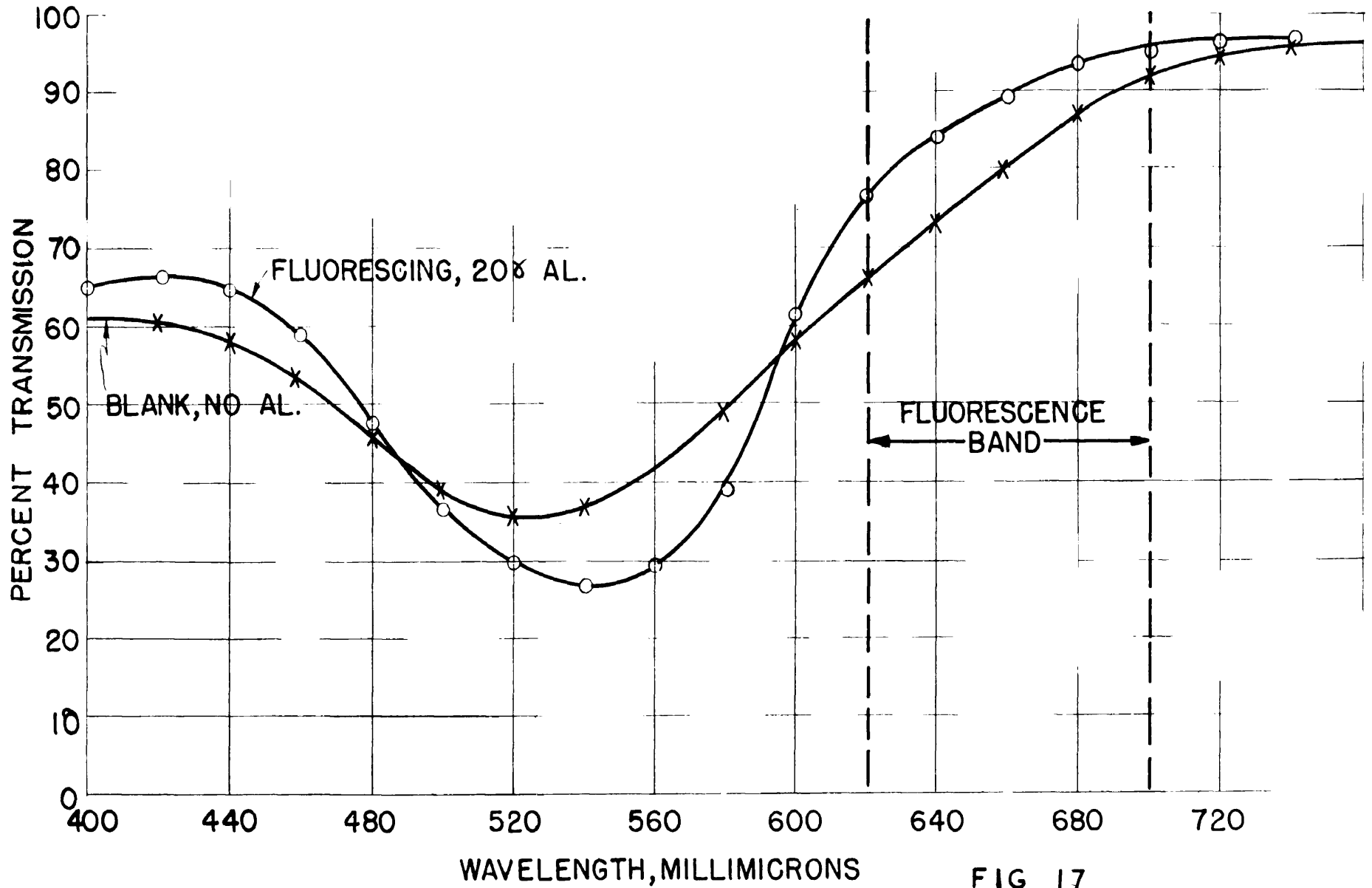
FIG 17

FIG. 18

NON-INTERFERENCE BY ZIRCONIUM IN SOLUTIONS CONTAINING 0.010 MG OF ALUMINUM
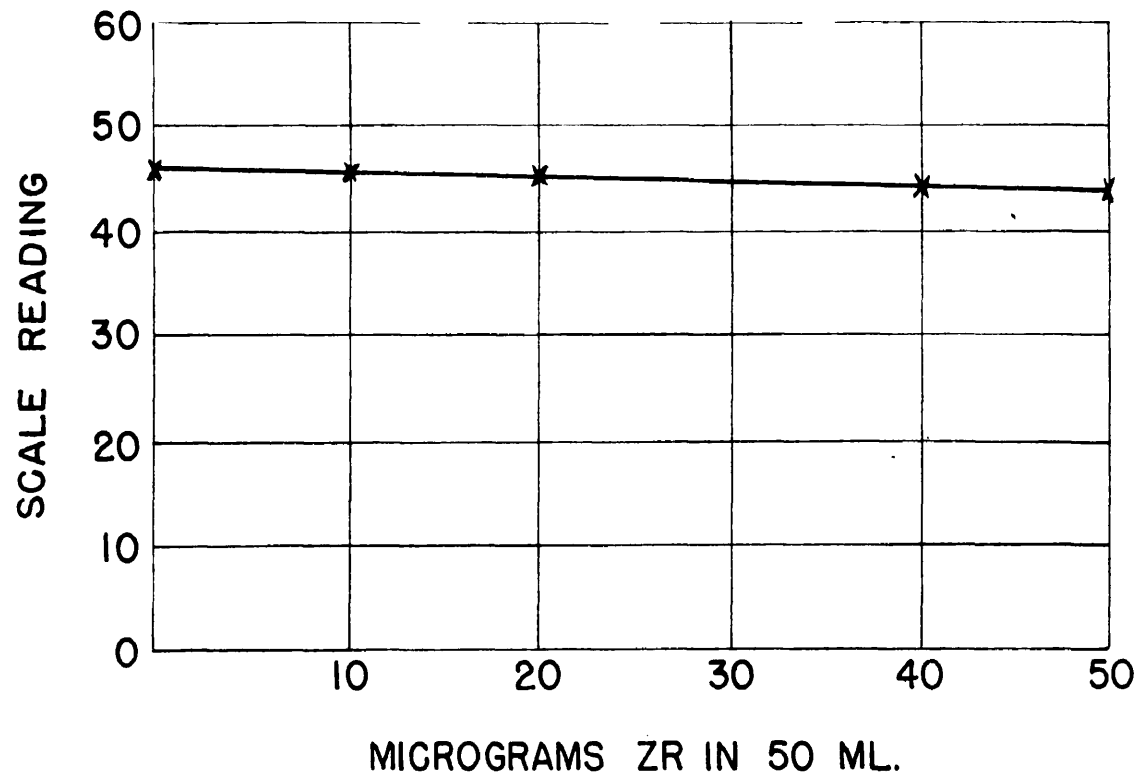
FIG 19

INTERFERENCE BY TITANIUM AND VANADIUM IN SOLUTIONS
CONTAINING 0.010 MG OF ALUMINUM
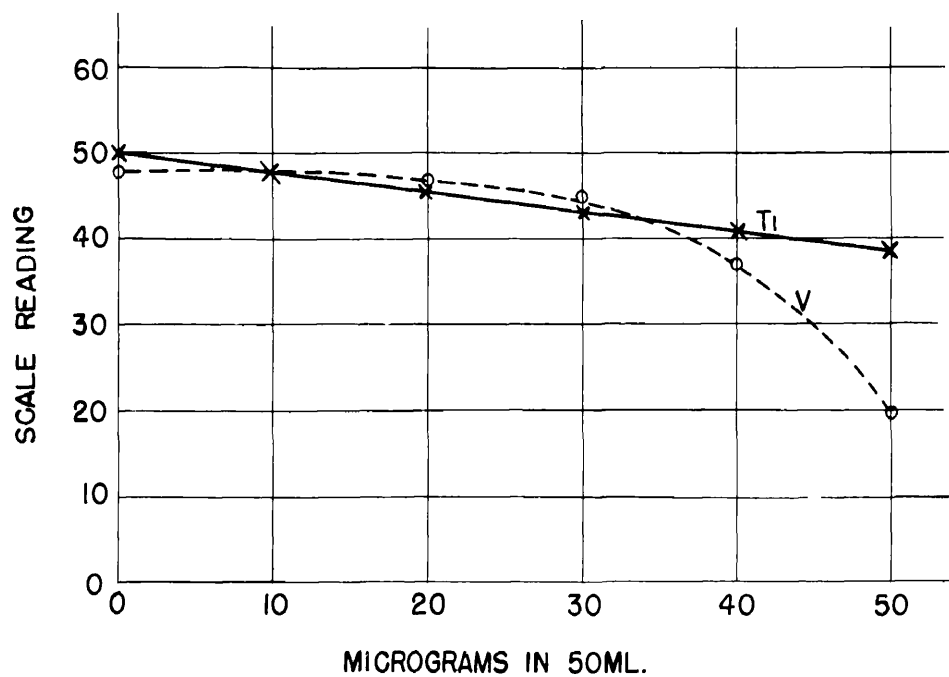
FIG. 20

