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AN INVESTIGATION OF THE VANADO MOLYBDATE COLORIMETRIC METHOD FOR THE DETERMINATION OF PHOSPHATE

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Introduction

In 1908 a colorimetric method for the determination of phosphate based on the reaction of a molybdate with a vanadate and a phosphate was published by Misson (1). A yellow coloured solution is formed when an acidic solution of a mixture of a vanadate and a molybdate is added to an orthophosphate solution. It is thought that the coloured component is phosphovanadomolybdic acid, $H_3PO_4.VO_3.11MoO_3$, but the exact constitution is uncertain. The usefulness of the colorimetric procedure based on this colour reaction is however unaffected.

The method has been put forward for the analysis of ores, plain carbon steels, (2, 3, 4, 5, 6.) plant materials (7) biological materials (8) and fertilisers (9, 10.).

Experimental and Discussion

The most accurate way of using colorimetric analysis is by the differential technique, that is, comparison of the unknown solution with an accurately known standard solution by measurement of the two colours, or more strictly the optical densities.

The differential technique is most accurately applied to solutions differing in composition by small amounts of the order of 1% concentration. A more useful method, and one which has been adopted in this work, is based on a calibration graph drawn for a short range about the concentration of a selected reference standard.

Apparatus

The work described was carried out using a Beckman DU Spectrophotometer. Readings on the instrument were made using 1 cm. cells for all determinations.

The error introduced by badly matching cells can be overcome by several methods. One method involves the addition or subtraction of a certain fixed difference determined by filling the two cells with the same solution and reading the optical density difference. This method is not favoured for the followi reason.

if d_1 is the optical density measured in cell 1.

d_2 is the optical density measured in cell 2.

L is the length of cell 1

$L + \Delta L$ is the length of cell 2

c is concentration of solution

Then $d_1 = KLc$

$d_2 = K(L + \Delta L)c$

$d_2 - d_1 = K\Delta Lc$

It will be seen therefore that for two cells of slightly different optica path the difference in optical density varies with the concentration for a fixed difference ΔL in cell length.

The method that was favoured in the work described was as follows :- Two cells were arbitrarily marked A and B; cell A was filled with the standard reference solution; cell B was filled with the solution of unknown concentration and the optical density difference was measured. Cell B was then filled with the reference standard, cell A was filled with the unknown solution and the optical density difference again measured. The arithmetic mean of the two readings wa taken as the true optical density difference. This technique was used in the preparation of all the calibration graphs and for all the subsequent work on the determination of phosphate in a number of fertiliser samples.

The same technique was used in measuring the effect of ions of impurities. This technique of reversing the cells, although requiring a little more time, yields the true optical density figure despite changes in concentration or in the condition of the optical surfaces of the cells.

The Beckman Instrument

Some measure of the range of the instrument is shown in Fig. 1. The instrument was balanced for different wavelengths using the appropriate slit width with the sensitivity control at its clockwise maximum, curve 1, and the sensitivity control at the anticlockwise maximum, curve 2. All readings were obtained on an air path with no cell in the beam.

It can be noted that there is a rapid increase in slit width as the wavelength is reduced below 360 mμ. This is due to the rapid fall off in intensity of the light emitted by the tungsten lamp at wavelengths below this figure. The region botween 400 mμ and 650 mμ represents the region of maximum output of the lamp.

Phosphovanadomolybdate Colour Reaction

The vanadate molybdate reagent used in this work was that advised by Hanson (9).

It was used as a composite reagent, a mixture of the two salts acidified with nitric acid. Details of the preparation of the reagent are given at the end of the text. The optimum conditions for colour development were given by Quinlan and De Sesa (4) using perchloric acid to acidify the solution as:

acid	0.4 Normal
Mo	0.02 - 0.06 Molar
V	1 - 4 Millimolar

and 7 - 46 p.p.m. P_2O_5 for 1 cm cells.

The quantities suggested at the end of the text using the Hanson reagent are:-

acid	0.66 Normal
Mo	0.034 Molar
V	2.6 Millimolar

and 70 p.p.m. P_2O_5.

It was found that exactness of measurement of the quantity of reagent was not critical but should be to at least 1 ml. The absorption of a coloured solution containing 1 mg. P_2O_5/100 ml. is shown in Fig. 2, between the wavelengths of 360 mμ and 600 mμ using the diluted reagent as standard zero. It can be seen that by choosing a suitable wavelength, almost any desired degree of sensitivity can be obtained.

When balancing the Beckman instrument with standard solutions of fixed optical density it is possible to achieve balance at fixed settings of the slit width and sensitivity control. Each of these settings is interdependent. If one is changed the other must also be changed to compensate. The slit width is calibrated. The response of the instrument which is a measure of the sensitivity varies with the slit width. This response is defined as the deflection of the needle for a change in the transmission of one division. The response is measured in units equal to the reciprocal of the change in percentage transmission which causes a needle deflection of one division.

The response at 420 mμ for various concentrations of P_2O_5 is shown in Fig. 3.

The method of procedure was to balance the instrument with a coloured solution of the required concentration at the lowest possible value of the slit width and to measure the difference in percentage transmission for a deflection of the needle of 10 divisions. This measurement was repeated at various slit widths up to the maximum slit possible. The procedure was repeated for various concentrations. If the instrument is to be read with certainty to 0.1% transmission, and if one stipulates a needle deflection of $\frac{1}{2}$ scale division for a change in transmission of 0.1%, the instrument response required would be 5. The horizontal line represents this response and the abscissae of the points of intersection are the slit widths necessary at the various concentrations to obtain this response. It may be noted that the response increases as the slit width increases and also that a greater slit width is required for a given response as the concentration increases.

Optimum Phosphate Concentration for Analysis

It follows from theoretical considerations that in general the higher the optical density of the solutions being measured the greater the accuracy. For if

d_s is the optical density of a coloured solution A relative to the solvent,

d_r is the optical density of a similar reference solution B of known concentration.

d_m the measured optical density difference between B and A.

then $d_m = d_s - d_r$

In making the optical density measurements the optical densities of the specimen and reference are arranged so that the difference is small and is read on the most open part of the optical density scale.

For a solution obeying the Beer-Lambert law

$d = KcL$ where d is the optical density

K is a constant

c is the concentration

L is the length of the light path

$$\text{Fractional error} = \frac{\triangle c}{c} = \frac{\triangle d_s}{d_s} = \frac{\triangle d_m}{d_s}$$

where $\triangle c$ is the smallest measurable difference in concentration, and $\triangle d_m$ is the smallest measurable difference in optical density and may be defined as the instrument error. For a given optical density difference d_m, the precision increases with d_s, the optical density of the coloured solution, up to the limit imposed by deviation from the Beer-Lambert law.

The following treatment is similar to that used by Neal (11) for the selection of the optimum concentration for the colorimetric estimation of titanium.

If:-

d_1 and d_2 are the optical densities of solutions 1 and 2,

c_1 and c_2 are the concentrations of solutions 1 and 2,

I_o is the intensity of incident radiation,

I_1 and I_2 are the intensities of radiation transmitted through solutions 1 and 2,

K is a constant depending on the nature of the solution being measured,

L is the length of the light path

Then by definition:-

$$d_1 = \log_{10} I_o/I_1 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$d_2 = \log_{10} I_o/I_2 \quad \ldots\ldots\ldots\ldots\ldots (2)$$

According to the Beer-Lambert law:-

$$d_1 = Kc_1L \quad \ldots\ldots\ldots\ldots\ldots (3)$$

$$d_2 = Kc_2L \quad \ldots\ldots\ldots\ldots\ldots (4)$$

from equation (1) : $I_o/I_1 = 10^{d_1}$ ..... (5)

from equation (2) : $I_o/I_2 = 10^{d_2}$ ..... (6)

from (5) and (6) : $I_2/I_1 = 10^{(d_1-d_2)}$

$$= 10^{KL(c_1-c_2)}$$

$$= 10^{KLc_1(1-\alpha)}$$

$$= 10^{d_1(1-\alpha)} \ldots\ldots (7)$$

where α = ratio of the concentrations = c_2/c_1

from (7) : $1 - I_2/I_1 = 1 - 10^{d_1(1-\alpha)}$

or $\Delta I/I_1 = 1 - 10^{d_1(1-\alpha)}$

where $\Delta I = I_1 - I_2$

If $c_2 > c_1$, then solution 1 is used as the reference solution and the instrument adjusted to read 100% transmission with solution 1 in the light beam.

$$\text{Thus } \Delta I = 100\,(1 - 10^{d_1(1-\alpha)})$$

where ΔI is expressed as percentage transmission.

Curve A. fig. 4 is the graph of ΔI plotted against optical density for $\alpha = 1.25$. As d increases ΔI increases becoming maximum at d = infinity.

