# THE ESTIMATION OF CHLORINE IN WATER BY THE *o*-TOLIDINE METHOD.

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The practice of chlorinating the water supplies of large towns is fast becoming almost universal. On account of the harmful effects of chlorine on the human system and its bleaching action on coloured fabrics, it is very desirable to have a reliable method for the accurate estimation of the small quantities of free chlorine usually present in chlorinated water supplies.

Of the various methods which have been suggested from time to time the best known is the *o*-tolidine method which depends on the yellow coloration produced by the addition of *o*-tolidine to a solution containing free chlorine. This method was developed by Ellms and Hauser (*J. Ind. Eng. Chem.*, 1913, **5**, 915; 1914, **6**, 553) and was subsequently adopted by the American Public Health Association in their standard methods for water analysis. Considerable work has been done concerning the sensitivity of the method as well as its applicability under different conditions. Ellms and Hauser reported that the method yielded positive tests with chlorine up to a minimum concentration of 0·005 part per million (p.p.m.) in aqueous solution, and that there was a gradation of colour with increasing concentrations of chlorine. They proposed a set of permanent colour standards for comparison by the use of solutions of potassium dichromate and copper sulphate of various concentrations. Further, they found that the presence of iron salts or nitrites in the sample of water to be tested did not interfere with the accuracy of the chlorine test unless they were present in rather unusual quantities, namely, to the extent of more than about 1 p.p.m. and 0·09 p.p.m. respectively. Buswell and Boruff (*J. Amer. Waterworks Assoc.*, 1925, **14**, 384; *Br. Chem. Abstr.*, 1926, **B**, 174) confirmed the results of Ellms and Hauser and obtained accurate results in the estimation of chlorine in concentrations 0·02—0·2 p.p.m. by employing the permanent colour standards suggested by the latter authors. Hopkins (*J. Ind. Eng. Chem.*, 1927, **19**, 744) found that although stable salts of manganese like the chloride or the sulphate did not interfere with the estimation of chlorine by the *o*-tolidine method, the presence of permanganate or manganous hydroxide even in very small concentrations rendered the method quite unsuitable. McCrumb (*J. New England Water Works Assoc.*, 1927, **41**, 386; *Br. Chem. Abstr.*, 1928, **B**, 38) emphasised the need for maintaining a pH value of 2 or less in the solution under test because the colour producing substance was a H° indicator giving the desired yellow colour only when the acidity of the solution corresponded to that value. He also devised a comparator set with the help of which he claimed that it was possible to avoid interference due to turbidity and the presence of salts of iron, manganese and nitrites in the sample. Anselmi and Calo (*Annali. Chim. Appl.*, 1930, **20**, 410; *Br. Chem. Abstr.*, 1930, **B**, 1170) investigated several methods for the estimation of chlorine and found the *o*-tolidine method to be the most satisfactory. They recommended its use in estimating quantities ranging from 0·02 to 0·2 p.p.m. and the starch iodide method for higher concentrations. McCrumb and Kenny (*J. New England Water Works Assoc.*, 1928, 42, 410; *Br. Chem. Abstr.*, 1929, **B**, 114) investigated the development and fading of the colour in samples exposed to direct sunlight and found that the results obtained were unreliable unless the sample was kept protected from sunlight in brown bottles. Hanal and Jaffè (*Analyst*, 1932, **57**, 308) noticed the interference of nitrites in the estimation of chlorine by this method and suggested that it should be applied only after ensuring the absence of nitrites by a preliminary test with *m*-phenylenediamine hydrochloride.

The method of testing employed by all the above workers was on the lines originally suggested by Ellms and Hauser (*loc. cit.*), which consist in the addition of 1 c.c. of *o*-tolidine reagent (1 g. in 1 litre of dilute HCl) to 100 c.c. of the sample under examination. A yellow colour is produced if free chlorine is present in the sample and since this colour deepens gradually for about 3 minutes, and then remains unchanged for about 30 minutes, it is matched after the expiry of 5 minutes with the colours given by solutions containing known quantities of chlorine or with the specified potassium dichromate standards. It appears from the preceding account that the estimation of chlorine especially in low concentrations is attended with uncertainties due to (*a*) interfering substances such as salts of iron and manganese and nitrites, (*b*) time required for colour to attain maximum intensity, (*c*) fading of the colour after a certain period, and (*d*) effect of sunlight as well as temperature on the rate of development of colour. This investigation was undertaken with a view to obtain additional data regarding the nature and extent of interference from the above sources and to devise a procedure by following which reasonably accurate results could be obtained.