EFFECT OF VSW CONCENTRATION ON FLUORESCENCE INTENSITY
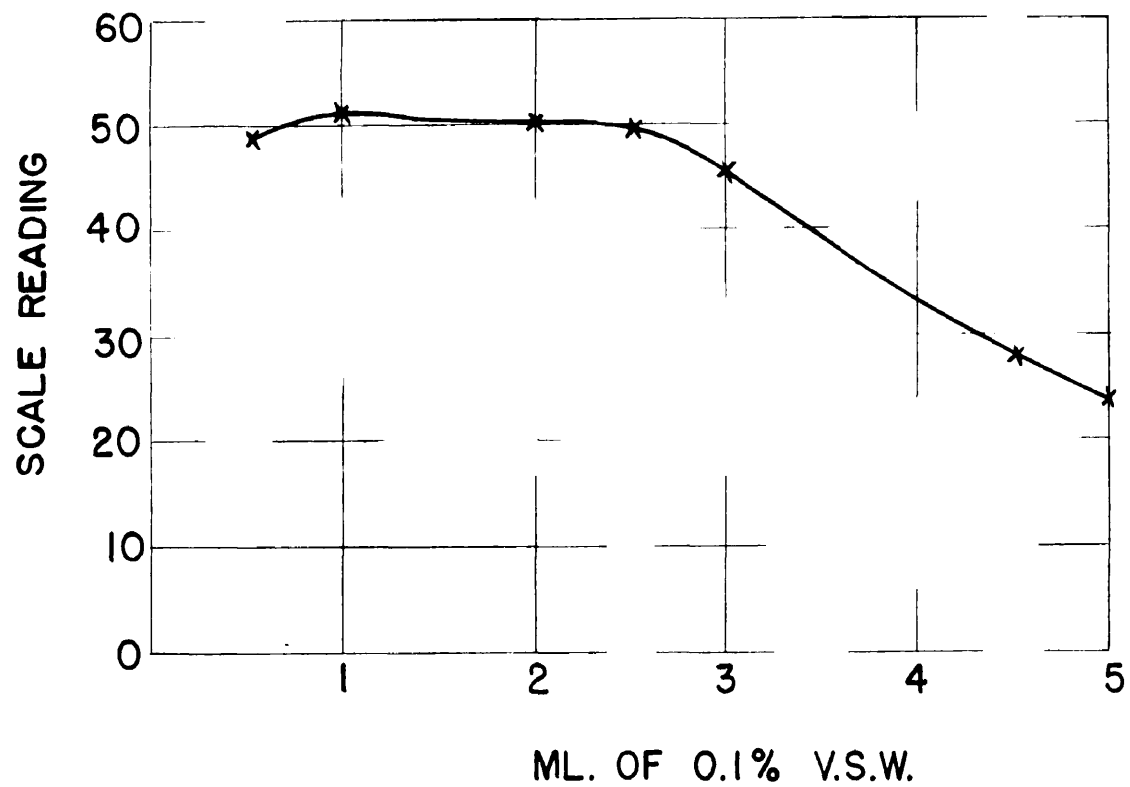
FIG 21

EFFECT OF pH ON VSW. FLUORESCENCE INTENSITY
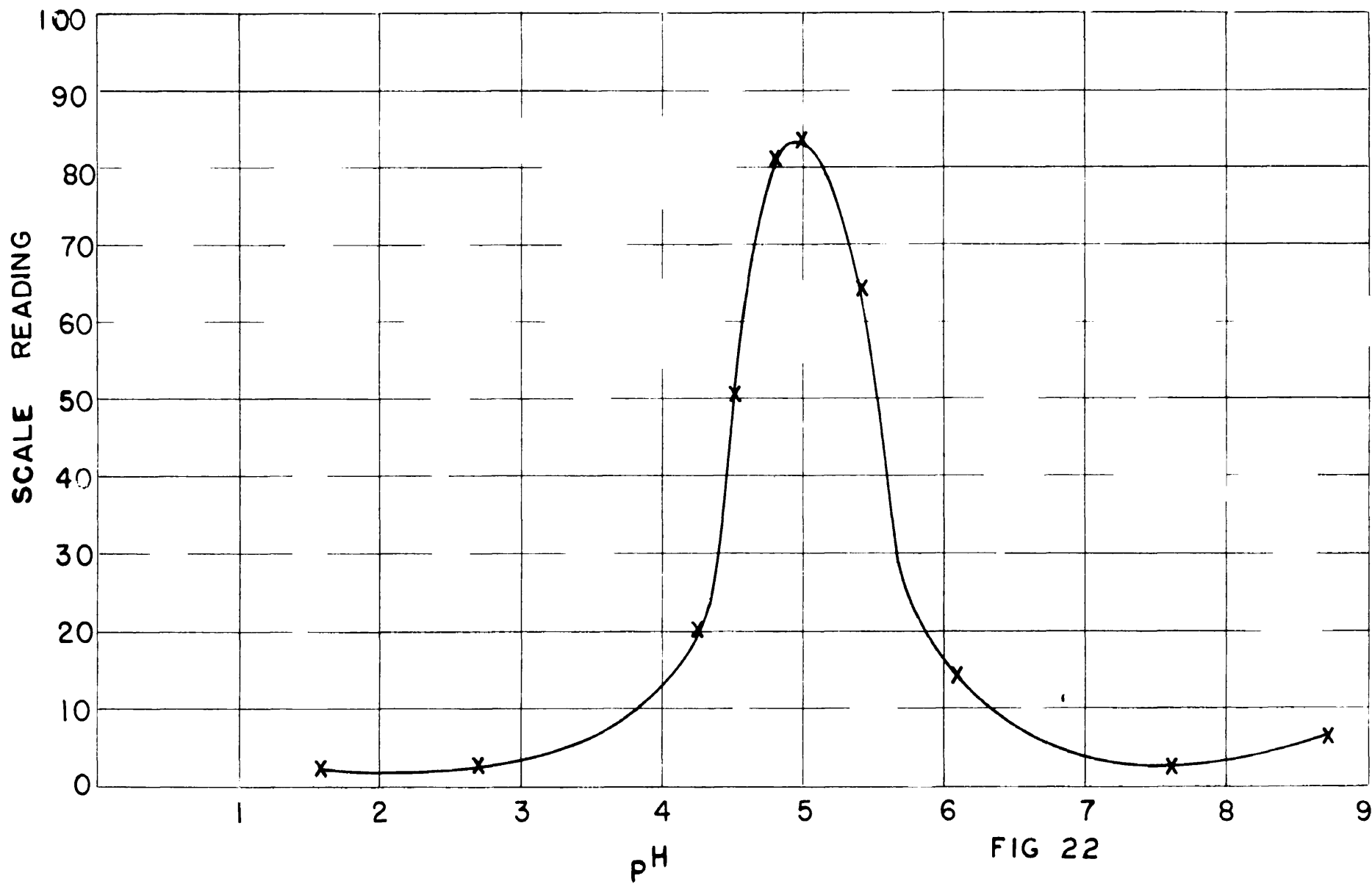
FIG 22

DEPENDENCE OF VSW FLUORESCENCE ON ALUMINUM CONCENTRATION
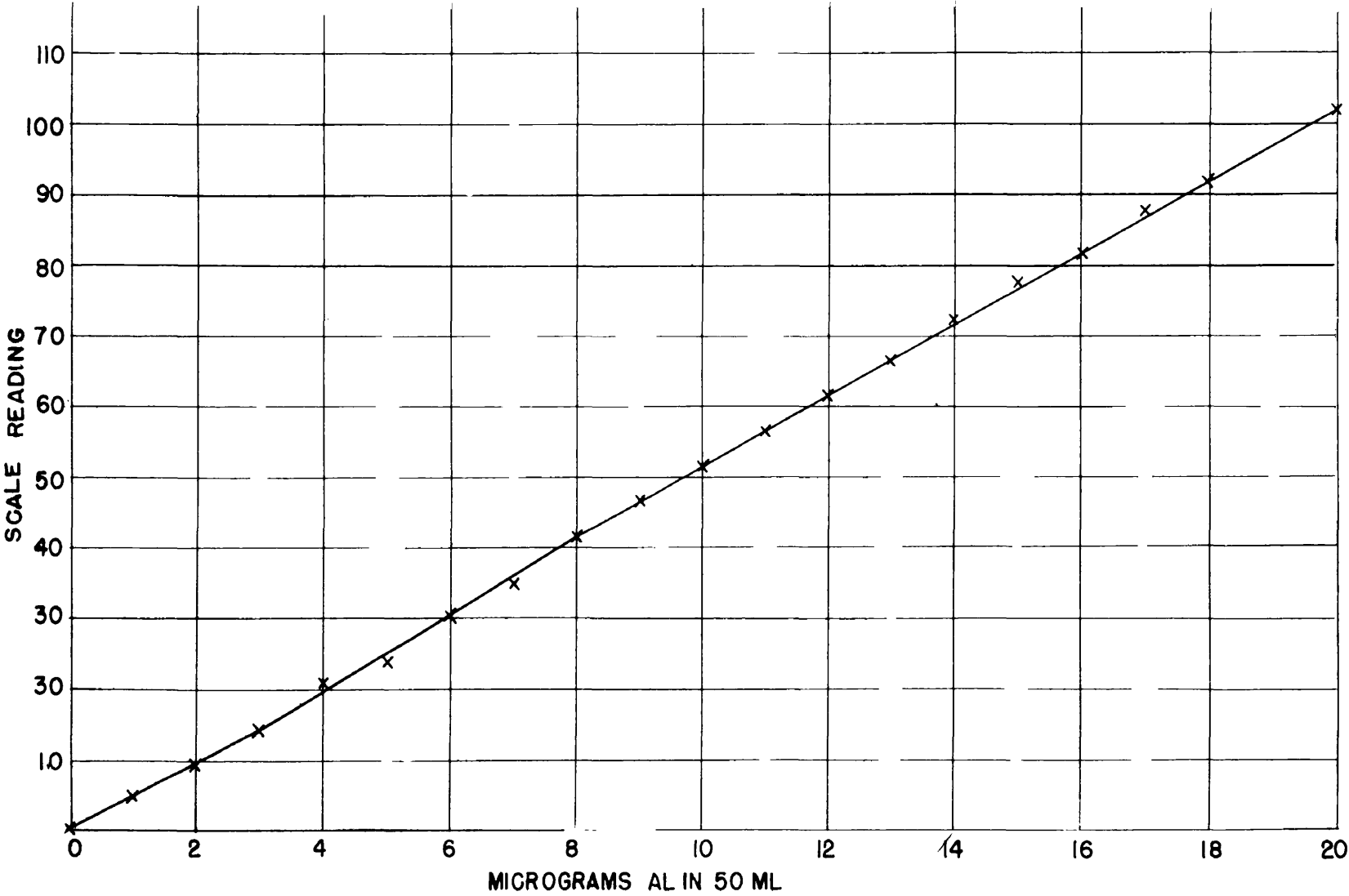
FIG. 23

DEPENDENCE OF VSW FLUORESCENCE ON ALUMINUM CONCENTRATION
(HIGH RANGE)