Curve B. is the graph of the experimental results in which the ΔI for pairs of solution of $\alpha = 1.25$ was plotted against the optical density. There is

a marked deviation from the Beer-Lambert law for values of d greater than 1.5 and $\triangle$I reached a maximum at a concentration of about 7 mg. P_2O_5 /100 ml. It can be simply shown that the accuracy is proportional to $\triangle$I for a given value of α and that the criterion for the best calibration curve is that it has the greatest $\triangle$I for a given value of α. The accuracy of a determination of a concentration is defined as the product of the concentration corresponding to a point on the calibration curve and the slope of the curve at that point. If the error in determining $\triangle$I is constant for all values of $\triangle$I.

$$\text{the slope } S = \frac{d(\triangle I)}{dc} = \frac{\triangle I}{c_1 - c_2}$$

where $\triangle$I is the transmission ratio of the solution of concentration c_1 and c_2.

$$\text{Accuracy} = \frac{\triangle I}{c_1 - c_2} \times \frac{c_1 + c_2}{2}$$

$$= \triangle I \cdot \frac{(1+\alpha)}{2(1-\alpha)}$$

Hence the accuracy is proportional to $\triangle$I at constant α and the greatest accuracy is obtained when $\triangle$I is greatest for a given value of α. These conclusions led us to select the concentration range about 7 mg. P_2O_5/100 ml. for calibration of the Beckman instrument. This concentration lies conveniently at about the mid position of the range of concentration obtained from our normal products by the procedure recommended at the end of the text using conventional pipettes.

Development of Colour

On addition of the reagent solution to a phosphate solution the colour is rapidly developed at ordinary temperatures. A coloured solution containing 1 mg P_2O_5/100 ml. derived from pure KH_2PO_4, was compared with a reagent blank. (See fig. 5). It is seen that full development of the colour is complete after 15 min. and it remains virtually stable for at least 24 hours although there is a slight increase in intensity. A solution containing 5 mg. P_2O_5/100 ml. was found to give the same reading as the initial reading after 5 days if compared with a standard of the same age. If, however, the solution after standing for 24 hrs. was compared with a freshly prepared solution of the same concentration the optical density reading at 420 mμ of the older solution was found on average to be 0.023 greater than the new solution. This is of no significance however, if the solutions used for determinations are of the same age.

Variability of Reading Instrument

In Table 1. a list is given of readings taken on the reagent blank.

Variability of Reading Instrument (Cont'd.)

Table 1.

Wavelength 420 mμ Slit 0.03 mm.

Reference cell A containing diluted reagent solution.

Readings on cell B containing same solution.

-0.001	+0.005	-0.001	+0.001	0.000
+0.002	+0.007	-0.004	+0.003	-0.002
+0.003	+0.007	-0.003	-0.001	+0.001
+0.004	+0.007	-0.002	+0.002	-0.004
+0.008	-0.001	+0.001	+0.001	-0.003
+0.005	-0.001	-0.001	+0.002	-0.002
+0.005	-0.003	-0.001	+0.002	+0.001
+0.006	-0.003	0.000	+0.001	+0.001

mean + 0.001; Standard Deviation 0.003

Two cells A and B containing the same solution were used. A was used to zero the needle and the reading obtained on B. B was emptied and recharged after each reading.

The standard deviation is 0.003 so that about 95% of all readings should lie within 0.006 of the mean reading. For a solution of 5mg. P_2O_5/100 ml. of optical density 1.1, if the same error is obtained, the coefficient of variation would be of the order of 0.27%.

Temperature Variation

Table 2.

Temperature °C	Optical Density
13.8	0.388
18.8	0.389
20.6	0.392
20.9	0.389
25.4	0.389
26.8	0.392

This may arise in two ways, differences between the temperatures of individual cells, and daily variations in the laboratory temperature in which the pair of cells are at the same temperature but may be different for different days.

Table 2. shows the results for the variation between pairs. A standard was made up of the diluted reagent and compared with a coloured solution containing 1 mg. P_2O_5/100 ml. which had been allowed to stand for 24 hours to ensure stability of colour. Both solutions were cooled in the cells by exposing them to the outside temperature and then reading the optical density at 420 mμ. Readings were made at various temperatures while the cells were warming up. It was concluded that there was no significant difference in the comparative optical density of two solutions caused by variation of the temperature over the normal range of room

temperatures.

The difference in optical density between solutions in cells at different temperatures is more difficult to determine experimentally and no figures are available for differences due to this cause. That it may be significant is shown by Curve A. in fig. 6. A cell was filled with water and placed in position in the instrument; the instrument was switched on 30 minutes before the cells were inserted. The rise of temperature with time is shown. It was found, contrary to expectations, that the temperature of a solution in a cell warmed in the instrument did not fall rapidly to the ambient temperature if the cell were removed from the instrument.

Fig. 6 curves B and C show the pattern of behaviour for a cell exposed in the instrument for 5 minutes, and allowed to stand in the room for 5 minutes, then replaced in the instrument for 5 minutes, and so on, as might be obtained in the case of a standard solution if the cell were not emptied and recharged frequently during a long series of determinations.

It is shown that there is an overall rise in temperature caused by slight heating of the cell compartment.

Cell Positioning

Accuracy is required in setting the cell in the carrier. Unless the cell is each time perpendicular to the light beam, the length of the light path through the absorbing medium will vary. Suppose that the normal to the cell makes a small angle i with the incident light beam. If μ is the refractive index of the absorbing medium, the fractional error δ in the path is given by

$$i = \mu \sqrt{2\delta}$$

As the cell can be set to within 1° the error should be negligible. A number of readings were obtained for the optical density of a solution in one cell containing 5 mg. P_2O_5 /100 ml. measured relative to the same solution in another cell, on gently attempting to twist the cell in the carrier.

It was concluded that negligible error arises from this cause.

Dependence of Reading on Technique of Filling and Emptying Cells

There are various techniques of filling and emptying cells.

One method is by draining with a pipette and refilling with the required solution. Figures were obtained when a solution of 4 mg. P_2O_5/100 ml. was replaced by one containing 5 mg. P_2O_5/100 ml. using this technique. It was shown that at least 4 changes of solutions were necessary before the correct value was obtained.

Another technique is to empty the cell by inverting and refilling. About

3 changes were necessary to obtain the correct reading, when this technique was adopted.

The Reagent

Concentration of Acid

It has been shown (3) that the intensity of the colour produced depends on the concentration of the acid present. The relationship between colour intensity or optical density and the acid normality of the final coloured solution is shown in Fig. 7.

It is seen that the colour intensity is constant for a range of acidity between 0.55N and 0.85N and that it is more intense at lower concentrations of acid and less intense for higher concentrations.

The standard solution used contained 7 mg. P_2O_5/100 ml. and 30 ml. of the Hanson reagent, and had an acidity of 0.68N.

Concentration of Molybdenum and Vanadium

The relationship between optical density and molybdenum and vanadium concentrations is shown in Fig. 8. It is seen that for a solution containing 7 mg. P_2O_5/100 ml. a minimum of 2.5×10^{-2}M molybdenum and 1.5×10^{-3}M vanadium is required in the final coloured solution. The reference standard solution used in the former case contained 2.4×10^{-3}M vanadium and in the latter case 3.4×10^{-2}M molybdenum, and the acidity in both cases was 0.68N.

Effect on Ions other than Phosphate, found in Phosphate Fertilisers

Although many ions are found in commercial fertilisers in trace amounts, the materials investigated, both anions and cations were those that are found in relatively large amount, originating in the superphosphate or filler, or those ions that are added as basic ingredients of the fertiliser or as reagents in the extraction and preparation of the phosphate solutions for analysis.

The ions examined were ferric iron, potassium, aluminium, calcium, ammonium, sulphate, silicate, citrate, chloride, borate, fluoride and fluosilicate.

The effect of these ions on a solution containing 7 mg. P_2O_5/100 ml. derived from pure KH_2PO_4, and 30 ml. of the Hanson reagent was examined. The ranges of concentration of the ions were based on the average content of the ions in superphosphate in the case of impurities and on the added amounts of ions such as ammonium, potassium and chloride found in compound fertilisers. The citrate ion range was based on the quantity of citric acid used in the extraction of a basic slag according to the British Official Method of extraction for analysis. All these ranges were calculated relative to a phosphate quantity

of 7 mg. P_2O_5. A list is given in Table 3.

None of the ions had significant interference on the range investigated except citrate and iron. Silicate was found to interfere if the coloured solutions were allowed to stand for 24 hours. A slightly higher optical density was developed. A silicate in the absence of phosphate was found to develop a faint colour when mixed with the reagent and allowed to stand for 24 hours. The behaviour of the solutions containing ferric iron is shown in figure 9, and the behaviour of those containing citrate is shown in figure 10.

All the measurements were made at a wavelength of 420 mμ.

Table 3.

