INVESTIGATIONS OF LINEAR STARCH-HALIDE COMPLEXES

by

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INTRODUCTION AND LITERATURE REVIEW

The color reaction of solutions of iodine and iodide anion with starch dispersions has been known for more than 150 years. Hanes (1) seems to have been the first to postulate the structure of the starch iodine complex as a helical arrangement of linear starch around iodine molecules with hydroxyl groups extended outward, so that iodine is in an essentially hydrocarbon surrounding. Rundle et al. (2) suggested in 1944, that the helix coil consisted of six glucose residues per loop with each loop enclosing one iodine molecule, by showing that dry linear starch takes up 26% of its weight in iodine vapor. The x-ray powder diagram yields a unit cell which confirms the helical structure of the complex. Szejtly et al. (3) are of the opinion that in aqueous solution linear starch assumes the shape of a loose or deformed helix. The long molecules of amylose appear to form several short segments of 110- 130 glucose units rather than one long helix per starch molecule. The short segments are connected by random segments. Therefore, the dissolved amylose complex molecules contain more than one independent polyiodide chain (3). The random segments between helical segments are assumed by Watanabe (6) to be composed of 14 glucose units. Others, (4) feel that the linear starch molecules are in the extended form and coil only in the presence of iodine or similar compounds.

Triiodide ions are thought to enter the interior of the helix loops yielding a polyiodide "rod" with the amylose helix tightening around the rod, reinforced by hydrogen bonding (5). Watanabe et al. (6) found that the polyiodide rod is composed of 11 iodine molecules with both ends in the I_3^- form: $I_3^-(I_2)_9I_3^-$. If this is consistent with six glucose units per helical coil, the helical segment will be composed of 66 glucose units provided that one iodine molecule per turn of the helix is maintained (6).

Lambert and Zitomer (7,8) postulate that the complex is formed by initial iodine penetration of one or more triiodide ions. Under these conditions more than one triiodide per starch helix must be present before a blue color will be produced.

Ono et al. (9) found that the iodine linear starch reaction required an aqueous medium of at least 26 moles/liter of water to form a blue color. When the reaction in water is followed spectrophotometrically the 290 and 255 mμ peaks due to triiodide are suppressed with the addition of starch to the solution (10). The extinction coefficients of these peaks are:

	I_3^-	Starch Complex
288 mμ	40,000	7,000
355 mμ	26,400	12,000
620 mμ	-----	43,000

Formation of the blue complex depends upon the iodine and iodide concentrations, the concentration of the amylose, and the degree of polymerization in the starch molecules. As noted by Laitinen (11), the work of Lambert (12) indicates that linear starch interacts with triiodide in solution and that excess iodide is not required to give a blue color. In 1960, Miyazaki (13) found that the blue maximum of the complex shifts to a lower wavelength as the amount of iodide is increased. Baldwin et al. (14) concluded that increasing the iodine concentration shifts the 620 mμ maximum to shorter wavelengths. When iodine and iodide concentrations are changed simultaneously the migration shows both the effects of iodine and iodide. Sufficient amounts of both must be present to produce a linear relationship between the color intensity and the amount of starch (14). At low concentrations of iodide, an increase in the concentrations does not change the maximum wavelength of absorptions for the complex, but does increase the intensity of the absorption. With high

concentrations of iodide, the wavelength maximum shifts significantly to the lower wavelengths with an accompanying decrease in the maximum absorption (32). Similar results were obtained by the addition of NaCl, methanol, and dimethyl sulfoxide.

Lambert (15) found that the reagent is nearly pH independent at pH values below 7. At a pH of approximately 7.5 a white precipitate, $Cd(OH)_2$ is formed if CdI_2 is used to prepare the starch to prevent degradation and as a source of iodide. Jarowenko (5) states that hydrolytic breakdown of starch begins at pH 2.5. Lambert (15) studied the temperature dependence of the starch iodine complex formation. More intense color developed at cooler temperatures but regardless of the temperature the color developed in 15-20 minutes, if below the retrogration temperature of the starch. Except for very precise work, temperature control is not critical.

The effect of chloride ion has been studied by Miyazaki (13), who showed that addition of chloride to definite amounts of the amylose-iodine complex increased the absorption of the complex.