## EXPERIMENTAL.

*Preparation of Materials.*—The chlorine required for preparing the solutions for estimation was obtained from a steel cylinder containing liquid chlorine.

The pure water employed for the preparation of solutions of chlorine was of the conductivity grade and was obtained by distillation from an alkaline permanganate solution, an all-glass apparatus with a silica condenser being employed for the purpose.

The *o*-tolidine reagent was prepared in the manner recommended by Boruff (*J. Amer. Waterworks Assoc.*, 1928, **20**, 401; *Br. Chem. Abstr.*, 1928, **B**, 246) by dissolving 1 g. of *o*-tolidine in 1 litre of dilute (7·5 p.c.) hydrochloric acid and by using it, 0·01 p.p.m. of chlorine could be detected with certainty.

Solutions with low concentrations of chlorine, *viz.*, less than 1 p.p.m. were always freshly prepared by diluting a stronger solution which had been accurately standardised iodimetrically by titration with sodium thiosulphate using starch as indicator. Comparison of intensities of colour could be performed when the solutions were kept in Nessler jars, but most of the data obtained in this work were obtained with the help of a simple type of colorimeter.

*Rate of development and fading of the colour and influence of temperature on same.*—To 100 c.c. of a sample of water containing 0·2 p.p.m. of chlorine kept in a Nessler jar, 1 c.c. of *o*-tolidine reagent was added and the liquid agitated by a glass stirrer. Part of the liquid was then transferred to the colorimeter tube which had a tap at the side to facilitate withdrawal of small quantities of the solution, and matched against the permanent standard solution (0·2 p.p.m) kept in the other tube at a constant level. The matching was done at regular intervals from the start by noting the height of the column of the test solution required to produce the same colour intensity as the standard, this being done by either withdrawing a part of the liquid from the tube or adding some more of the test solution from the Nessler jar. Duplicate readings usually agreed to within 2 m.m. but since three or four readings were obtained for each setting and at least two experiments were always performed, the accuracy of the measurements was considered to be sufficient for our purpose.

The results obtained in two sets of experiments carried out at 20° and 30° respectively are shown in Table I as well as in Fig. 1.

TABLE I.

| Time minutes | Standard cm. ($h_0$) | Test cm. ($h_1$) | Colour intensity $1/h_1$ | $h_0/h_1$ | Temp. |
|---|---|---|---|---|---|
| 2 | 14.0 | 16·0 | 0·063 | 0·88 | 30 |
| 3 | ,, | 15·0 | 0·067 | 0·93 | 30 |
| 5 | ,, | 14·5 | 0·069 | 0·97 | 30 |
| 5 | ,, | 17·3 | 0·058 | 0·81 | 20 |
| 10 | ,, | 14·2 | 0·070 | 0·99 | 30 |
| 10 | ,, | 15·9 | 0·063 | 0·88 | 20 |
| 15 | ,, | 14·2 | 0·070 | 0·99 | 30 |
| 20 | ,, | 14·2 | 0·070 | 0·99 | 30 |
| 20 | ,, | 14·9 | 0·067 | 0·94 | 20 |
| 25 | ,, | 14·2 | 0·070 | 0·99 | 30 |
| 30 | ,, | 14·2 | 0·070 | 0·99 | 20 |
| 35 | ,, | 14·5 | 0·069 | 0·97 | 30 |
| 45 | ,, | 15·0 | 0·067 | 0·93 | 30 |
| 45 | ,, | 14·2 | 0·070 | 0·99 | 20 |
| 60 | ,, | 15·5 | 0·064 | 0·90 | 30 |
| 60 | ,, | 14·5 | 0·069 | 0·97 | 20 |
| 75 | ,, | 17·1 | 0·059 | 0·82 | 30 |
| 90 | ,, | 18·4 | 0·055 | 0·76 | 30 |
| 90 | ,, | 15·6 | 0·064 | 0·88 | 20 |
| 120 | ,, | 21·3 | 0·047 | 0·66 | 30 |
| 120 | ,, | 17·8 | 0·056 | 0·79 | 20 |
| 150 | ,, | 24·7 | 0·040 | 0·57 | 30 |
| 150 | ,, | 20·4 | 0·049 | 0·69 | 20 |