SCALE READING

MICROGRAMS AL IN 50 ML.
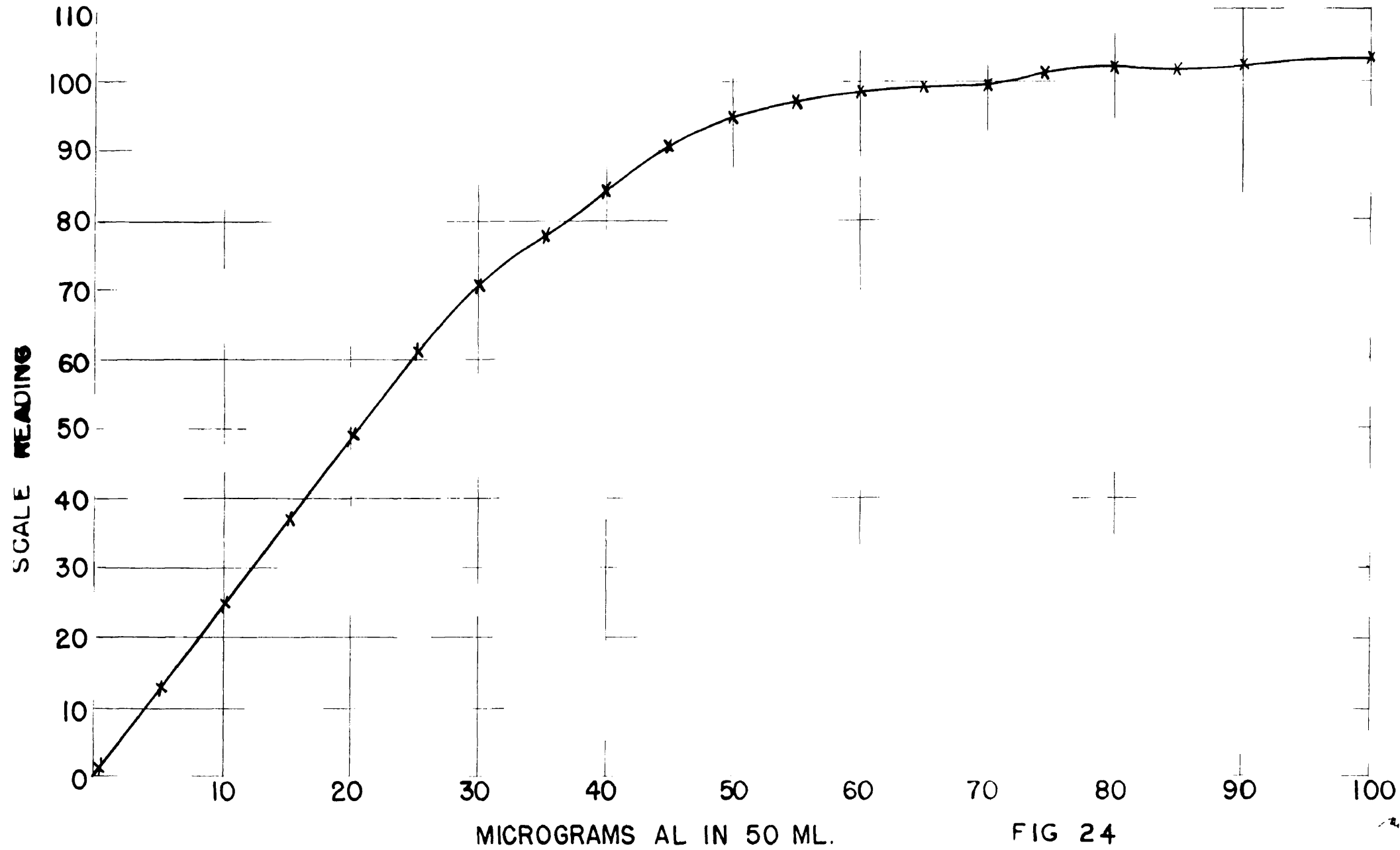
FIG 24

DEPENDENCE OF VSW FLUORESCENCE ON ALUMINUM CONCENTRATION
(LOWEST RANGE)
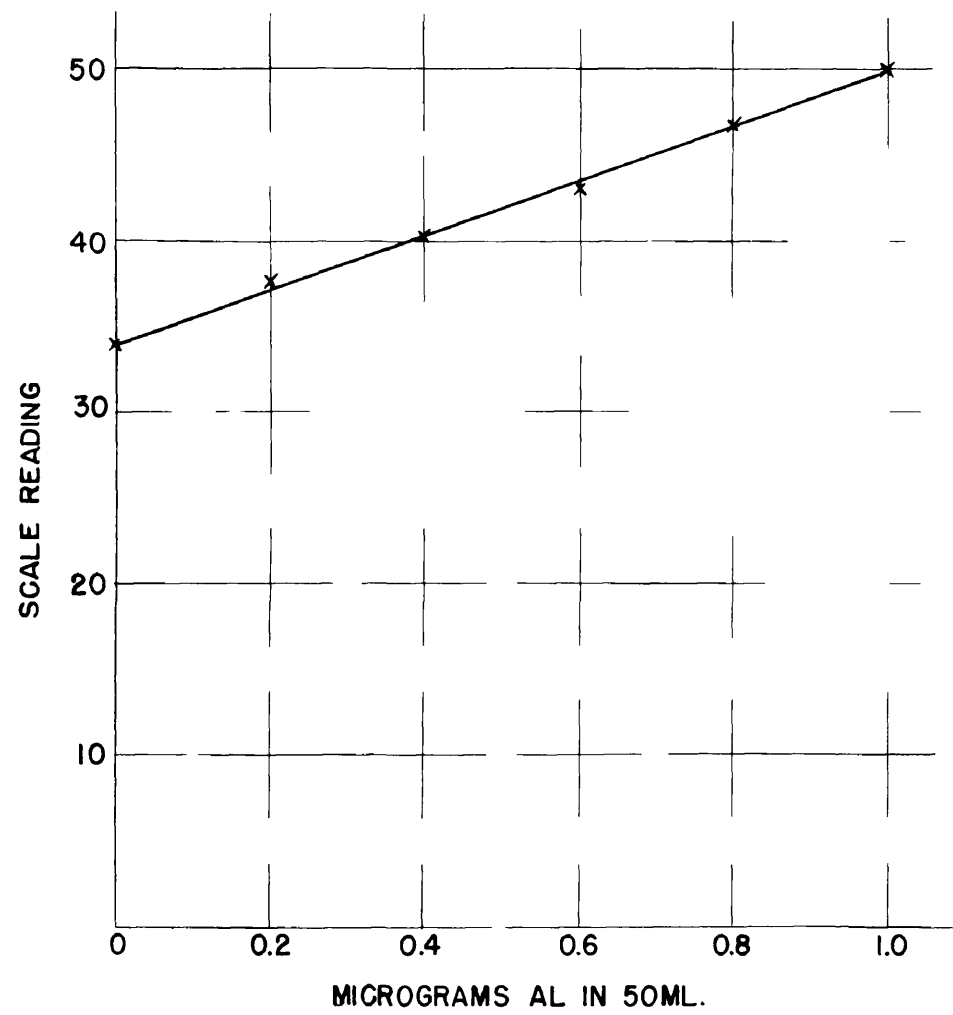
FIG. 2 5

TRANSMISSION OF PRIMARY AND SECONDARY FILTERS
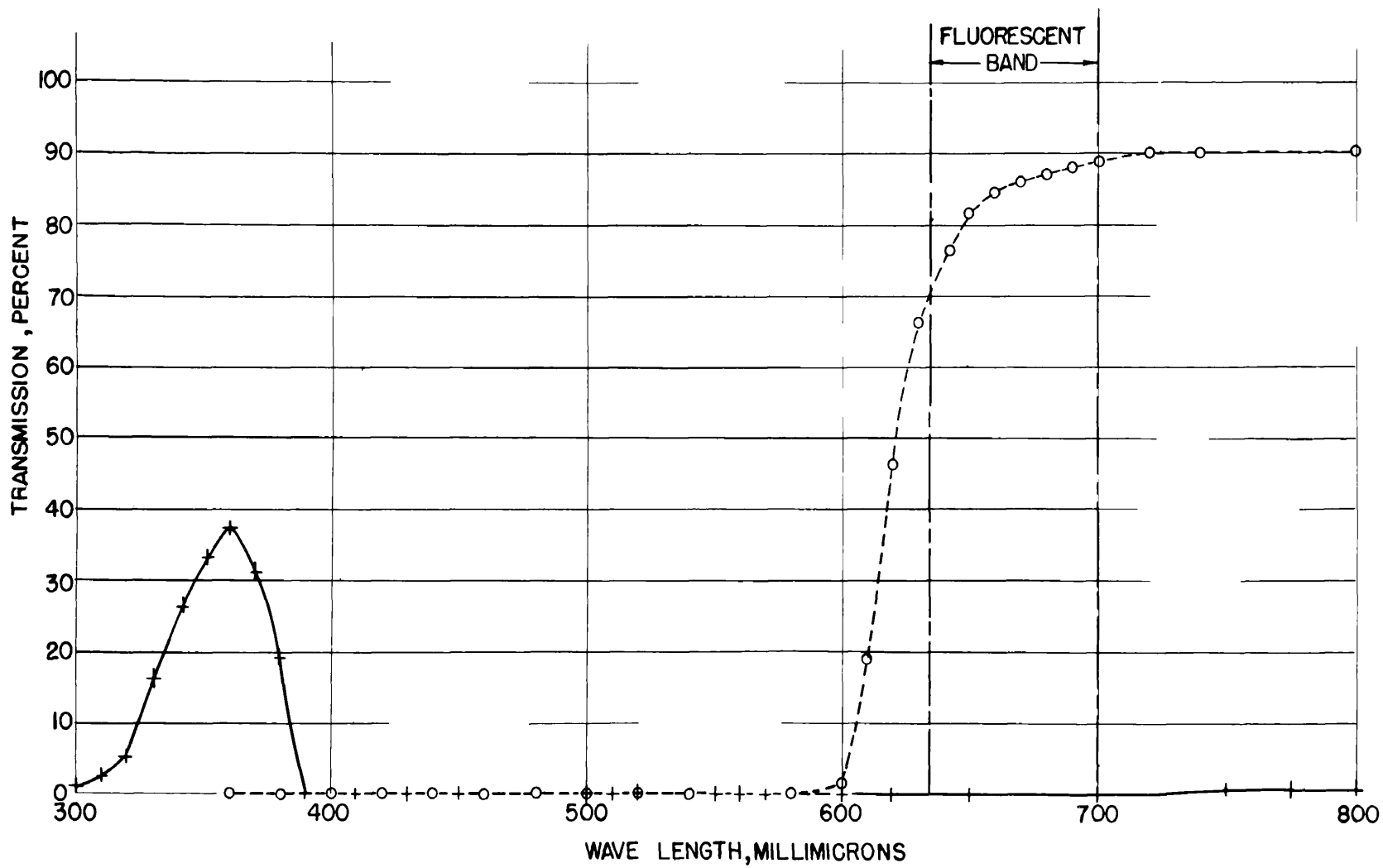
FIG. 26
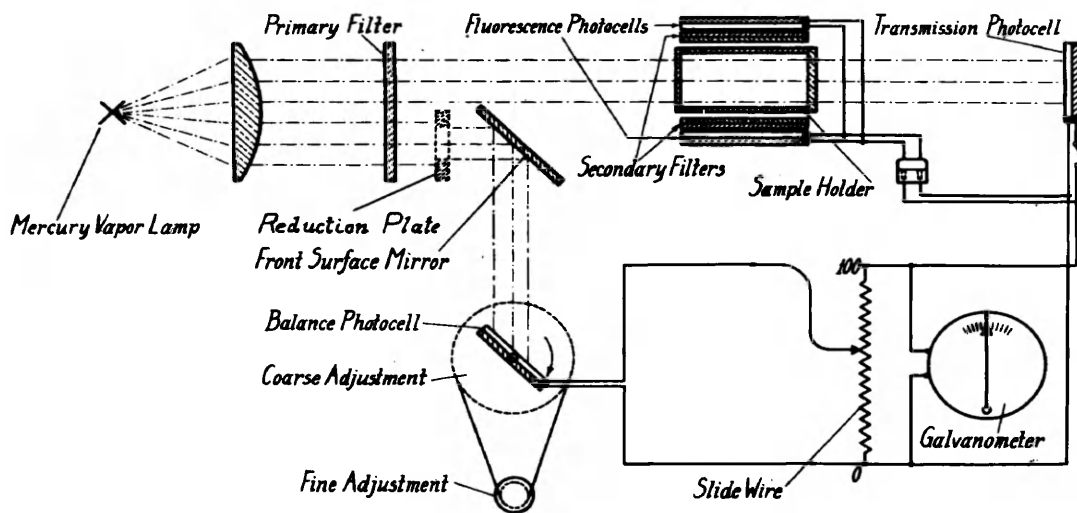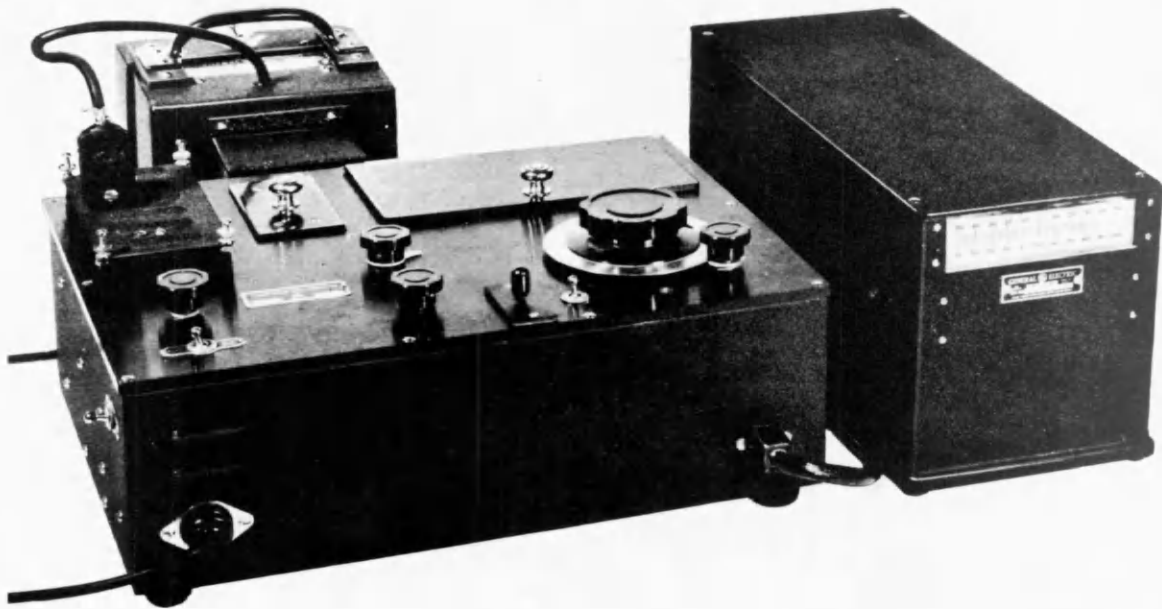
LUMETRON FLUORESCENCE METER - MOD. 402 EF