Senti et al. (16) have shown that amylose complexes with bromide ion in a ratio of one mole of potassium bromide to two glucose units. The KBr complex was thought to fit the helical explanation similar to I_2 complexation (16). Greenwood and Rossetti (17) studied the spectra of ICN^- complexed with starch to confirm the "chair" conformation for the glucose units. No other halide complexes have been confirmed. Minkus (18) found that linear starch complexes with fatty acids in a way similar to iodine, and that dipole forces are responsible for the molecular inclusion complex which finds the fatty acid in the center of the starch helix.

Bailey et al. (24) found that the wavelength of the maximum absorption of the amylose-iodine complex is related to the chain length of the amylose. The minimum chain length necessary for an observer to see the blue color is 45 glucose units (5). The wavelength of the absorption maximum is 540 mμ for the short chains of about 45 units and 610-675 mμ for the longer chains (19). The color of the complex seems to be mainly a function of the degree of polymerization in the lower polymerization range (5, 19). Above 72 glucose units the color is a function of triiodide concentration (5, 19). Gilbert and Marriot (29) state that ions of the type $3I_2 \cdot 2I^-$ must be present in a linear resonating form and that red complexes which are formed by the shorter amylose chains are due to their inability to stabilize an ion of this size (29).

Measurements of osmotic pressure have been widely used for determining the molecular weights of amylose, but more frequently the limiting viscosity number in dimethyl sulfoxide is used to calculate the viscosity-average molecular weight (6). The average molecular weight used in this study was calculated by Watanabe et al. (6) to be 10^6 g/mole. This is consistent with other values for potato starch amylose (20).

The line formed by plotting absorbances versus concentration for the iodine-starch reaction does not follow Beer's Law because it does not pass through the origin (12). The calibration curve for the determination of iodide by reaction with excess iodate and complexation with starch also shows a threshold (12). The threshold can not be overcome by increasing the iodide concentration, the starch concentration, or by changing the pH (12). Drey (22) has postulated that the reason for this constant threshold is caused by hydrolysis of iodine to hypoiodous acid and that a minimum concentration of hypoiodous acid is necessary before reaction of iodine with starch can occur.

Mokhnach et al. (23) found a characteristic IO^- absorbance band at 360 mμ in a starch iodine solution. They concluded that when starch is added to an aqueous iodine solution the following reactions take place:

$$I_2 + H_2O \longrightarrow IO^- + 2H^+ + I^-$$

$$I_2 + I^- \longrightarrow I_3^-$$

$$I_3^- + \text{linear starch} \longrightarrow \text{complex}$$

This sequence of reactions gives one explanation for the threshold concentration but has not been accepted without question.

Even though much has been studied about the reaction between starch and triiodide, neither the mechanism nor the actual complex species has been elucidated. This study was designed to derive as much information about the reaction of linear starch with triiodide as possible and to correlate it to the structure and reactions known at the present. Of primary interest was to find the number of iodine molecules per helical coil necessary to form the characteristic blue color of the complex and the influence of pH and iodide concentration upon the formation and the stability of the complex. The possibility of formation of a complex with other halides or polyhalides suggested work in this area.

EXPERIMENTAL:

Reagents: All solutions were prepared in deionized water unless otherwise noted. All chemicals used were of purest available grade and were used as obtained from the supplier.

Linear starch was recrystallized three times from n-amyl alcohol as per method of Lambert et al. (27). It was found to have a longer shelf life when sealed in a tightly stoppered container with a trace of n-amyl alcohol.

Cadmium iodide-linear starch reagent was prepared by addition of 11.00 g CdI_2 and 2.50 g of linear starch to a liter of water (15). The reagent was not heated as per Lambert (15) other than to warm the solution to dissolve the starch and form a clear solution.

Chlorine demand free water was prepared by irradiation of deionized water containing chlorine gas to sunlight for three days (28).

Tetramethylammonium tribromide, $(CH_3)_4NBr_3$, (26) was prepared by addition of 4.0 g of $(CH_3)_4NBr$ in a small quantity of 1:1 acetic acid and ethanol, to 4.0 g of bromine. Bright orange crystals of product were recrystalized from a warm solution of ethanol containing a little dissolved bromine. The product must be kept in a tightly stoppered container.

Tetraethylammonium diiodobromide, $(C_2H_5)_4NBrI_2$, (26) was prepared by addition of 4.70 g of finely powdered iodine to 2.50 g of $(C_2H_5)_4NBr$ dissolved in 40 ml of boiling ethanol. Upon cooling crystals of the product crystallized from the solution. These were recrystallized twice from hot ethanol to yield dark crimson crystals.