The results given in the above table and the curves in Fig. 1 indicate that a certain period of time elapses before the colour reaches

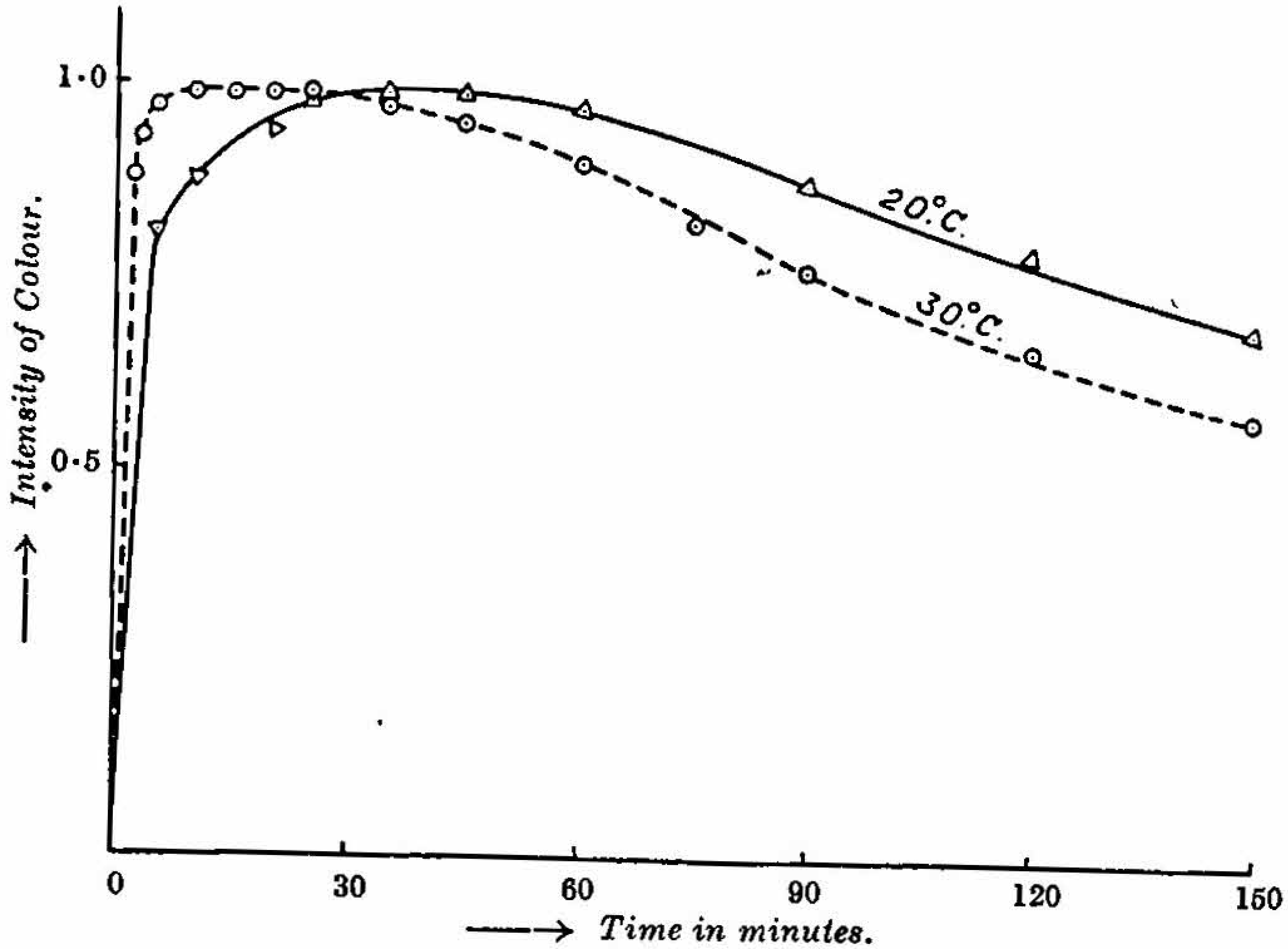

**Fig. 1.**

**Development and Fading of Colour with Chlorine (0·2 p.p.m.) at 20°C. and 30°C.**

its maximum intensity at which it remains steady for about 15 minutes and then begins to fade gradually. Further, it is apparent that the colour attains maximum intensity much more quickly at 30° than at 20° and that the fading process sets in at different intervals. It appears therefore necessary that whereas in experiments carried out at 20° the comparison should be made after about 30 minutes but within 45 minutes, in those at 30°, it should be done earlier, *viz.*, between 10 and 25 minutes. These conditions were adhered to in all our subsequent determinations.