FIG. 27
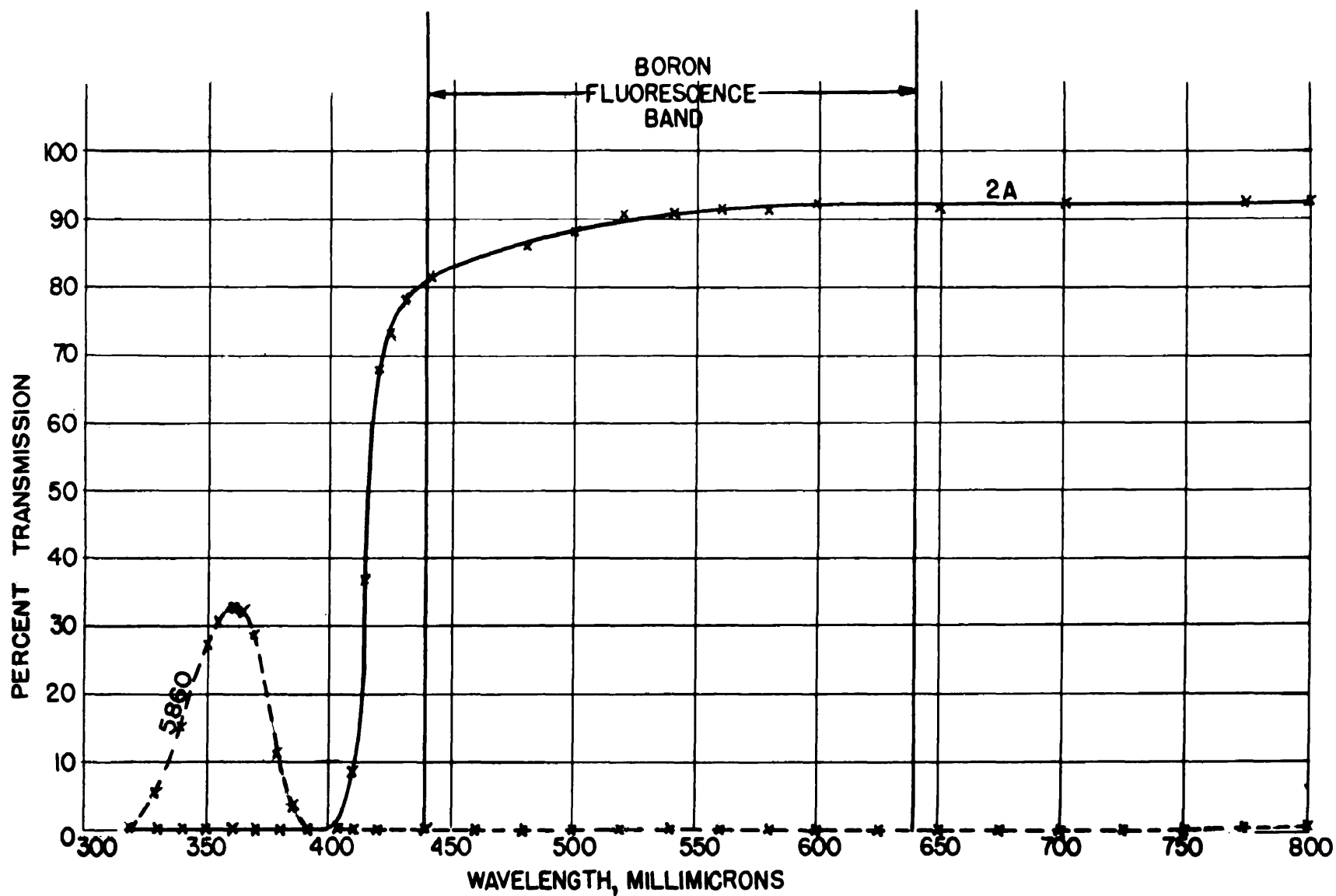
FIG. 30

CHANGE OF FLUORESCENCE WITH TIME. 0.010 MG OF BORON IN ETHANOL
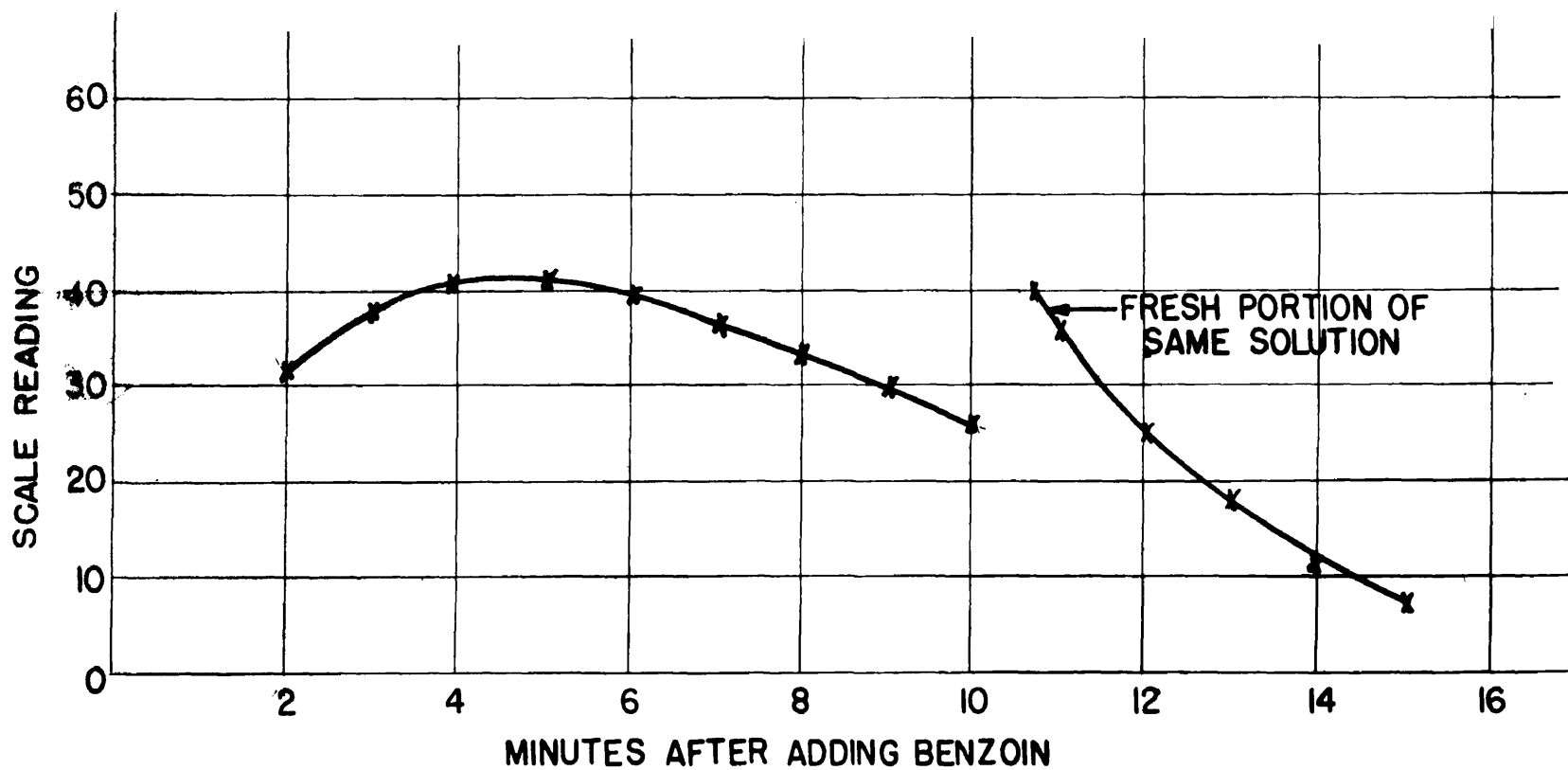
FIG. 31
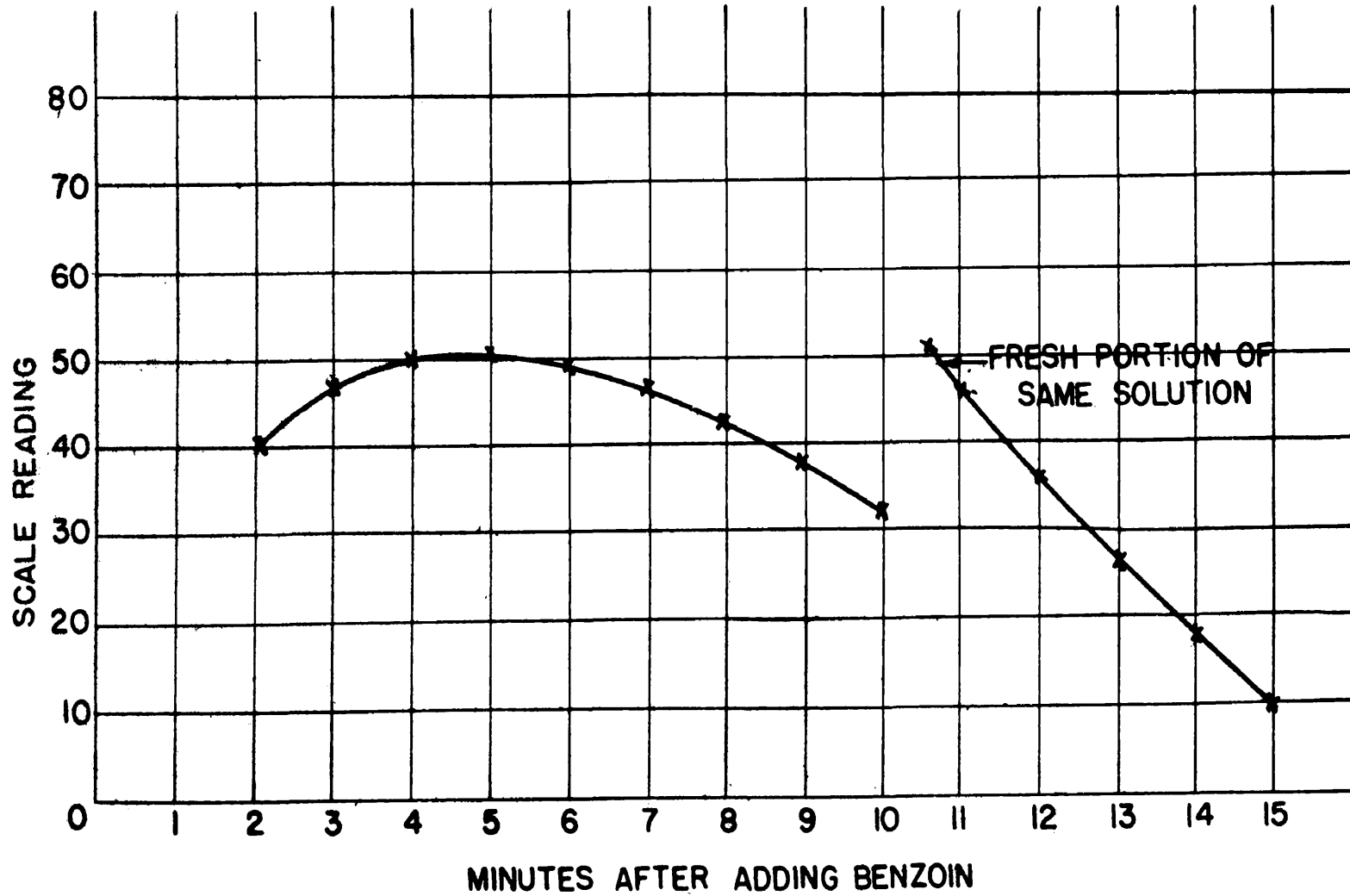
FIG. 32