Ion	Added as	Range mg./100 ml.
K^+ and Cl'	KCl	0 - 20 KCl
Fe^{+++}	$FeCl_3.6H_2O$ acidified with HCl	0 - 50 Fe
Al^{+++}	$AlK(SO_4)_2.12H_2O$	0 - 1 Al
Ca^{++}	$CaCl_2.6H_2O$	0 - 50 Ca
NH_4^+ and SO_4''	$(NH_4)_2SO_4$	0 - 100 $(NH_4)_2SO_4$
SiO_2''	acidified Na_2SiO_3 pH 1.4	0 - 17 SiO_2
Citrate	citric acid	0 - 300 citric acid
Citrate	neutral ammonium citrate	0 - 300 citric acid
BO_3'''	H_3BO_3	0 - 5 H_3BO_3
Na^+ and F'	NaF	0 - 1.4 F 0 - 1.6 Na
SiF_6	$MgSiF_6$	0 - 2.1 SiF_6

Preparation of Standard Phosphate Solution and Reagent

A phosphate solution containing 1 mg. P_2O_5 per 1 ml. was prepared as follows. Analar KH_2PO_4 was dried in an oven at 100°C for 2 hours and cooled in a desiccator. The dried KH_2PO_4 (1.9173g.) was dissolved in distilled water and made up to give 1 litre of Solution A.

The standard 7 mg. P_2O_5/100 ml. phosphate solution was made up in a 100 ml. class A volumetric flask using 30 mls. reagent, This standard was obtained by weighing out 7 mls. Solution A or diluting five-fold and measuring 35 mls. This measure was checked gravimetrically by first weighing 100 ml. made up in a class A volumetric flask and so determining the weight of 7 ml. The accuracy of the standard is of extreme importance.

The Reagent is prepared by dissolving Analar ammonium molybdate (20g.)

in distilled water (400 ml.) at 50°C. Analar ammonium vanadate (1g.) is dissolved in approximately 300 mls. water and concentrated Analar nitric acid (140 ml.) added. The molybdate solution is added slowly to the acid vanadate solution with mixing and the resultant mixture made up to 1,000 ml. with distilled water.

Method of Procedure for Phosphate Analysis

One method of taking aliquots for determinations is to take the solutions obtained by the British official methods for extraction of soluble and total phosphate and to dilute them in two stages to the required concentration. This technique is tedious and time consuming but may yield greater accuracy. It is considered desirable, however, to keep dilutions to a minimum. It was determined, therefore, to take larger portions of the original solutions with class A pipettes of capacity 5 mls. or over, and make up larger volumes of coloured solution using a standard concentration of 7 mg. P_2O_5/100 ml. In general, volumes of 250 ml. were prepared. The above concentration is about the mid-point of a range of concentrations obtainable by the British official methods of preparation from our products using pipettes of conventional capacities, and it has the advantage of having a higher optical density than the standard 5 mg. P_2O_5/100 ml.

Depending on the phosphate content of the fertiliser sample, an aliquot of the soluble or total phosphate solution was taken with a class A pipette so that the concentration of P_2O_5 in the final colour solution was about 7 mg. per 100 ml.

The taken aliquot was transferred to a 250 ml. volumetric class A flask with 75 ml. reagent and made up to the mark with distilled water. The solutions were allowed to stand for at least 15 minutes. The time for colour development is not of great importance so long as it is greater than a minimum of 15 minutes and that all the colour solutions are of the same age.

Measurement of Optical Density

The comparative optical densities were measured in 1 cm. cells. The cells are delicate and great care was taken in their handling and filling. The optical surfaces were not touched with the fingers and the cells were always stored clean. The most suitable material for polishing the outer surfaces was found to be a Selvyt cloth. The method of positioning cells and cell carrier was standardised, and was the same as the positioning used in calibration.

Two conditions arise in the application of the method.

(a) The optical density of the unknown solution 2 is greater than that of the reference solution 1.

In this case the instrument is balanced at zero on the optical density scale with the reference solution 1 and the optical density of 2 is measured.

Then C_2 conc. of solution 2.

C_1 conc. of solution 1.

d_1 measured optical density difference

$C_2 = Kd_1 + R + C_1$

Where K and R are constants for a linear calibration graph.

(b) The optical density of the unknown solution 3 is less than that of the reference solution 1.

The solution 3 must be used for the initial adjustment of the instrument and the optical density of the reference solution 1 is measured.

Then if C_3 conc. of unknown solution

d_2 = measured optical density difference

$C_3 = -Kd_2 + R + C_1$

R should be zero but in most calibrations is found to have a very small positive or negative value.

The wavelength chosen for calibration was 420 mμ to coincide with that suggested by Donald Schwehr and Wilson (10) and to give a reasonable range of phosphate concentrations, measurable by the instrument.

The standard phosphate was prepared from Analar KH_2PO_4 and the standard concentration chosen was 7 mg. P_2O_5 per 100 ml. i.e. 70 pts. P_2O_5 per million. The calibration graph plotted between 5 and 12 mg. P_2O_5/100 ml. was linear between 5 mg. and 9 mg. per 100 ml. and the linear relationship between optical density and concentration of P_2O_5 was calculated for these values by the method of root mean squares.

Expression (1) gives the value of the expression calculated.

Expression (2) gives the value of the expression calculated for the same solutions using different cells. It can be noted that there is close agreement between these calibrations.

Expression (3) is a calibration expression using a total phosphate solution of a Morocco superphosphate estimated by the Wilson method as standard.

Expression (4) is calculated for a similar set of results using a total phosphate solution of a Morocco superphosphate estimated by a Magnesium Ammonium Phosphate method as standard.

$C_2 = 4.6437d - 0.02273 + C_1$ ..... (1)

$C_2 = 4.6437d - 0.01898 + C_1$ ..... (2)

$C_2 = 4.6776d - 0.02263 + C_1$ ..... (3)

$C_2 = 4.6176d + 0.01718 + C_1$ ..... (4)

All the aliquots of the solutions were checked gravimetrically to the third place of decimals and were therefore adjusted very accurately. It can be seen that there are slight divergencies between the Magnesium Ammonium Phosphate estimated standard results, the Wilson method estimated standard results, and the KH_2PO_4 standard results, the KH_2PO_4 expression lying between the Wilson reference standard result and the Magnesium Ammonium Phosphate reference standard results. It should be noted, however, that the differences are very small.

Table 4.

Results on Superphosphate

Total Phosphate Instrument Beckman DU Spectrophotometer $c = 4.6437d - 0.01898 + 7.0$

		Colorimetric Method				Wilson Method	Difference
	Quantity of original solution/made up to/ quantity of reagent. ml.	Optical Density Difference (O.D.) Std. cell A	Std. cell B	Mean	$\%P_2O_5$	mean of 4 determinations $\%P_2O_5$	$\%P_2O_5$
Constantine Super	10/250/75	0.037	0.037	0.037	17.88	17.81	+0.07
Morocco Super	9/250/75	0.052	0.042	0.047	20.00	20.00	0.00
" "	"	0.054	0.047	0.051	20.05	20.06	-0.01
" "	"	0.052	0.044	0.048	20.01	19.95	+0.06
" "	"	0.034	0.022	0.028	19.75	19.77	-0.02
" "	"	0.028	0.013	0.020	19.66	19.84	-0.18
" "	"	0.042	0.025	0.033	19.82	19.92	-0.10
" "	"	0.037	0.035	0.036	19.86	19.87	-0.01
" "	"	0.064	0.020	0.042	19.93	19.87	+0.06
" "	"	0.065	0.017	0.041	19.92	19.93	-0.01
" "	10/250/75	0.186	0.181	0.184	19.59	19.60	-0.01
" "	"	0.218	0.212	0.215	19.95	19.95	0.00
						Mean Difference (irrespective of sign)	0.04

TABLE 5

Results on Superphosphate

Soluble Phosphate

Instruments: Beckman DU Spectrophotometer — c = 4.5386d − 0.01324 + 7.0
Unicam SP 600 Spectrophotometer — c = 4.6361d − 0.0283 + 7.0

Original solution diluted five-fold and 25 mls. taken.

	Colorimetric Method								Wilson Method	Difference for HNO3 treated solutions for Beckman results	Difference for untreated solutions for Beckman result
	Solutions treated with HNO3				Solutions untreated						
	Beckman		Unicam		Beckman		Unicam		Mean of 2 determinations		
	O.D.*	%P2O5	O.D.*	%P2O5	O.D.*	%P2O5	O.D.*	%P2O5	%P2O5	%P2O5	%P2O5
Morocco Super	0.017	17.66	0.017	17.63	0.015	17.64	0.013	17.58	17.70	−0.04	−0.06
" "	0.025	17.75	0.026	17.76	0.024	17.74	0.023	17.70	17.77	−0.02	−0.03
" "	0.009	17.57	0.009	17.53	0.006	17.53	0.003	17.46	17.61	−0.04	−0.08
" "	0.067	18.23	0.070	18.24	0.065	18.20	0.064	18.17	18.28	−0.05	−0.08
" "	0.059	18.14	0.060	18.12	0.057	18.11	0.058	18.10	18.15	−0.01	−0.04
" "	0.087	18.45	0.088	18.45					18.51	−0.06	
" "	0.030	17.80	0.031	17.79					17.85	−0.05	
										mean difference ± 0.04	mean ± 0.06 difference

Original solution undiluted straight aliquot of 5 ml. taken and treated with HNO3.