Tetramethylammonium dibromoiodide, $(CH_3)_4NBr_2I$, was prepared by the addition of 2.8 g of bromine, dissolved in twice its volume of acetic acid to 3.5 g of $(CH_3)_4NI$ in 35 ml of warm ethanol. Upon cooling the product

crystallized out of solution and was recrystallized from hot ethanol yielding reddish orange crystals (26).

Tetramethylammonium triiodide, $(CH_3)_4NI_3$, (26) was prepared by addition of 4.0 g of iodine and 3.1 g of $(CH_3)_4NI$ to hot ethanol. Upon cooling, crystals of the product separated with a dark metallic color.

EQUIPMENT:

Spectrophotometer: Perkin-Elmer Coleman 124, with recorder.

EXPERIMENTAL:

To assure uniformity in the way results were obtained, several conditions were used consistently throughout this research. All values represented in this paper are averages of five replicate determinations. A development time of 15 minutes was allowed for all reactions involving triiodide and linear starch reagent.

To determine the effect of the starch concentration upon the reaction of triiodide with linear starch, solutions containing triiodide in concentrations from 0.7 to 7.0 ppm were allowed to react with concentrations of starch reagent varying from 2.0 to 5.0 ml per 100 ml of total solution. Absorbance values were determined at the 615 mμ maximum.

The sensitivity of the linear starch-cadmium iodide reagent has not been conclusively established. To determine the sensitivity, chlorine demand free water was used to make all solutions. Triiodide solutions were made by dilution of 1000 ppm I_3^- stock solution. Concentrations of triiodide ranged from 1.7 to 0.2 ppm with 3 ml of the starch reagent per 100 ml total solution. Another method to get I_2 into solution is to oxidize the iodide in the starch reagent to I_2 with hypochlorite. Hypochlorite, from "Zonite", a commercially available 0.87% hypochlorite solution, was added to 3.0 ml of starch reagent and diluted to 100 ml with chlorine demand free water. Dilution of Zonite ranged from 10.0 to 0.01 ppm corresponding to 35.7 to 0.036 ppm I_2 produced in the solution by the oxidation process. The absorbance values of the solutions were determined at 615 mμ.

To determine the pH dependence of the reaction involving the formation of the starch-iodine complex, a solution of 6 ppm of I_3^- was complexed with a 3-ml sample of linear starch reagent and diluted to 100 ml. They were

acidified to pH values ranging from 1.0 to 6.58 with 0.1 N HCl and absorbance values were determined at 615 mμ.

It has been previously reported that the concentration of iodide in solution with the linear starch-triiodide complex has little effect upon the formation of the complex (12). As stock solutions of I_2 require an excess of iodide to make the iodine soluble, stock solutions of varying ratios of I_2 to I^- were prepared and diluted to the part per million range, after which absorbance values were compared. The concentration of I_2 was varied between 1.0 and 7.0 ppm and the ratios of I^- to these values were 15 to 100. Two ml of the starch solution were used for each 100 ml of total solution. Absorbance values were determined for each solution at the 615 mμ maximum.

The complex formed between linear starch and triiodide is a large anion which precipitates from solution in the presence of a cation. Cations of various sizes were allowed to interact with linear starch triiodide complex until precipitation was perceivable. The cations used to precipitate the complex were K^+, Cs^+, Rb^+, tetramethylammonium cation, $(CH_3)_4N^+$, tetrabutylammonium cation, $(C_4H_9)_4N^+$, tetrabutylphosphonium cation, $(C_4H_9)_4P^+$, and benzyltriphenylphosphonium cation, $PhCH_2(Ph)_3P^+$. In each case 50 ml of the starch complex was prepared by the addition of 3 ml of the linear starch-cadmium iodide reagent to 3 ml of 100 ppm triiodide and dilution to 50 ml with deionized water. The cations were added by titration of the complex solution with standard cation solutions until cloudiness of the precipitate could be seen.

Linear starch complexes with other halides and polyhalides were also studied. Tribromide, dibromoiodide, and diiodobromide salts were prepared as above and allowed to react with linear starch solution. The diiodobromide

decomposed in water solution to give starch solution the characteristic triiodide blue color, therefore, no further work was done with it. Starch solutions used with these systems were made by addition of 0.250 g of linear starch to hot water. The solutions were then filtered and diluted to 100 ml. The reagent became turbid after two to three days exposed to the normal atmosphere so to insure freshness of the solution it was prepared fresh daily.