CHANGE OF FLUORESCENCE WITH TIME, USING RESORCINOL AS ANTI-OXIDANT

FRESH PORTION OF SAME SOLUTION

SCALE READING

MINUTES AFTER ADDING BENZOIN
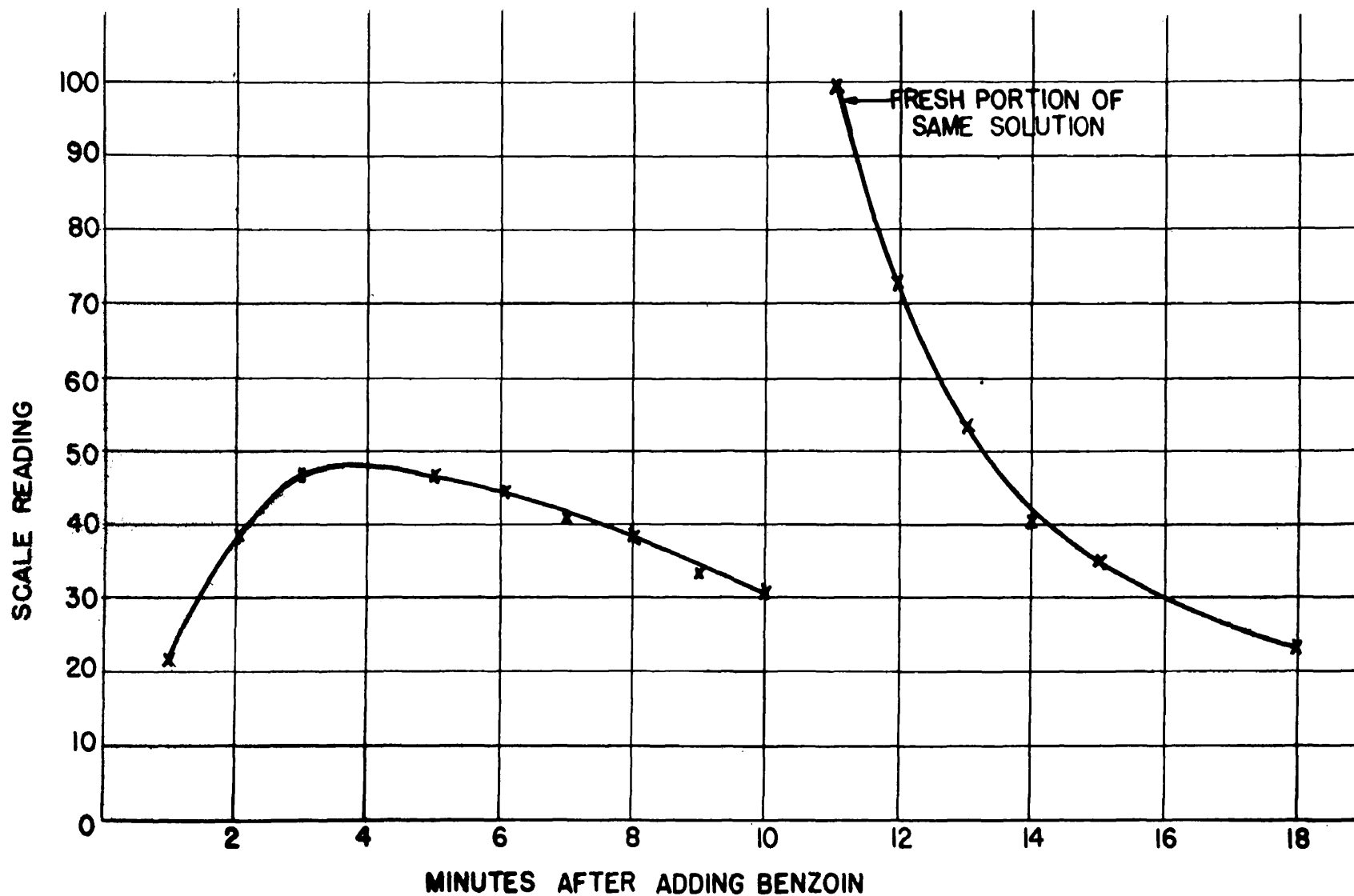
FIG. 33

CHANGE OF FLUORESCENCE WITH TIME. 0.010 MG OF BORON IN METHANOL
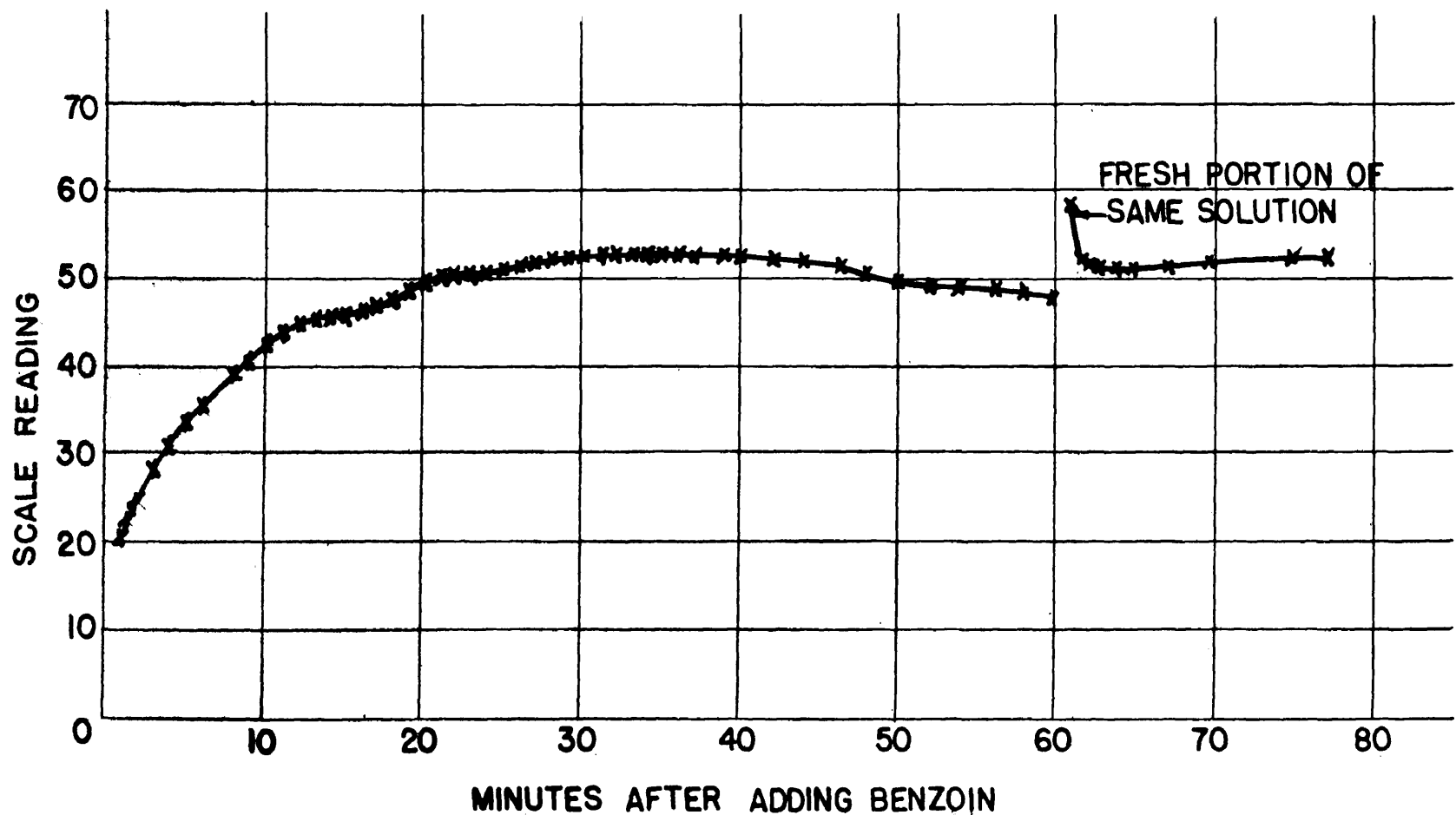
FIG. 34