Morocco Super	0.045	17.98	0.048	17.98		
" "	0.086	18.44	0.087	18.43	17.99	−0.01
" "	0.050	18.03	0.051	18.02	18.42	+0.02
" "	0.063	18.18	0.066	18.19	18.12	−0.09
" "	0.057	18.11	0.058	18.10	18.18	0.00
" "	0.007	17.55	0.008	17.52	18.16	−0.05
					17.49	+0.06
						mean ± difference 0.04

*O.D. − Optical Density Difference

± Irrespective of sign

Table 4 shows a number of results obtained on total phosphate solutions using this technique. The Wilson method results on the same samples are also tabulated. It can be seen that although there is sometimes a large difference in the optical density readings when the order of the cells is reversed, the mean of the two readings gives an accurate result.

Table 5 shows a number of results obtained for soluble phosphate determinations. Some of the colorimetric results were obtained using the above technique and some by five-fold dilution of the phosphate extract and taking an aliquot five times larger than in the former case. It was found also that if the phosphate extract were heated with nitric acid (1 ml. conc. Analar nitric acid to 25 mls. extract), slightly higher results were obtained which in general were closer to the Wilson method results. A Unicam SP 600 and a Beckman DU spectrophotometer were used to measure the optical densities of the solutions.

Table 6 shows a number of determinations of soluble phosphate in a sample of Morocco superphosphate with and without nitric acid treatment. Each result is a complete determination of the soluble phosphate in different portions of the same sample. They are not merely replicates of a single sample solution. The standard deviation is 0.05 for untreated solutions and 0.04 for treated solutions.

Table 6.

Results on a sample of Morocco Superphosphate

Untreated	After nitric acid treatment
$\%P_2O_5$	$\%P_2O_5$
18.33	18.34
18.35	18.33
18.41	18.41
18.47	18.45
18.40	18.39
18.35	18.43
18.39	18.39
18.32	18.39
18.42	18.39
18.42	18.42
18.44	18.44
Mean 18.39	Mean 18.40
Standard deviation 0.05	Standard deviation 0.04

Other Instruments

It will be observed in Table 5 that results have been obtained with a Unicam SP 600 spectrophotometer. It was found that the conditions established for the Beckman DU spectrophotometer could be directly applied to this instrument. This less elaborate spectrophotometer is equally suitable for phosphate fertiliser analysis and is simpler in operation. Calibration graphs for the above instruments are shown in Fig. 11.

Fig. 11 also shows two calibration graphs for a Spekker absorptiometer:-

(1) using a tungsten filament lamp and a Kodak filter giving maximum transmission at a wavelength of 430 mμ.

(2) using a mercury vapour lamp and a combination of Wratten No. 50 and Chance OB2 filters to isolate the 436 mμ line. It will be observed from these graphs that with the mercury vapour lamp, the instrument sensitivity is approximately doubled and that the graph is more nearly a straight line.

The use of a filter giving maximum transmission at a lower wavelength increases instrument sensitivity. This was found impossible with the filament lamp unless the standard phosphate concentration was reduced to the order of 1 mg. P_2O_5 per 100 ml. Even with the mercury vapour lamp, operation was more satisfactory with a 5 rather than a 7 mg. P_2O_5 standard.

A number of comparative tests have been made using the Spekker absorptiometer against the Wilson method and other instruments. Table 7 shows results for water soluble phosphate when testing the same aqueous extract of various samples of Morocco Superphosphate. The instruments used were (1) Spekker H.760 absorptiometer with tungsten filament lamp; (2) Beckman DU spectrophotometer; (3) Unicam SP 600 spectrophotometer.

Table 7.

	Spekker	Beckman	Unicam
	18.61	18.54	18.63
	18.56	18.44	18.64
	17.83	17.82	17.92
	17.67	17.73	17.78
	18.08	18.14	18.14
	18.40	18.39	18.40
	18.08	18.10	18.07
	18.33	18.26	18.27
	18.77	18.83	18.89
	18.08	18.06	18.06
Average	18.24	18.23	18.27

It is concluded that there is reasonable agreement between the three instruments.

Conclusions

The vanado molybdate colorimetric method is sufficiently precise for the determination of phosphate in fertilisers.

The greatest accuracy is obtained by using solutions of maximum optical density within the limits imposed by instrumental characteristics or deviation from the Beer-Lambert law.

The molybdenum and vanadium concentrations must be greater than a fixed minimum, but higher concentrations of these reagents cause no effect on the colour except for the slight additive colour due to the vanadate solution. A range of acidity is possible over which the intensity of the colour developed is constant.

Of the impurities commonly found in fertilisers, only iron and citrate ions showed significant interference in the range investigated.

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FIG. 1

RANGE OF BECKMAN INSTRUMENT FOR AIR PATH

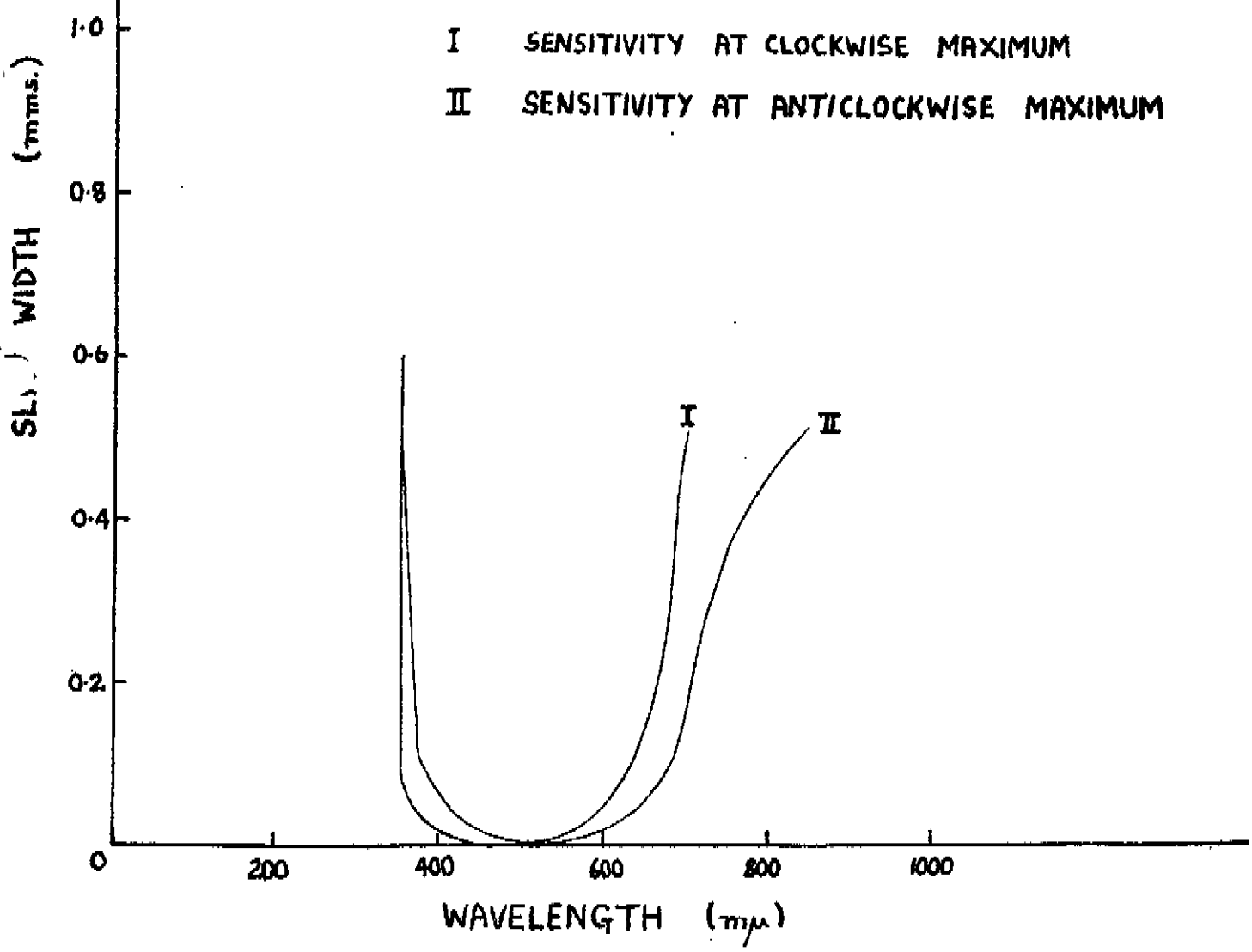

FIG. 2

VARIATION OF OPTICAL DENSITY WITH WAVELENGTH FOR A COLOURED SOLUTION CONTAINING 1 mg. P_2O_5 / 100 ml.