*Proportionality between colour intensity and chlorine concentration.*—Samples of water containing 0·1, 0·2,....up to 1·0 p.p.m. of chlorine in water were prepared in the manner mentioned earlier and the colours developed on the addition of *o*-tolidine to the various samples were matched in the colorimeter with dichromate solutions which according to the tables of Ellms and Hauser (*loc. cit.*) were equivalent to 0·2, 0·5 and 0·8 p.p.m. of chlorine. The three different colour standards mentioned above were taken in order that the colours compared might in every case be of the same order of intensity, as otherwise the matching operation would be inconvenient. The results obtained are shown in Table II and also in Fig. 2.

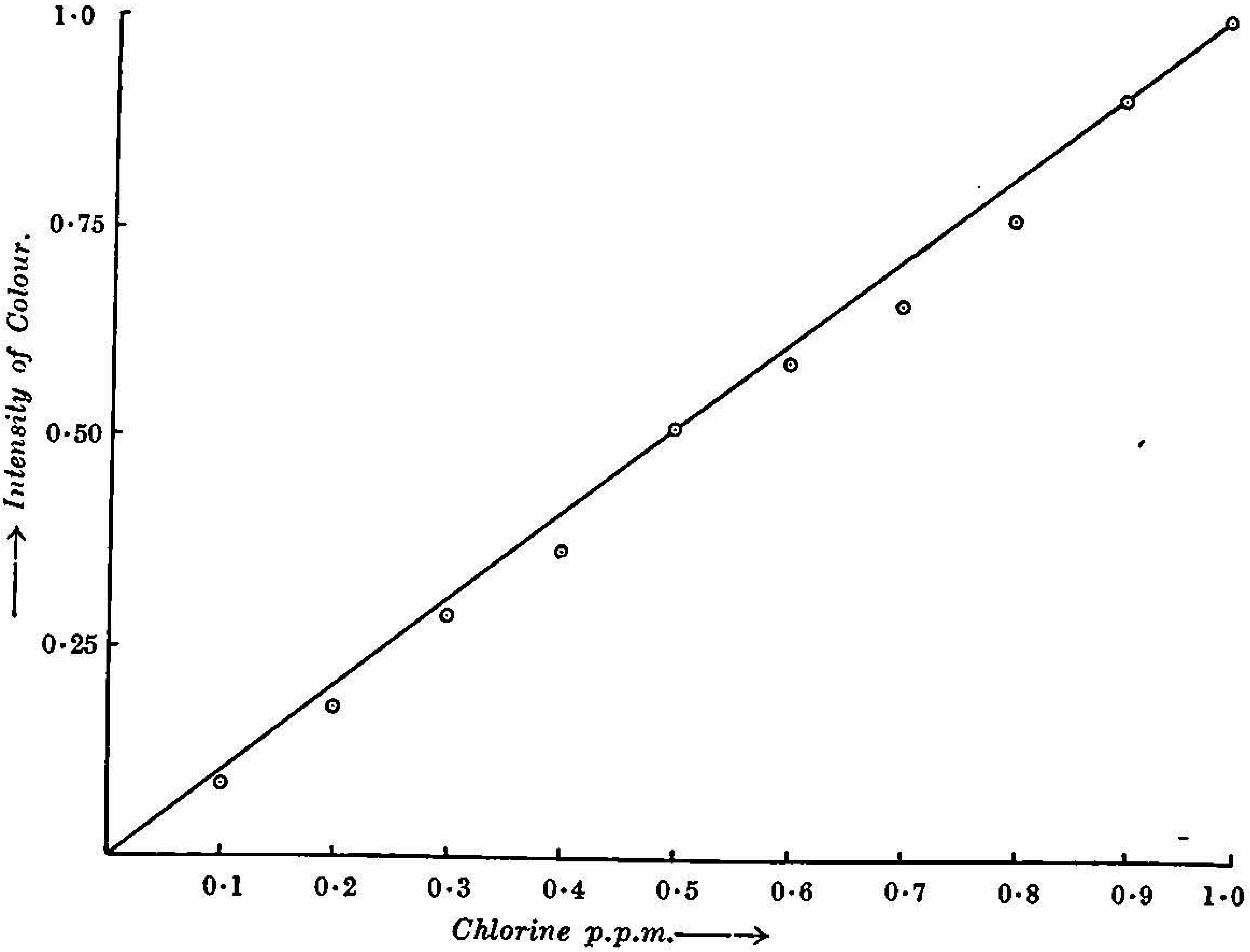

**Fig. 2.**

Variation of Intensity of Colour with strength of Chlorine Solution.

TABLE II.

| Permanent standard p.p.m. | Height of standard cm. | Chlorine p.p.m. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0·1 | 0·2 | 0·3 | 0·4 | 0·5 | 0·6 | 0·7 | 0·8 | 0·9 | 1·0 |
| | | Height of solution in cm. | | | | | | | | | |
| 0·2 | 11·0 | 22·0 | 11·0 | 6·9 | .. | .. | .. | .. | .. | .. | .. |
| 0·5 | 6·7 | .. | .. | 11·7 | 9·4 | 6·5 | 5·6 | .. | .. | .. | .. |
| 0·8 | 7·0 | .. | .. | .. | .. | .. | 9·1 | 7·9 | 6·9 | 5·9 | 5·1 |

The results given in the above table might be recalculated in order to express all the heights with reference to that of 0·2 p.p.m. solution, *viz.*, 11·0 cm., and the figures so obtained are given below in Table III.

## TABLE III.

| Chlorine p.p.m. | Height in matching tube $h$ | Colour intensity $1/h$ | $(1/h)/0\cdot527$ |
|---|---|---|---|
| 0·1 | 22·0 | 0·045 | 0·09 |
| 0·2 | 11·0 | 0·091 | 0·17 |
| 0·3 | 6·9 | 0·145 | 0·28 |
| 0·4 | 5·55 | 0·182 | 0·35 |
| 0·5 | 3·85 | 0·263 | 0·50 |
| 0·6 | 3·3 | 0·303 | 0·58 |
| 0·7 | 2·9 | 0·345 | 0·65 |
| 0·8 | 2·5 | 0·400 | 0·76 |