CHANGE OF FLUORESCENCE WITH TIME. 0.100 MG OF BORON IN METHANOL
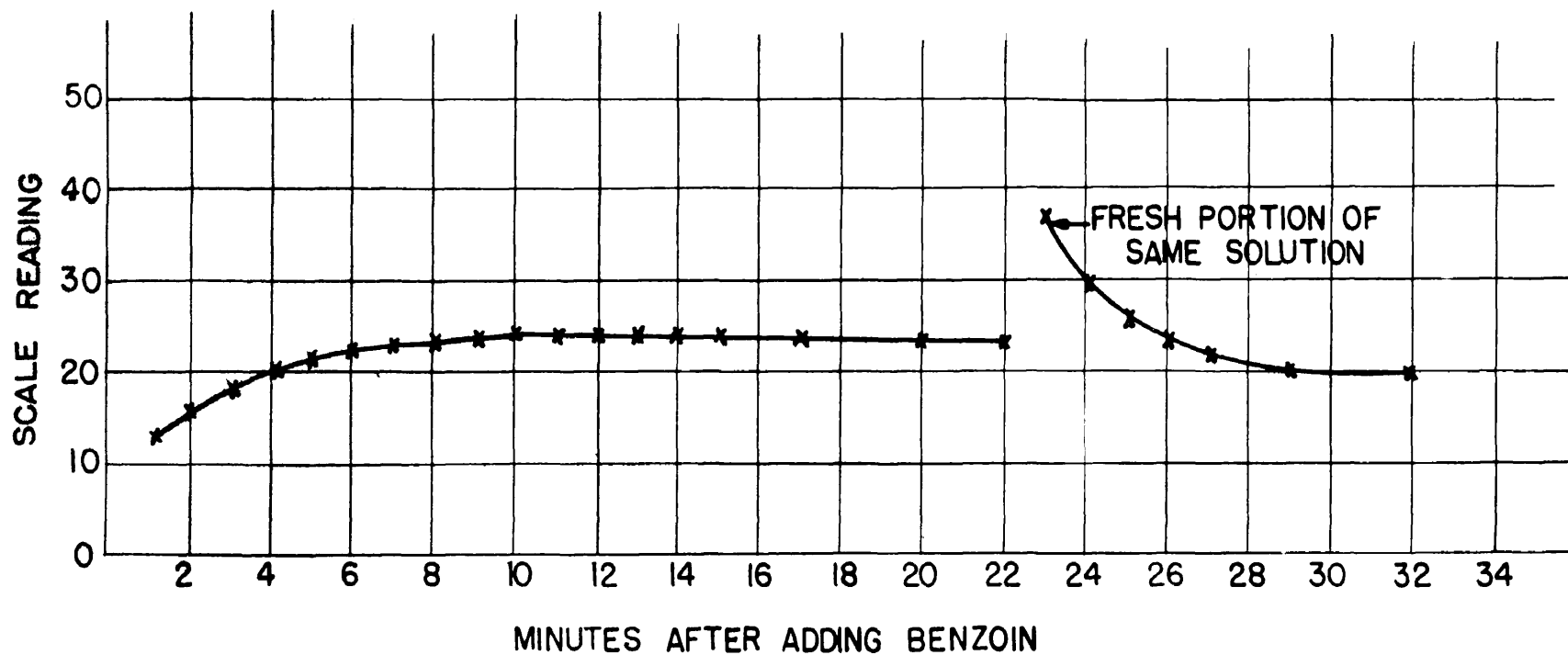
FIG. 35

EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON FLUORESCENCE

ML. OF 0.6N N_AOH IN 50 ML.
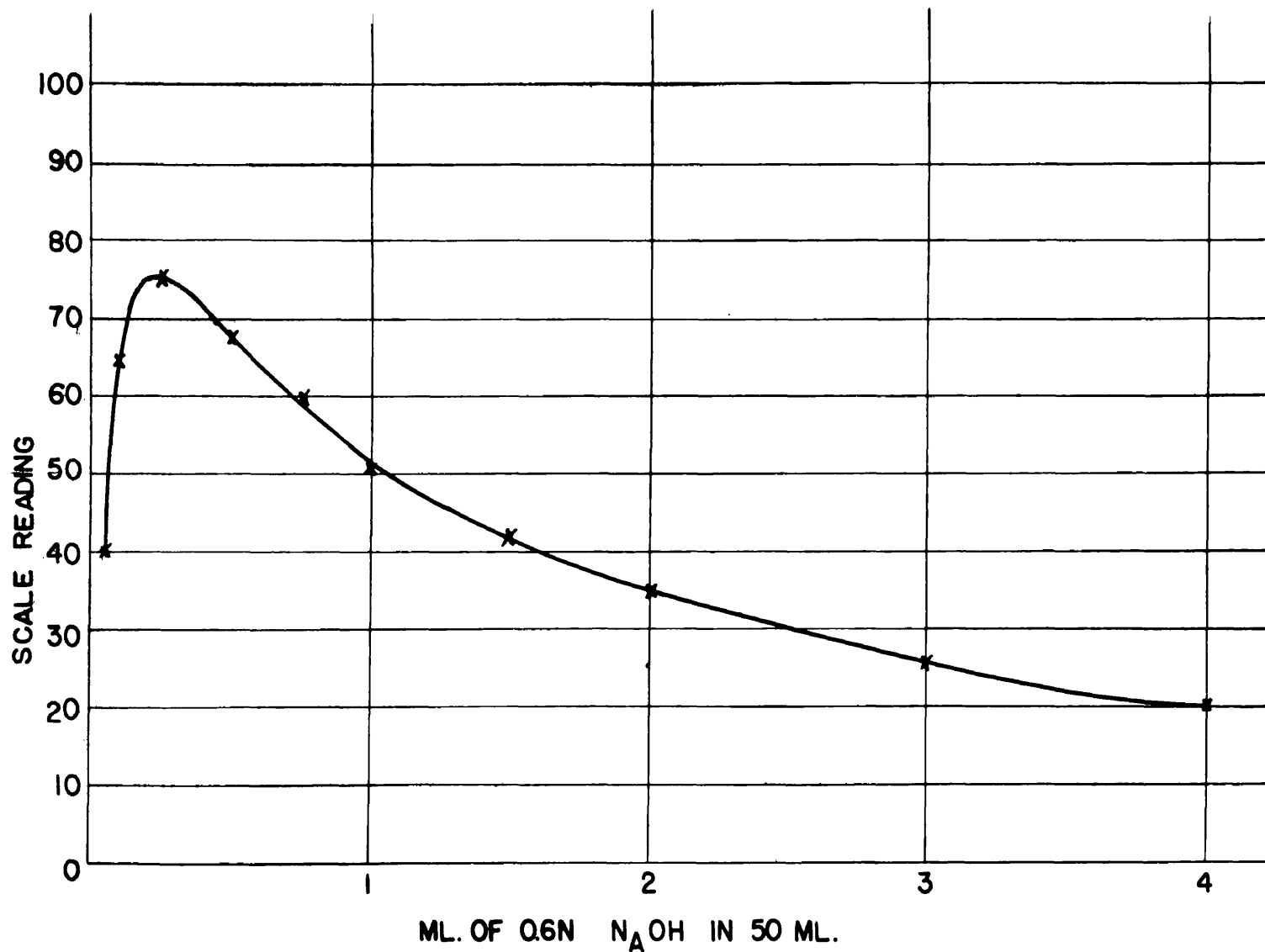
FIG. 36
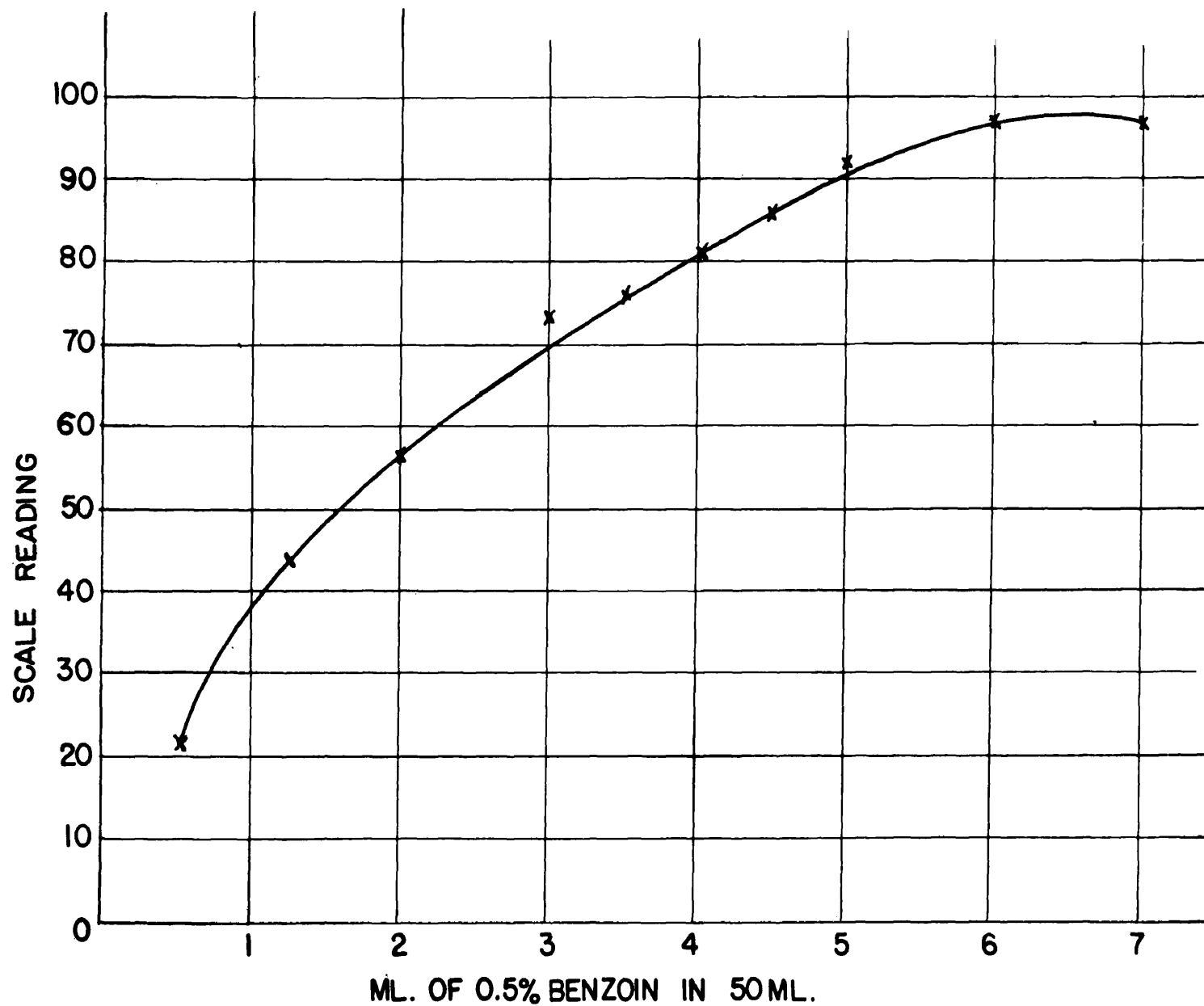
FIG. 37