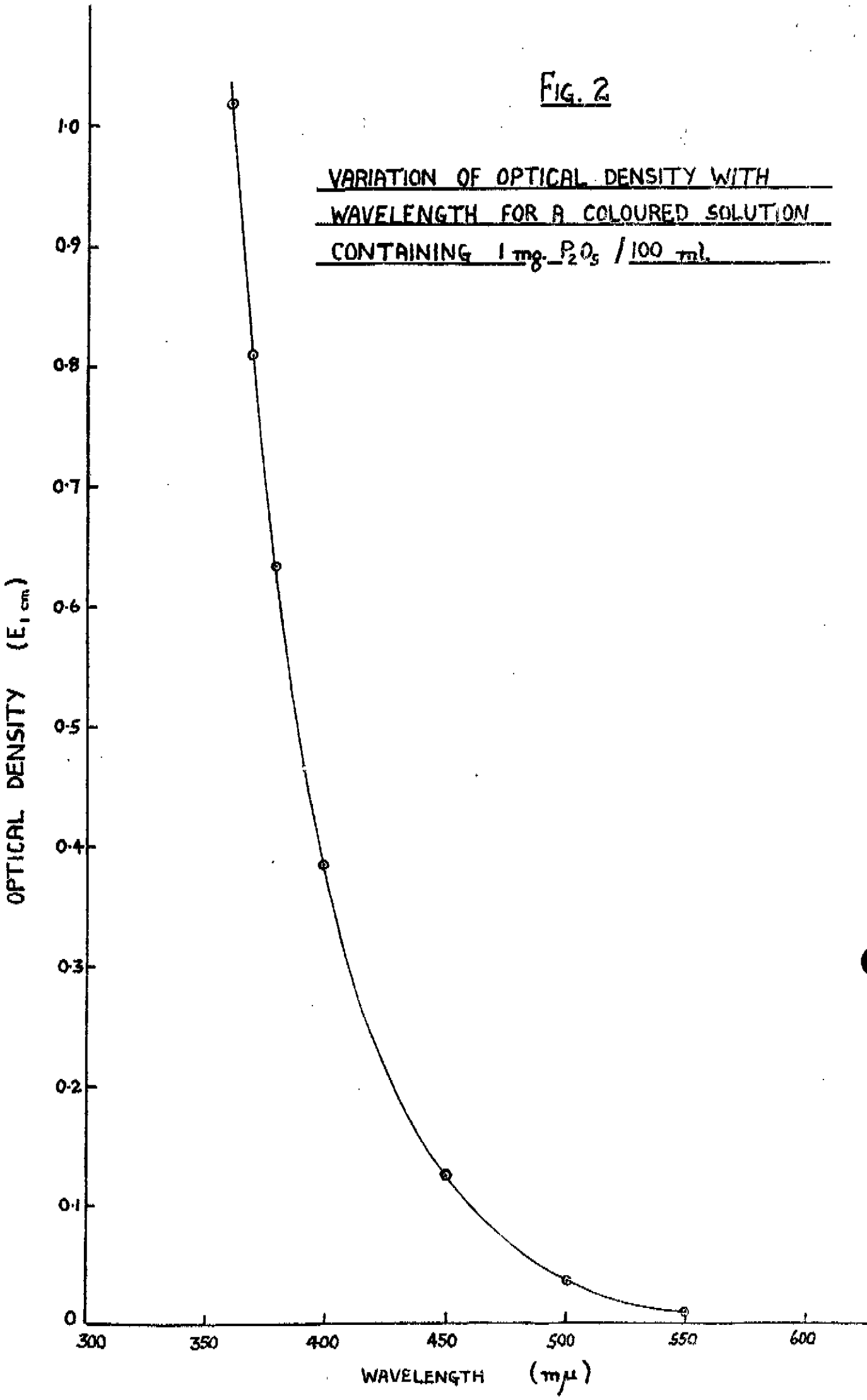

FIG. 3.

SENSITIVITY OF BECKMAN INSTRUMENT AT 420 mμ FOR VARIOUS CONCENTRATIONS OF PHOSPHATE

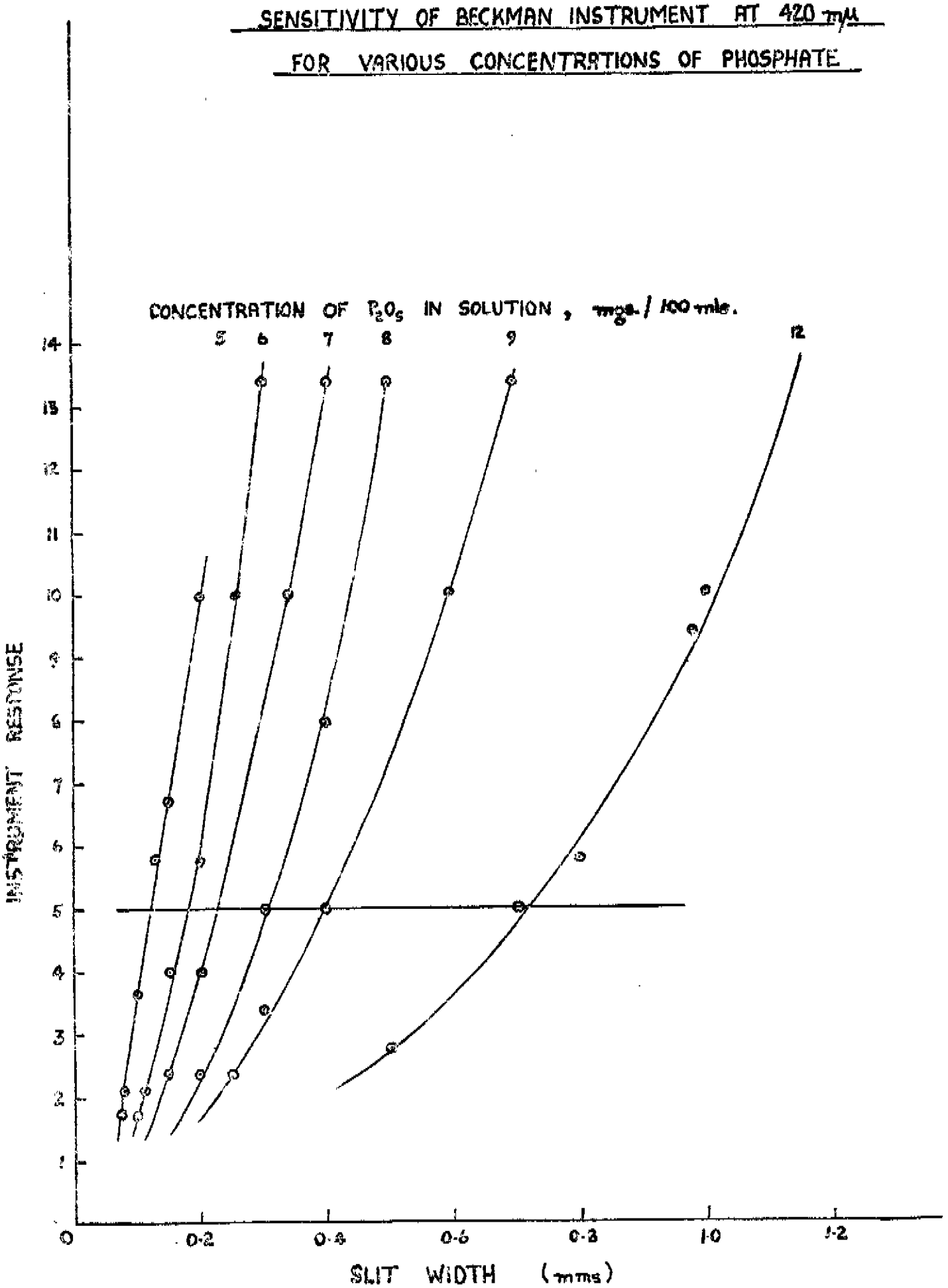

FIG. 4.