Tribromide was studied both complexed with starch and as the free tribromide in solution. Maximum absorbance readings at 257 mμ were recorded for tribromide concentrations of 50, 100, and 200 ppm in solution containing 3 ml of starch reagent and also for the pure tribromide solutions. Absorbance values were determined after 24 and 48 hours of development time to see if the tribromide might have a long development time. The pH of the tribromide solutions with starch was adjusted to values of 1, 2, 3, 4, 5, and 6 by dropwise addition of 0.1 N HCl and the absorbance values were recorded at 257 mμ.

The dibromoiodide system was studied in a similar manner and exhibited maximum absorbances for the pure dibromoiodide solution at 254 mμ and at 420 and 540 mμ for dibromoiodide with starch reagent in solution with it. Concentrations of dibromoiodide used were 50, 100, 200, and 300 ppm with 3 ml of starch reagent per 100 ml of total solution. Absorbance values were determined every two hours for a 48 hour period of time to observe the development of the maximum absorbance values for each absorption peak of the starch solution of dibromoiodide.

RESULTS AND CONCLUSIONS:

The effect of the starch concentration upon the formation of the triiodide complex is reflected in Figs. 1 and 2. Figure 1 shows the limits of the starch complexing with triiodide. Two ml of starch reagent contains 5.0×10^{-6} moles of linear starch (molecular weight estimated to be 10^6 g/mole) and 6.0×10^{-4} moles of CdI_2. Point A in Fig. 1 is at about 5.5 ppm of triiodide and is the intersection of the line representing the concentration of triiodide before complexation is complete, and the line after complete complexation has occurred. For 2.0 ml of the starch per 100 ml of standard triiodide solution, both figures show an absorbance of 0.74 as the constant value of the absorbance after complexation is completed. Two ml of starch complexing with 5.5 ppm triiodide gives 2.16×10^{-5} moles of I_2 per 5.0×10^{-9} moles of starch. This compares to Watanabe et al. (6) who obtained a value of 2.1×10^{-5} moles of I_2 per 2.0×10^{-8} moles of amylose. When 3 ml and 5 ml of starch reagent were used no limiting value could be seen in the 0 to 2 absorbance range. Therefore, unless otherwise noted, 3 ml of starch reagent was used per 100 ml of total solution throughout the remainder of the analysis.

The sensitivity of the linear starch-CdI_2 reagent to I_2 was determined by complexation of a standard KI_3 solution with linear starch reagent. The minimum concentration at which the blue color was visually detectable was accepted as the sensitivity of the reagent. When chlorine demand free water was used, a blue color could be seen at 0.2 ppm I_3^- but no absorbance value could be recorded. The 0.3 ppm solution gave an absorbance of 0.08 at 615 mμ. Hypochlorite, commercially available as "Zonite", 0.87%, was used to oxidize I^- to I_2 directly in the solution, which then forms the triiodide complex