| 0·9 | 2·15 | 0·476 | 0·90 |
| 1·0 | 1·985 | 0·527 | 1·00 |

It is seen from Table III and more clearly from Fig. 2 that the intensities of colour developed in solutions of chlorine are roughly proportional to their chlorine concentration in the range studied.

*The reliability of the method in presence of salts of iron and manganese and nitrites.*—The reliability of the *o*-tolidine method in presence of ferric salts was investigated as follows: Several lots of chlorine water of known concentration (0·2 p.p.m.) were freshly prepared and to these were added a standard solution of ferric sulphate in such quantities that chlorine solutions (0·2 p.p.m.) containing various known quantities of iron up to 3·3 p.p.m. were obtained. *o*-Tolidine reagent was added to these solutions and the colorimetric comparison made with the permanent standard solution (0·2 p.p.m.) at definite intervals for a period of 2½ hours. The results obtained are shown in Table IV and also in Fig. 3.

### TABLE IV.

*Chlorine solution employed : 0·2 p.p.m.*

| Time minutes | Fe (p.p.m.) | | | | |
|---|---|---|---|---|---|
| | 0·0 | 0·28 | 0·56 | 1·40 | 2·80 |
| | Intensity of colour | | | | |
| 2 | 0·88 | 0·90 | 0·69 | 0·75 | 0·84 |
| 3 | 0·93 | .. | .. | .. | 0·96 |
| 5 | 0·97 | 0·95 | 0·81 | 0·92 | 1·07 |
| 7 | .. | .. | .. | 0·96 | .. |
| 8 | .. | .. | .. | .. | 1·24 |
| 10 | 0·99 | 0·98 | 0·89 | 1·07 | 1·40 |
| 15 | 0·99 | 1·00 | 0·96 | 1·20 | 1·70 |
| 20 | 0·99 | .. | .. | 1·36 | 2·09 |
| 25 | 0·99 | 1·00 | 1·05 | 1·52 | 2·50 |
| 30 | .. | .. | .. | 1·69 | .. |
| 35 | 0·97 | .. | .. | .. | 2·74 |
| 40 | .. | 1·00 | 1·12 | .. | .. |
| 45 | 0·93 | .. | .. | 2·09 | 3·04 |
| 1 hr. | 0·90 | 0·91 | 1·12 | 2·30 | 3·18 |
| 1¼ ,, | 0·82 | .. | 1·06 | .. | .. |
| 1½ ,, | 0·76 | 0·84 | 0·99 | 2·75 | 3·42 |
| 2 ,, | 0·66 | 0·69 | 0·84 | .. | .. |
| 2½ ,, | 0·57 | 0·49 | .. | .. | .. |