PERCENTAGE TRANSMISSION AS A FUNCTION OF OPTICAL DENSITY

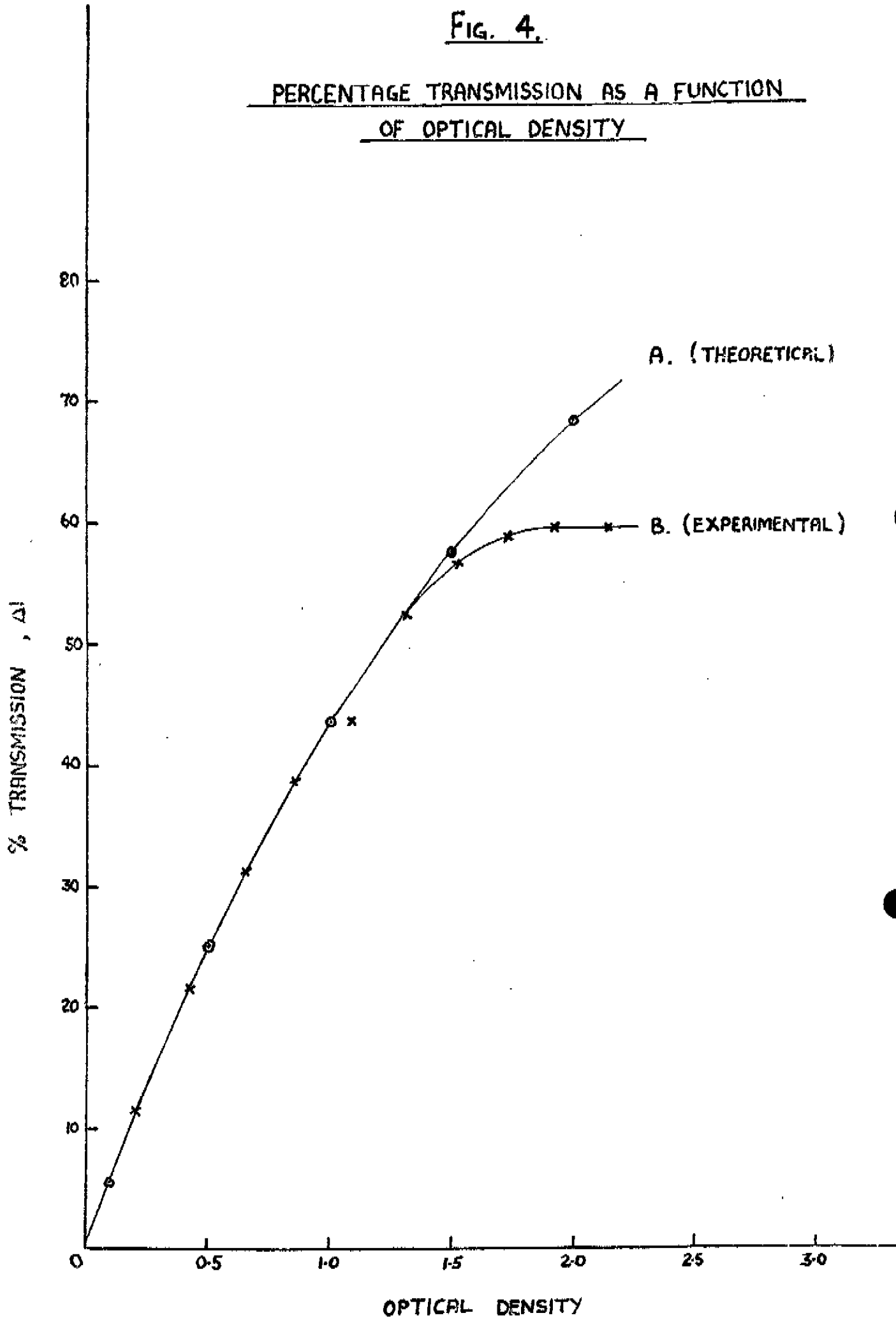

Fig. 5.

BEHAVIOUR OF COLOUR SOLUTION WITH TIME

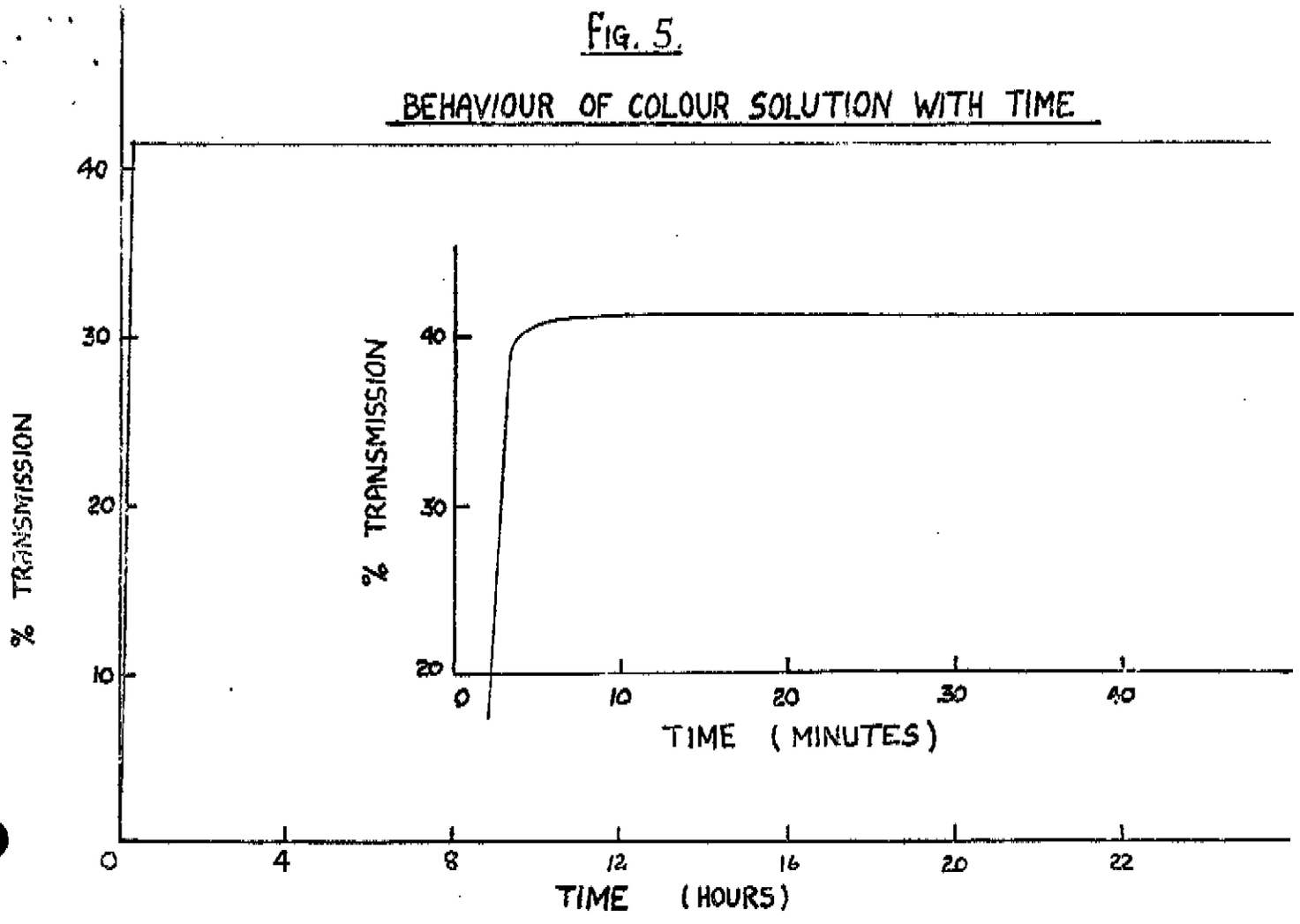

Fig. 6.