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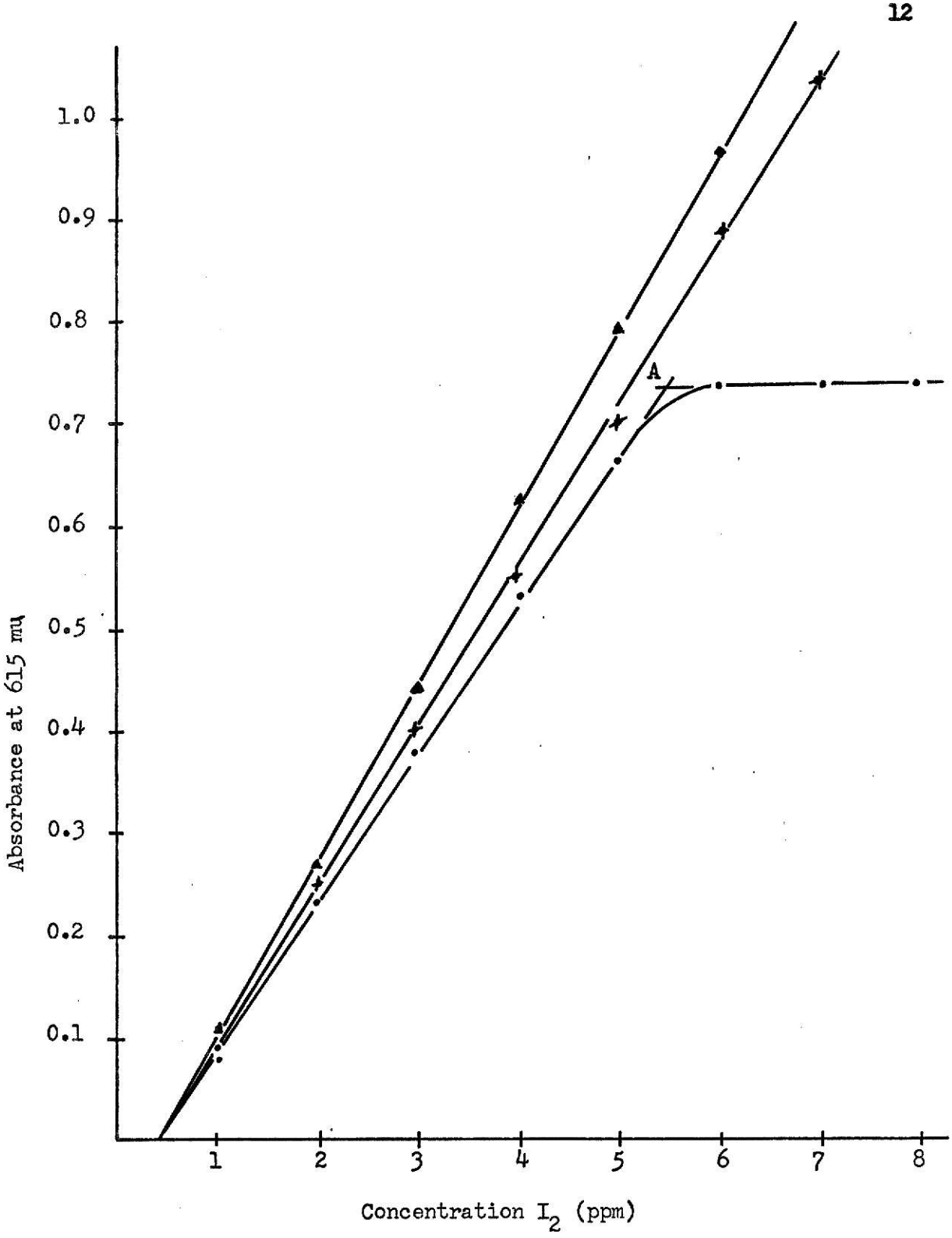

Fig. 1: Concentration versus Absorbance for I_3^--linear starch solutions with 2 ml (--•--), 3 ml (--x--), and 5 ml (--▲--) starch reagent per 100 ml of total solution.