The figures given in the above table and the curves in Fig. 3 clearly indicate that the results obtained are accurate only if iron is present in quantities not exceeding 0·28 p.p.m. while larger quantities of iron interfere in the determinations and the results obtained by comparison at the stage of maximum colour intensity are abnormally high. This

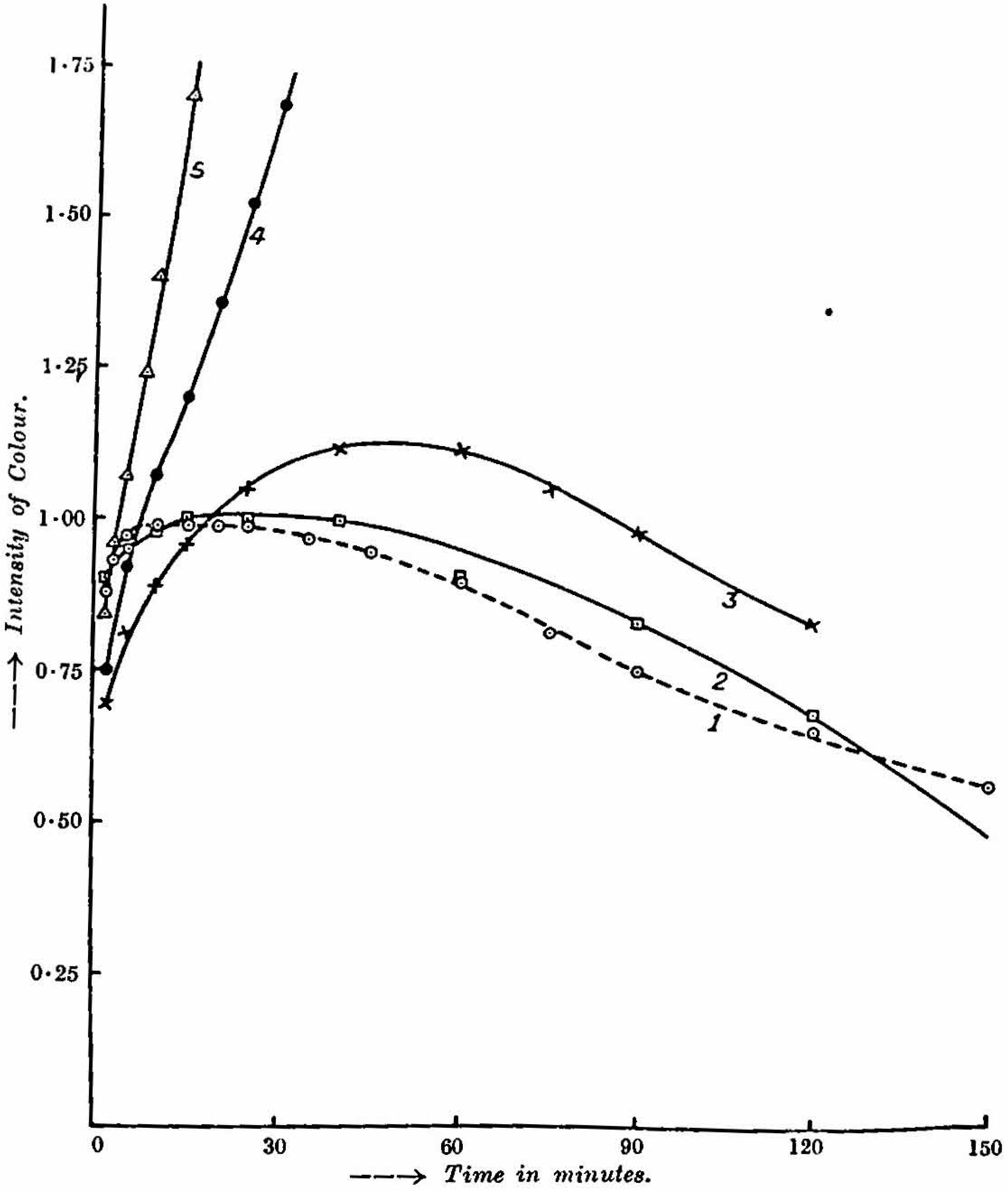

**Fig. 3.**

The Influence of Iron on the Estimation of Chlorine.