TEMPERATURE IN CELLS AS FUNCTION OF TIME

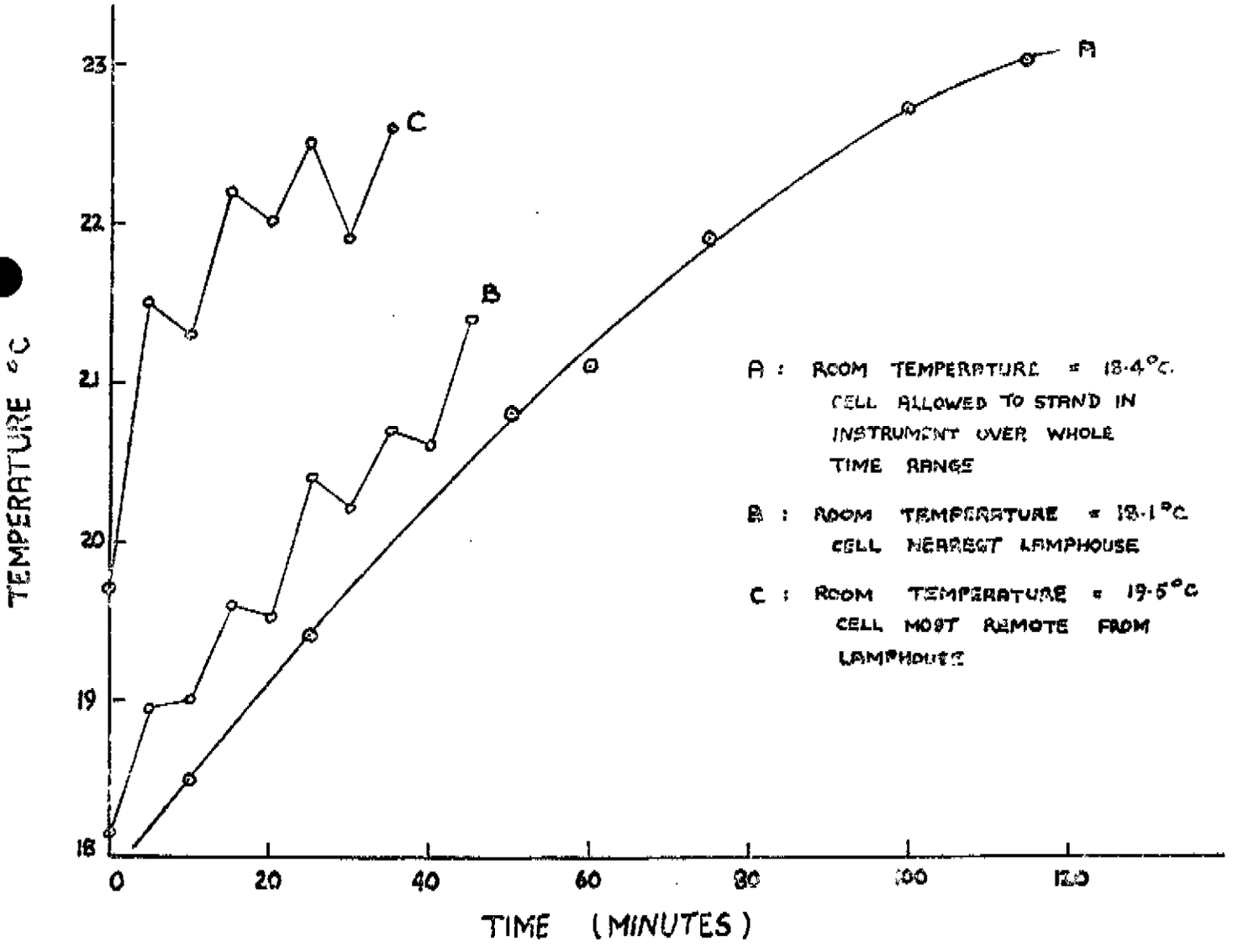

FIG. 7.

COLOUR DEVELOPMENT AS A FUNCTION OF ACIDITY

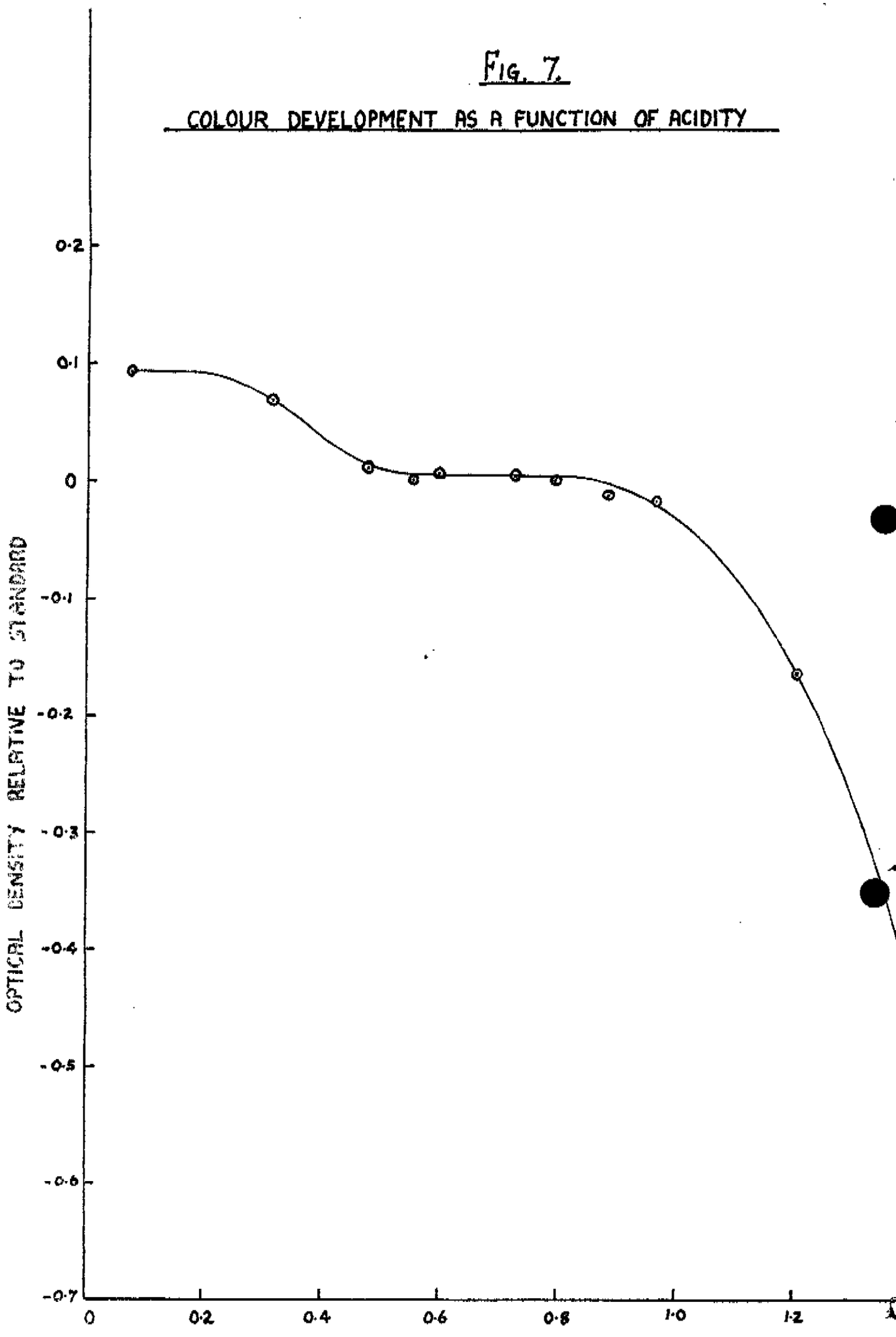

FIG. 8.

COLOUR DEVELOPMENT AS A FUNCTION OF REAGENT CONCENTRATION

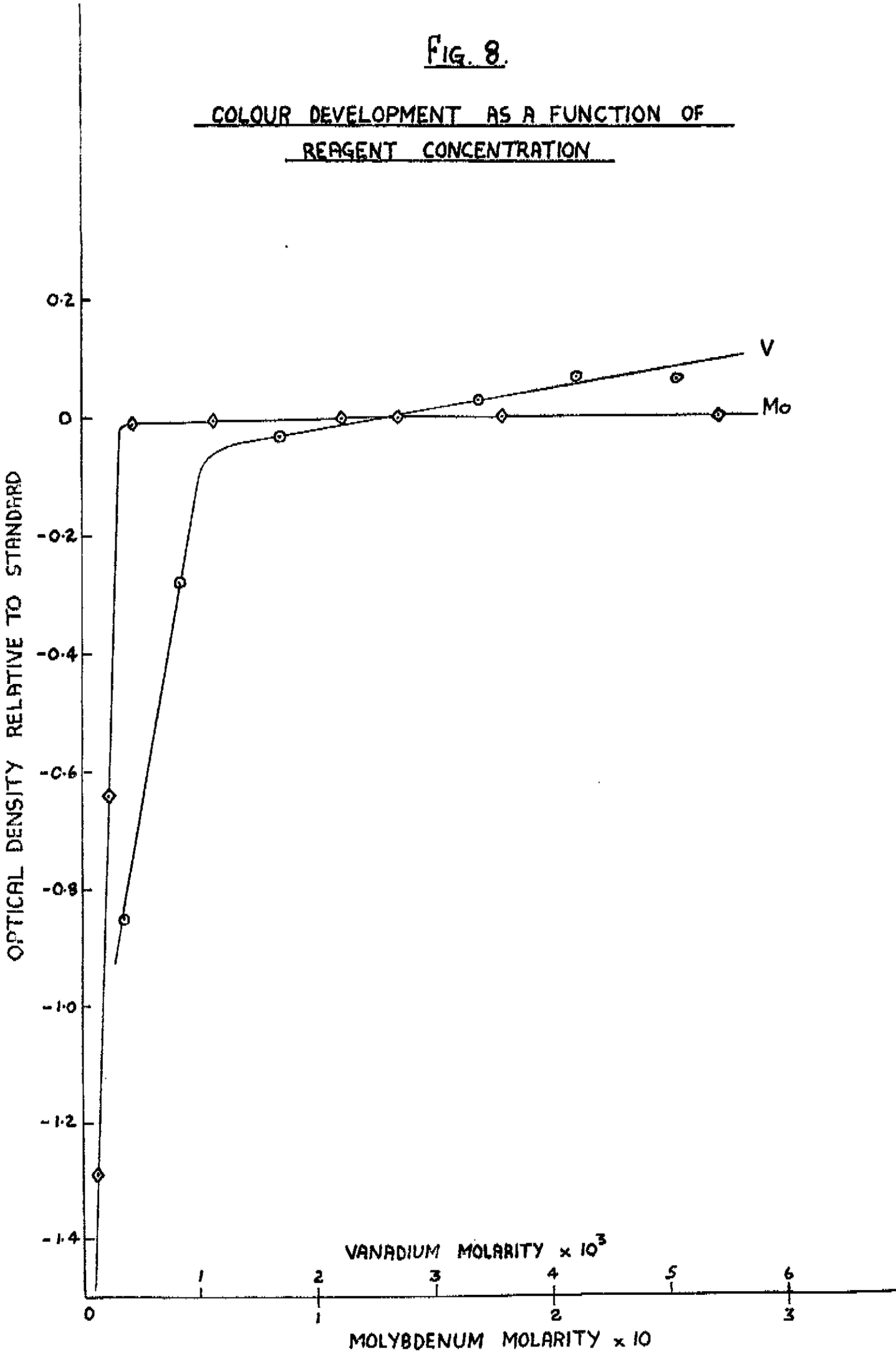

FIG. 9.