EFFECT OF WATER CONCENTRATION ON FLUORESCENCE
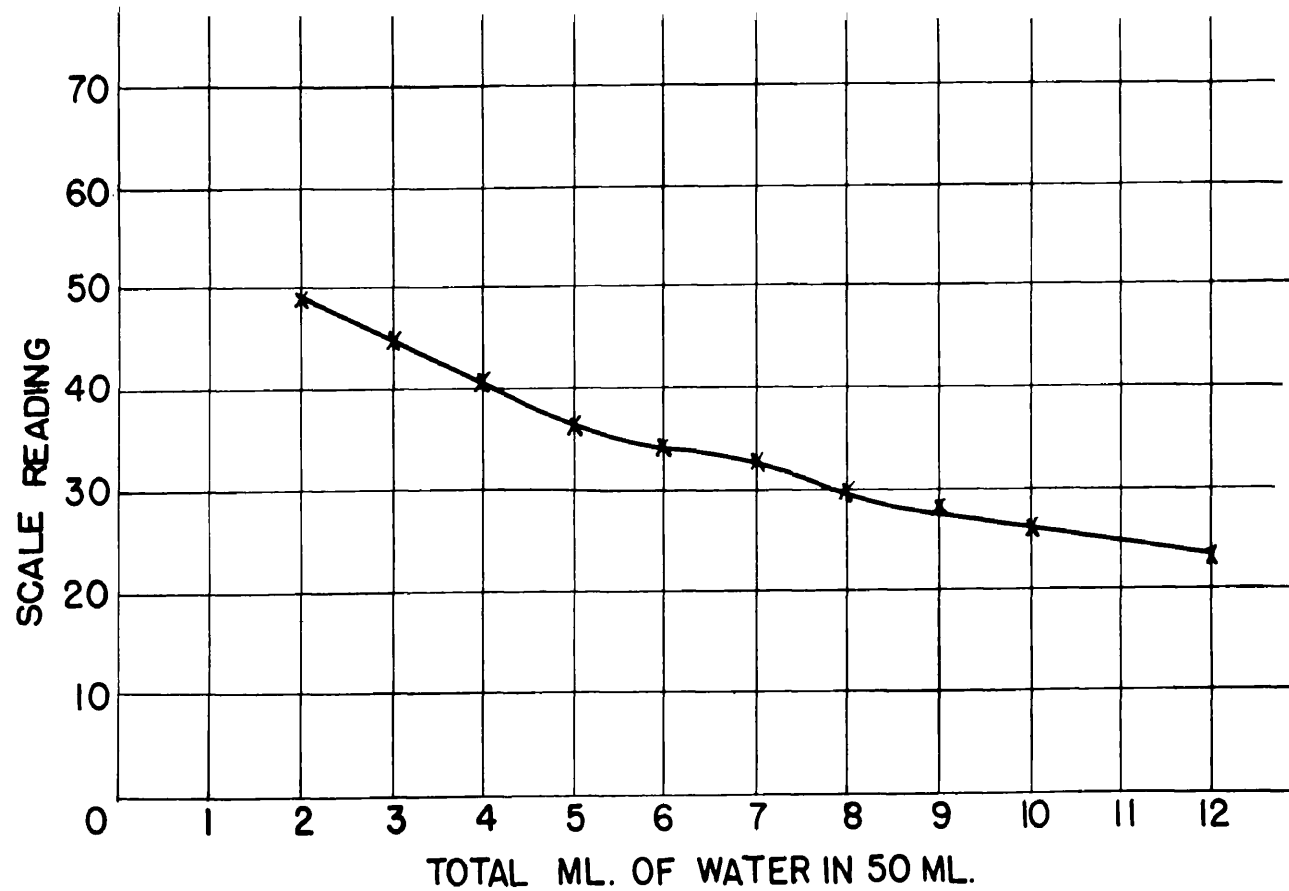
FIG. 38
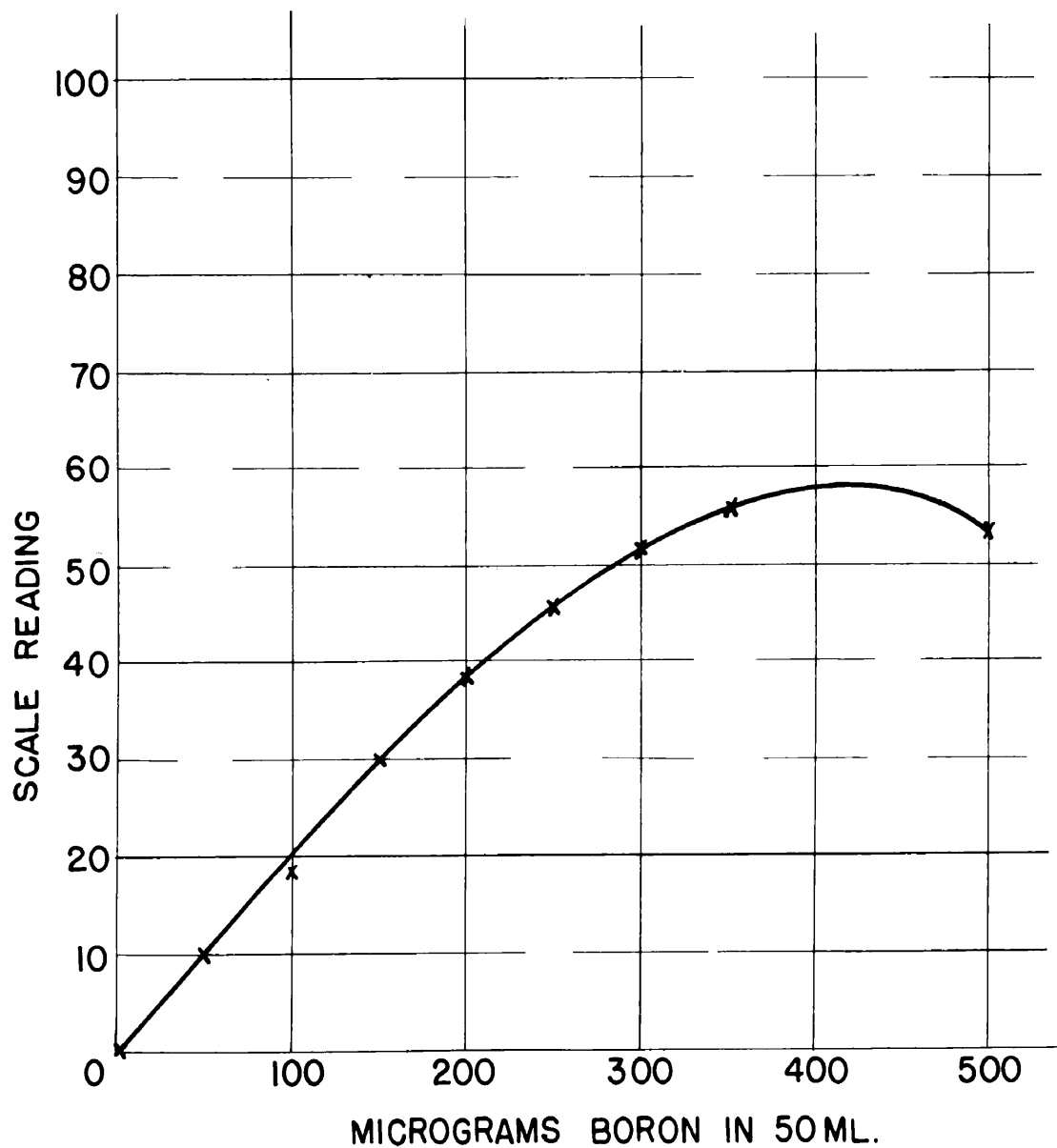
FIG. 39