1—Chlorine (0·2 p.p.m.)
2— do. do. + Iron (0·28 p.p.m.)
3— do. do. + do. (0·56 do. )
4— do. do. + do. (1·40 do. )
5— do. do. + do. (2·80 do. )

is at variance with the observation of Ellms and Hauser (*loc. cit.*) that correct results could be obtained in presence of iron up to a maximum concentration of 1 p.p.m.

The next point to be investigated was whether the high values obtained in presence of iron could be corrected for, if the iron content of the solution was known and also the colour intensity which that quantity of iron would produce with *o*-tolidine in water entirely free from chlorine. This was done as follows:—To several lots of distilled water contained in Nessler jars was added a standard solution of ferric sulphate in such quantities that solutions containing respectively 0·28, 0·56, 1·40 and 2·80 p.p.m. of iron were obtained. To these solutions *o*-tolidine was added and the coloration developed was matched against a permanent colour standard. The results obtained are shown in Table V.

TABLE V.

| Time minutes | Fe (p.p.m.) | | | |
|---|---|---|---|---|
| | 0·28 | 0·56 | 1·40 | 2·80 |
| | Intensity of colour | | | |
| 10 | .. | .. | .. | 0·19 |
| 15 | .. | .. | 0·15 | 0·35 |
| 20 | .. | .. | 0·22 | .. |
| 25 | .. | .. | 0·30 | 0·57 |
| 30 | .. | .. | 0·36 | 0·77 |
| 45 | .. | 0·23 | 0·67 | 1·22 |
| 60 | .. | .. | 1·00 | 1·71 |
| 75 | .. | 0·37 | 1·31 | .. |
| 90 | 0·20 | .. | 1·49 | 2·60 |
| 105 | .. | 0·51 | 1·73 | .. |
| 120 | 0·25 | .. | .. | 3·11 |
| 135 | .. | 0·63 | 2·03 | .. |
| 150 | 0·29 | 0·68 | 2·03 | 3·11 |
| 180 | 0·28 | .. | .. | 2·98 |
| 210 | .. | 0·58 | 1·61 | .. |
| 240 | 0·24 | .. | .. | 2·59 |

The results given in Table V indicate that a coloration is produced on the addition of *o*-tolidine to water containing iron even in such small concentrations as 0·28 p.p.m. although a considerable period elapses before it is noticeable. With higher concentrations of iron the development of colour is more rapid.

A few experiments carried out on the same lines as mentioned above showed conclusively that manganese sulphate, even when present in high concentrations (100—1000 p.p.m.) did not interfere with the accuracy of the chlorine determination.

The extent to which nitrites interfere was ascertained by carrying out a few experiments in which small quantities of nitrites were added to a chlorine solution of known concentration (0·2 p.p.m.). The colour produced by *o*-tolidine in presence of nitrites was brownish and could not be matched with the dichromate standards. This point was not investigated further because it was evident that even small concentrations of nitrites rendered the estimation difficult.

## SUMMARY.

The following points have been elucidated from a study of the *o*-tolidine method for the estimation of chlorine :—

(1) The colour developed on the addition of *o*-tolidine to solutions of chlorine in water takes an appreciable time to attain maximum intensity at which it remains steady for some time, and then fades gradually, the rates of the two processes depending on the temperature of the solution.

(2) The most suitable time for making the comparison of colour intensities depends on the temperature and is between 10–25 minutes at 30° and 30–45 minutes at 20°.

(3) The presence of ferric ion in solution yields high results except when it is present in concentrations of less than about 0·3 p.p.m. Attempts to devise a correction factor for this interference were unsuccessful.

(4) The method is inapplicable to samples containing nitrites even in low concentrations.

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