EFFECT OF IRON ON COLOUR DEVELOPMENT

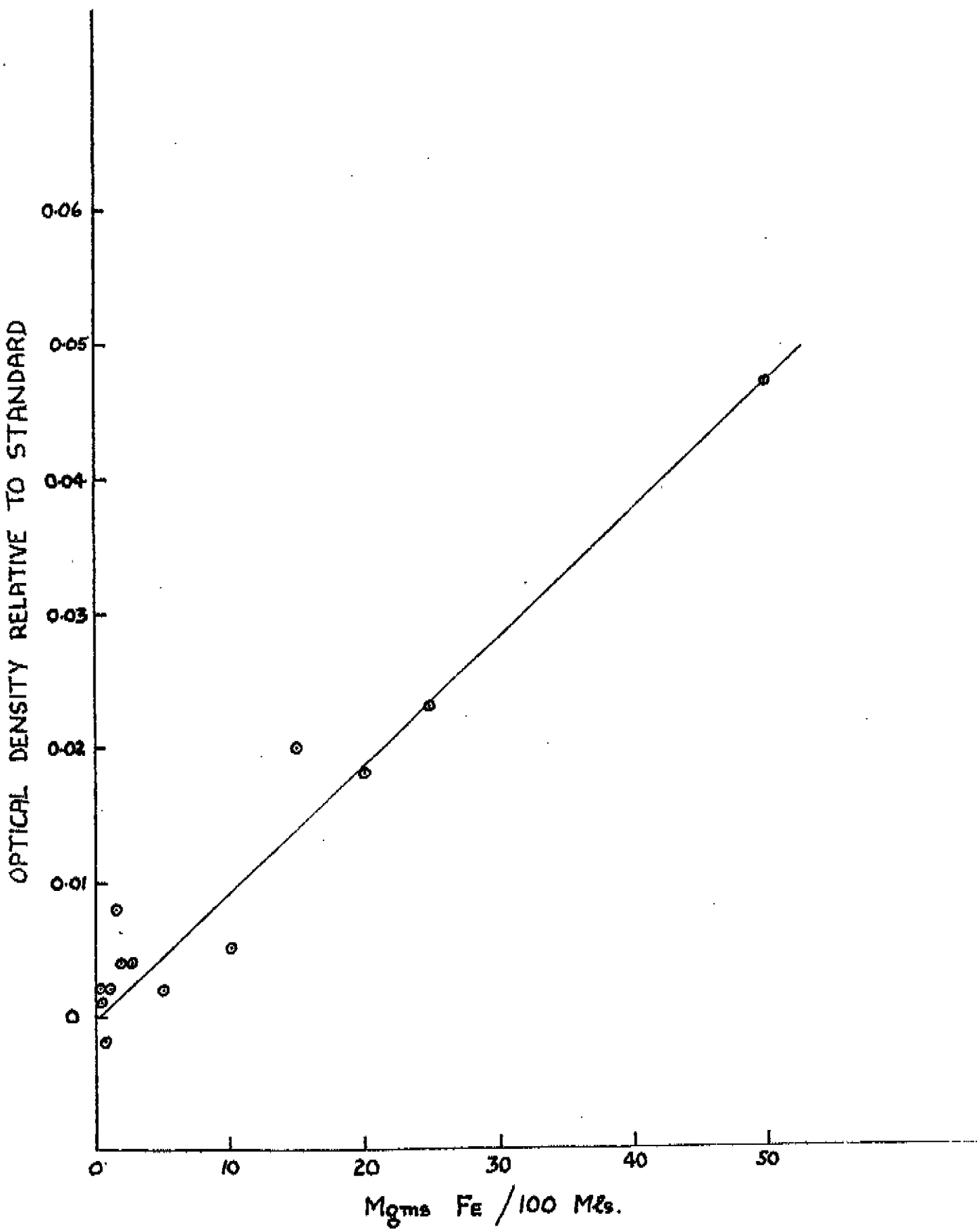

Fig. 10.

EFFECT OF CITRATE ION ON COLOUR DEVELOPMENT

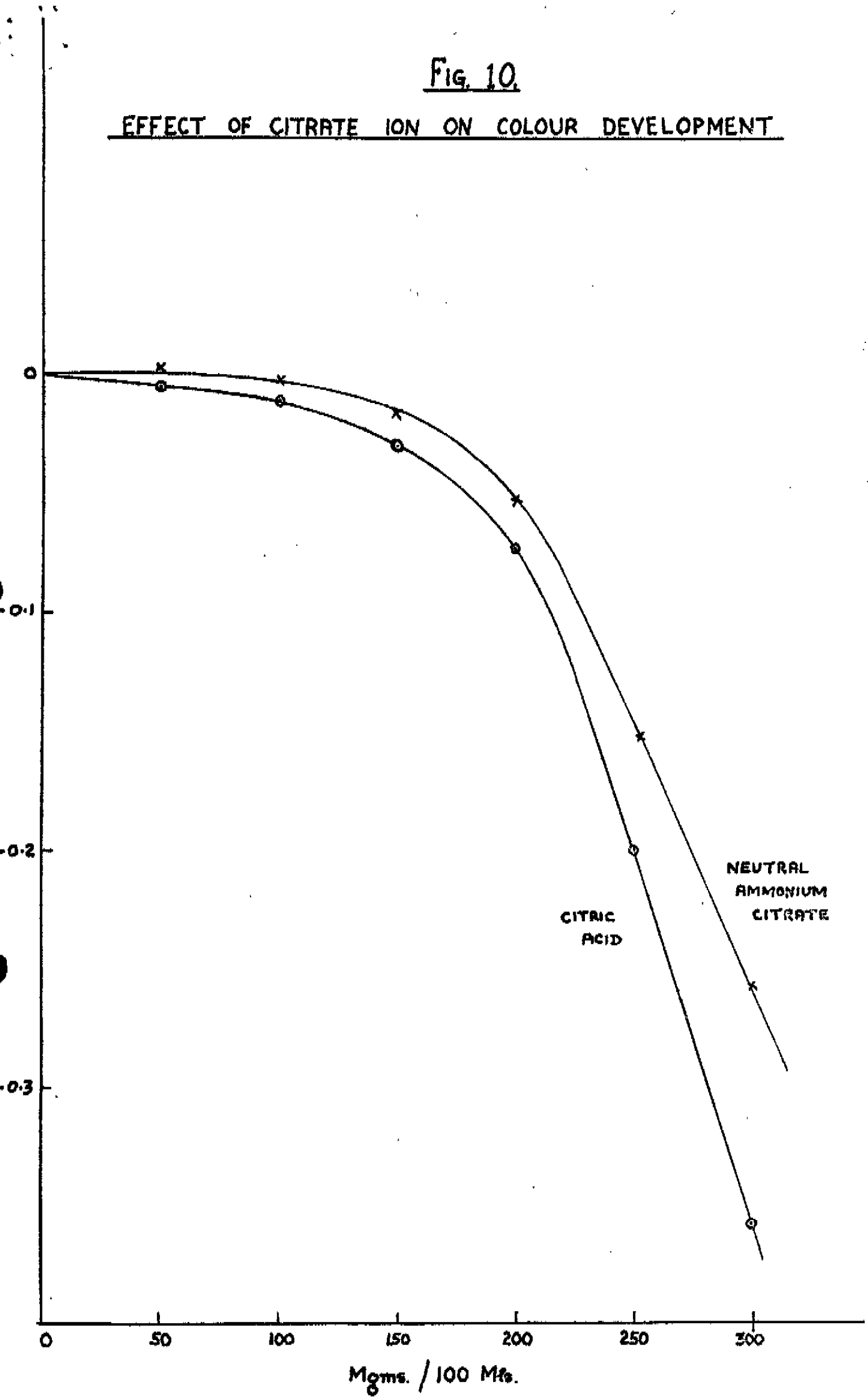

Fig. 11

CALIBRATION GRAPHS