RELATION OF FLUORESCENCE TO BORON CONCENTRATION, MIDDLE RANGE

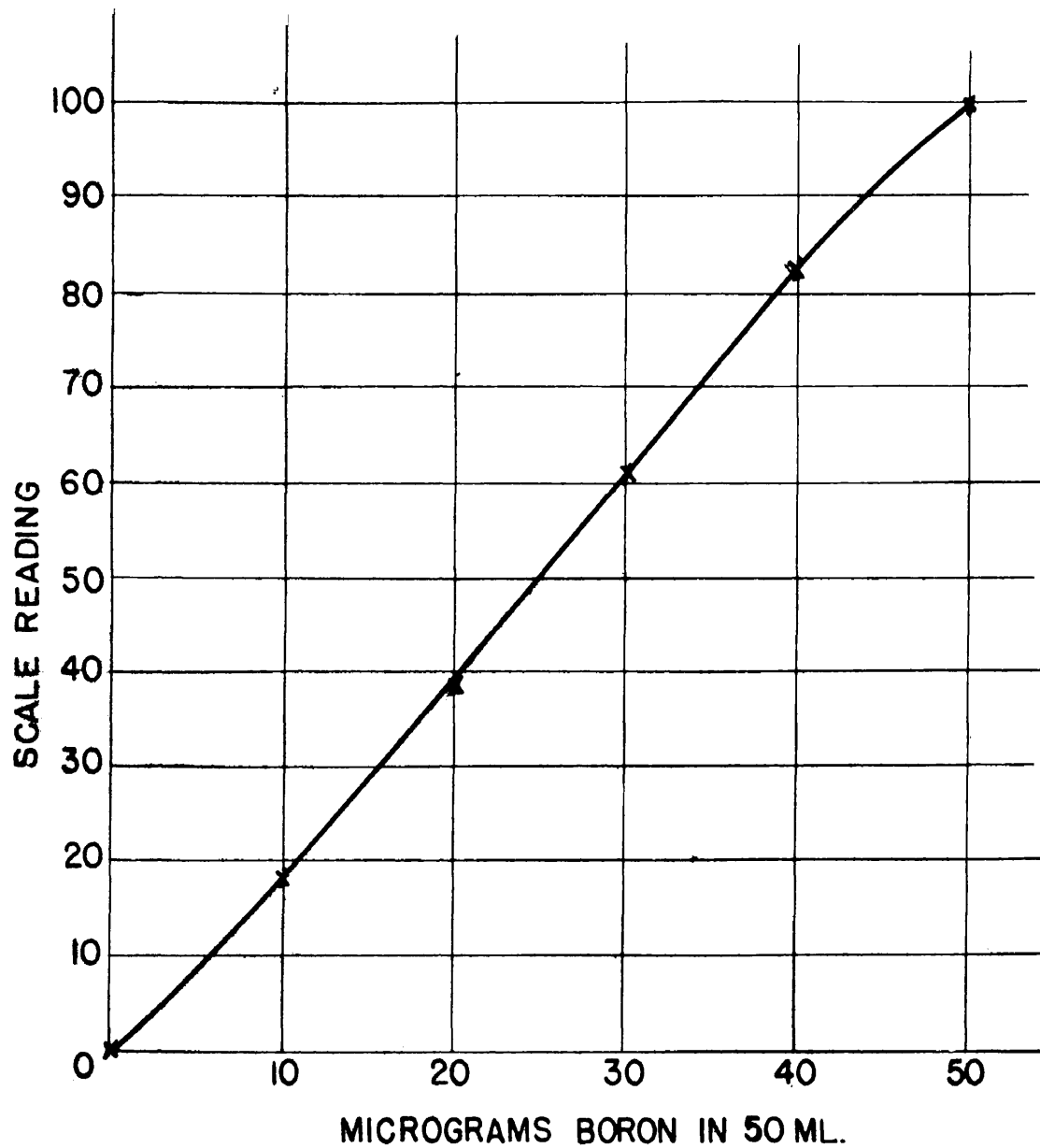FIG. 40

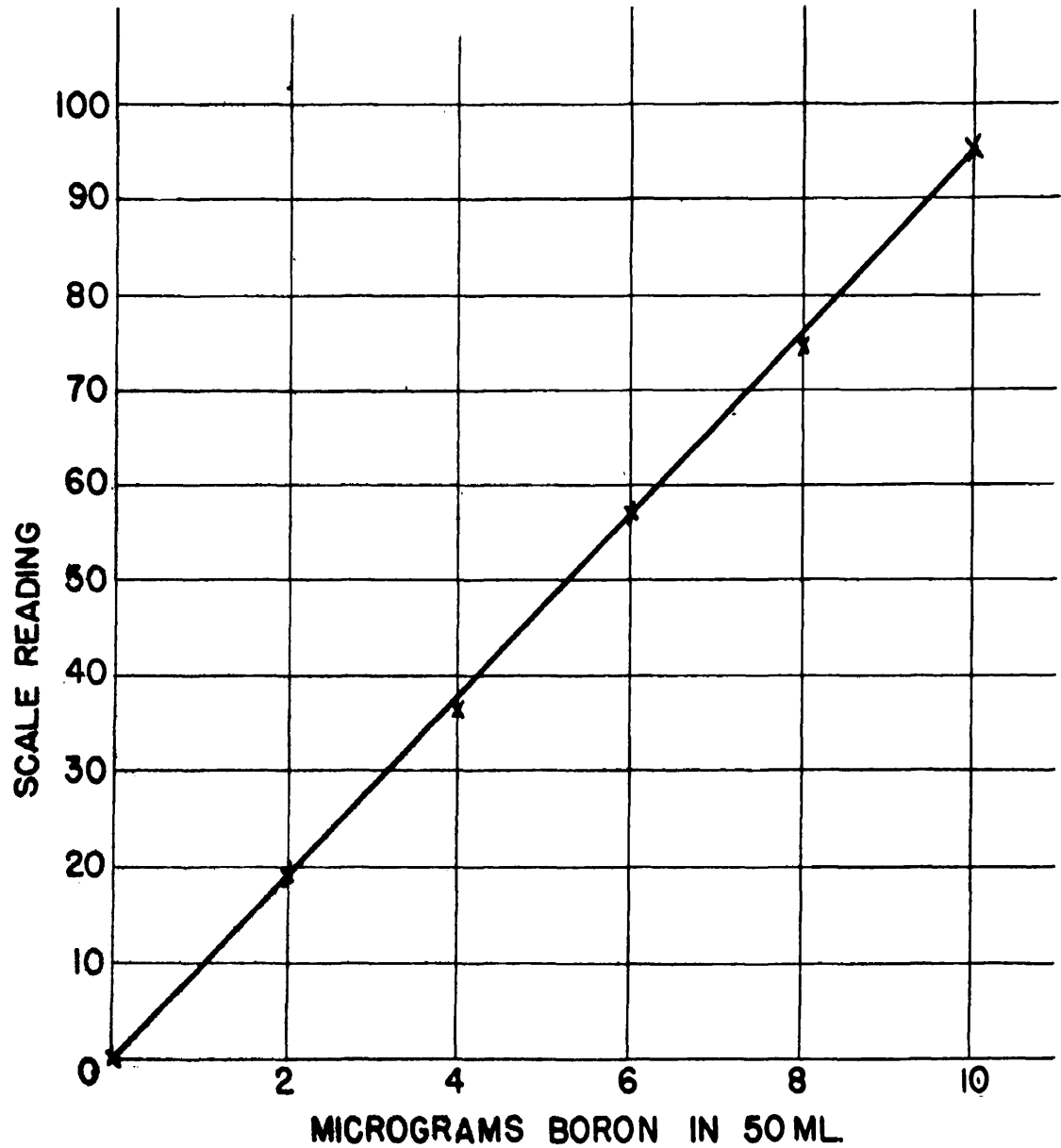# RELATION OF FLUORESCENCE TO BORON CONCENTRATION, LOW RANGE

FIG. 41

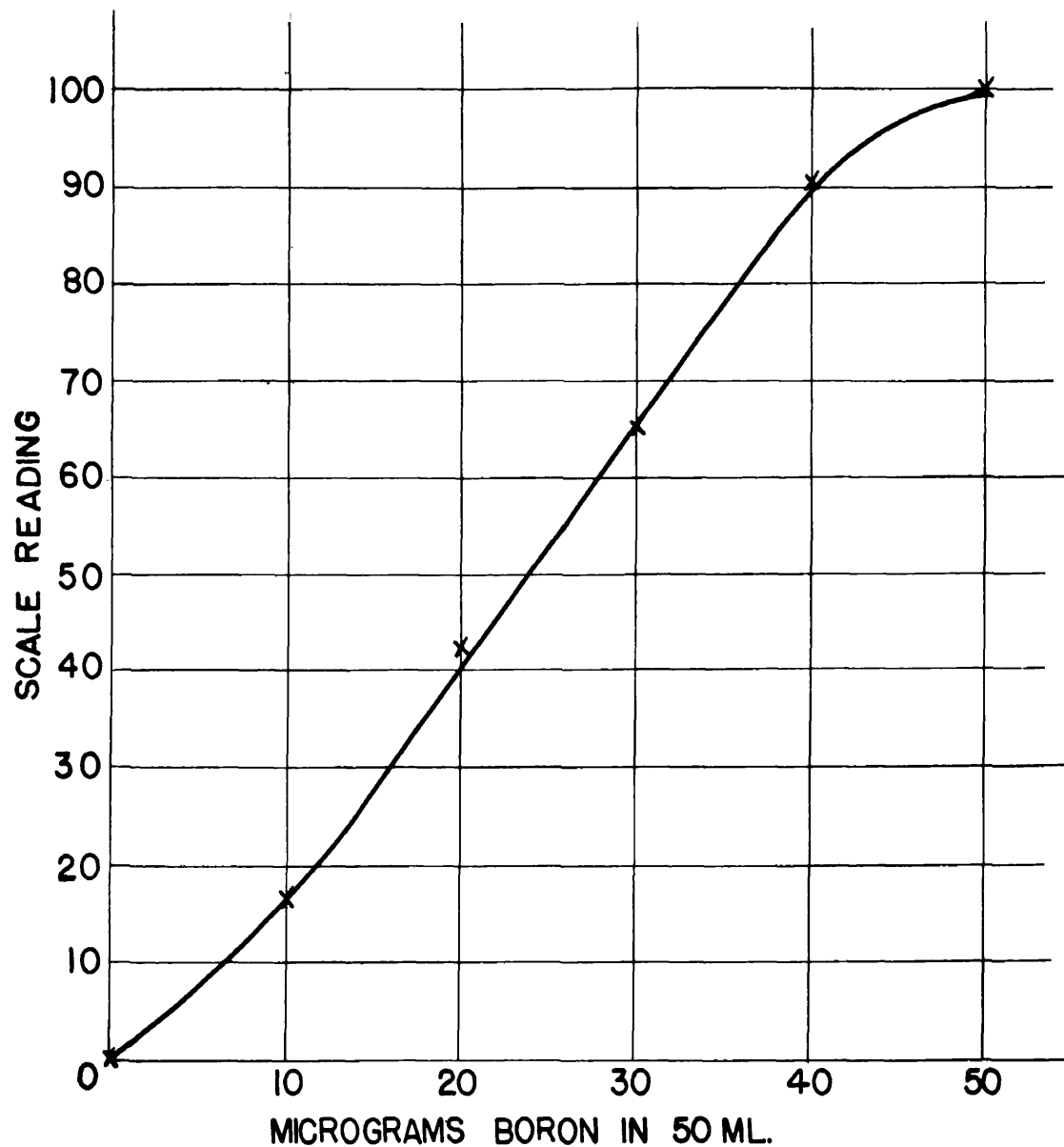RELATION OF FLUORESCENCE TO BORON CONCENTRATION, IN ISOPROPYL ALCOHOL

FIG. 42

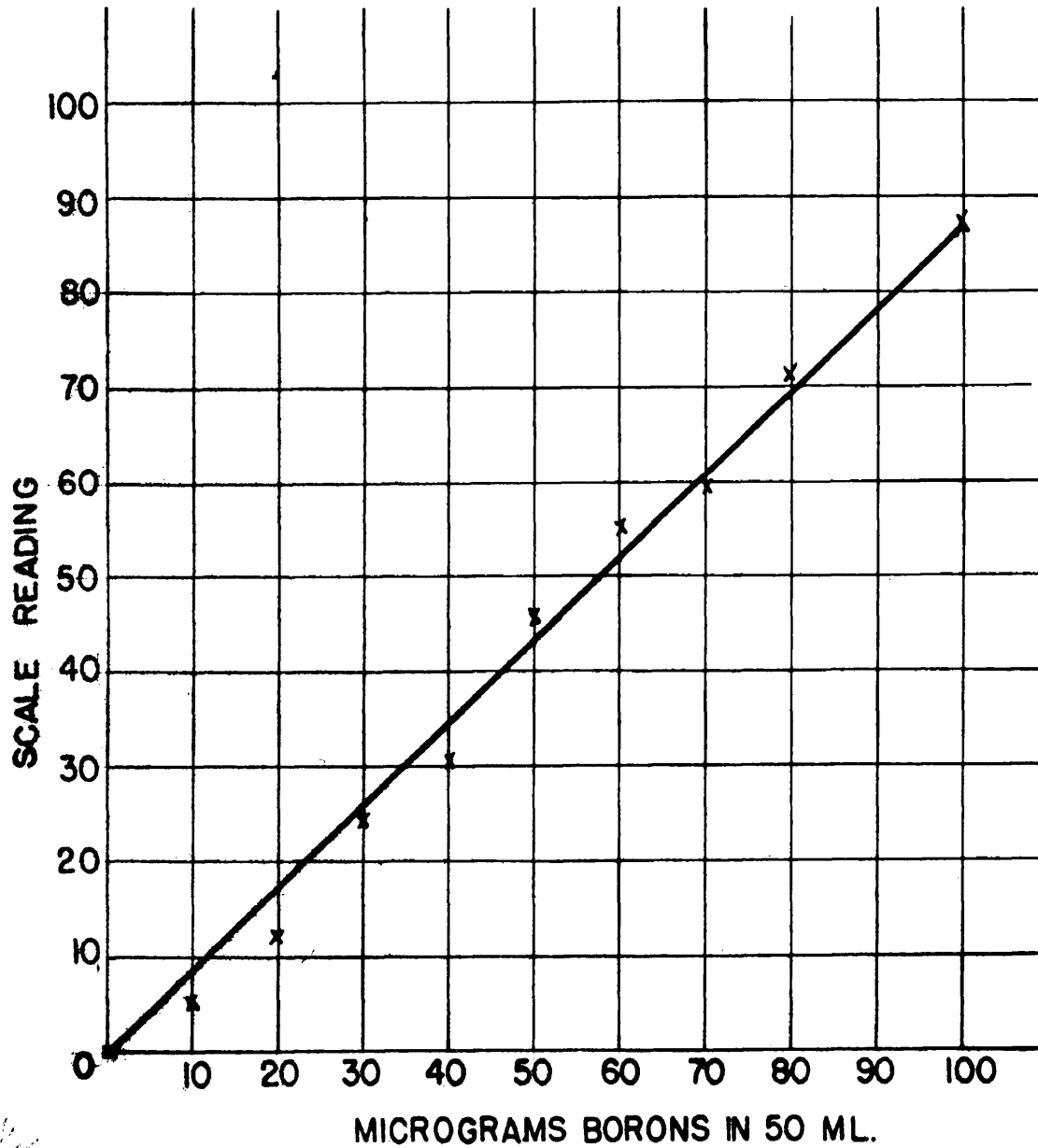# RELATION OF FLUORESCENCE TO BORON CONCENTRATION, IN METHYL ALCOHOL

FIG. 43

VITA

Alfred Weissler was born March 13, 1917 in New York
City. He was educated in the public schools and James Monroe High School of that city. After attending the College
of the City of New York from 1932 to 1936, he received the
B. S. in 1936. His graduate study at the University of Wisconsin in 1937-8 earned him the M. S. in 1938. In 1941 he
was married to Miss Pearl Goldman. The degree of Ph. D. was
conferred on him in 1946. His address is 2958 Second Street,
S. E., Washington 20, D. C.

His publications include:
"Determination of germanium in steel," Ind. Eng.
          Chem., Anal. Ed., 16, 311 (1944).
"Bobby's interest in chemistry," J. Chem. Ed.,
          21, 447 (1944).
"Simultaneous spectrophotometric determination
          of titanium, vanadium, and molybdenum,"
          Ind. Eng. Chem., Anal. Ed., 17, 695
          (1945).
"Spectrophotometric determination of titanium in
          steels," Ind. Eng. Chem., Anal. Ed., 17,
          775 (1945).

His present position is as chemist at the Naval Research
Laboratory, Washington, D. C. Previously, he was a science
teacher in the New York City high schools, a chemist at the
U. S. Customs Laboratory in New York, and a U. S. Railway
Postal Clerk in New York.