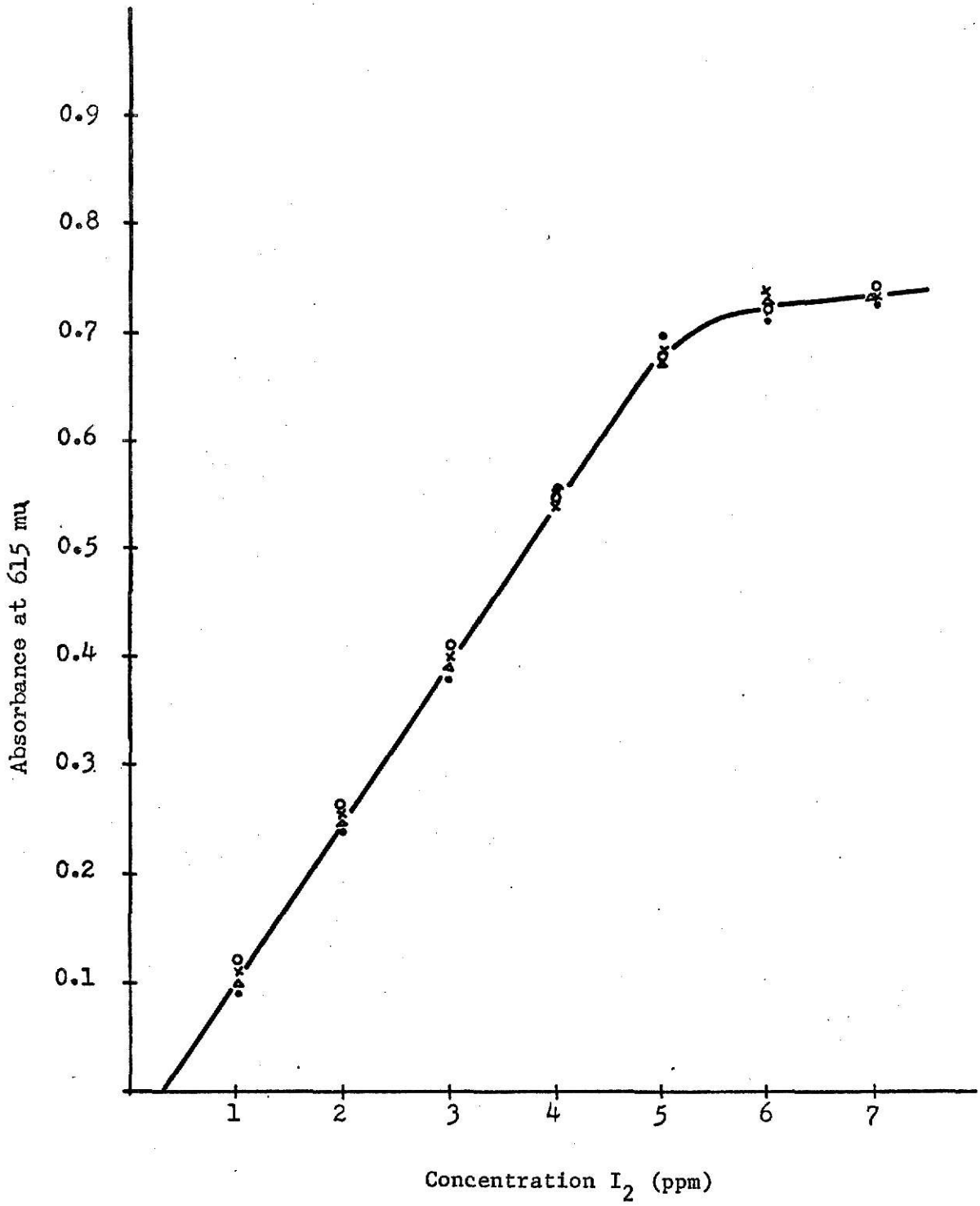

Fig. 2: Concentration versus Absorbance for I_3^--linear starch solutions with varying amounts of I^-. I_2/I^- ratios are 25 (--·--), 30 (-- --), 58 (--x--), and 100 (--o--). Two milliliters of starch reagent was used for each 100 ml of total solution. Each data point is the average of 5 determinations.

with linear starch. It was found that the complex formed by this method, made with chlorine demand free water, gave a definite blue color at 0.1 ppm ClO^- but no color at 0.01 ppm, which would correspond to 3.57 and 0.36 ppm of I_2 respectively. Therefore, both methods gave the same range for the detection limit for the starch reagent.

The pH effects upon the linear starch triiodide complex are shown on Fig. 3. Six ppm of I_2 with 3 ml of starch reagent were used per 100 ml of total solution and the pH was adjusted to values between 1 and 6.5. Absorbance values remained constant at 0.8, with only a slightly detectable increase at pH 2, therefore the system was considered essentially independent of the pH below the value of 7.0. The absorbance values were recorded immediately after acidification of the complex solution. If the solutions were allowed to stand a few minutes hydrolysis of the starch might occur yielding false absorbance values. This could be the reason for the slight increase of pH around 2, since hydrolysis begins around this point.

The concentration of iodide has essentially no effect upon the reaction of linear starch and iodine as shown by Fig. 2. The solution of iodine and starch reagent contained concentrations of iodine from 1.0 to 7.0 ppm and varying concentrations of iodide were added to the iodine solution before complexation occurred. Since 2.0 ml of starch were used per 100 ml of total solution the solutions contained 15.2 ppm iodide due to the CdI_2 in the starch reagent. This amount is residual in all the solutions and the iodide from the iodine solutions was added to this base amount to get the I_2/I^- ratios. Ratios of 25, 30, 58, and 100 were used with concentrations of I_2 ranging from 0.7 to 7.0 ppm. The absorbance values of the solutions, measured at 615 mμ, are plotted on Fig. 2. This graph yields essentially one line which indicates that

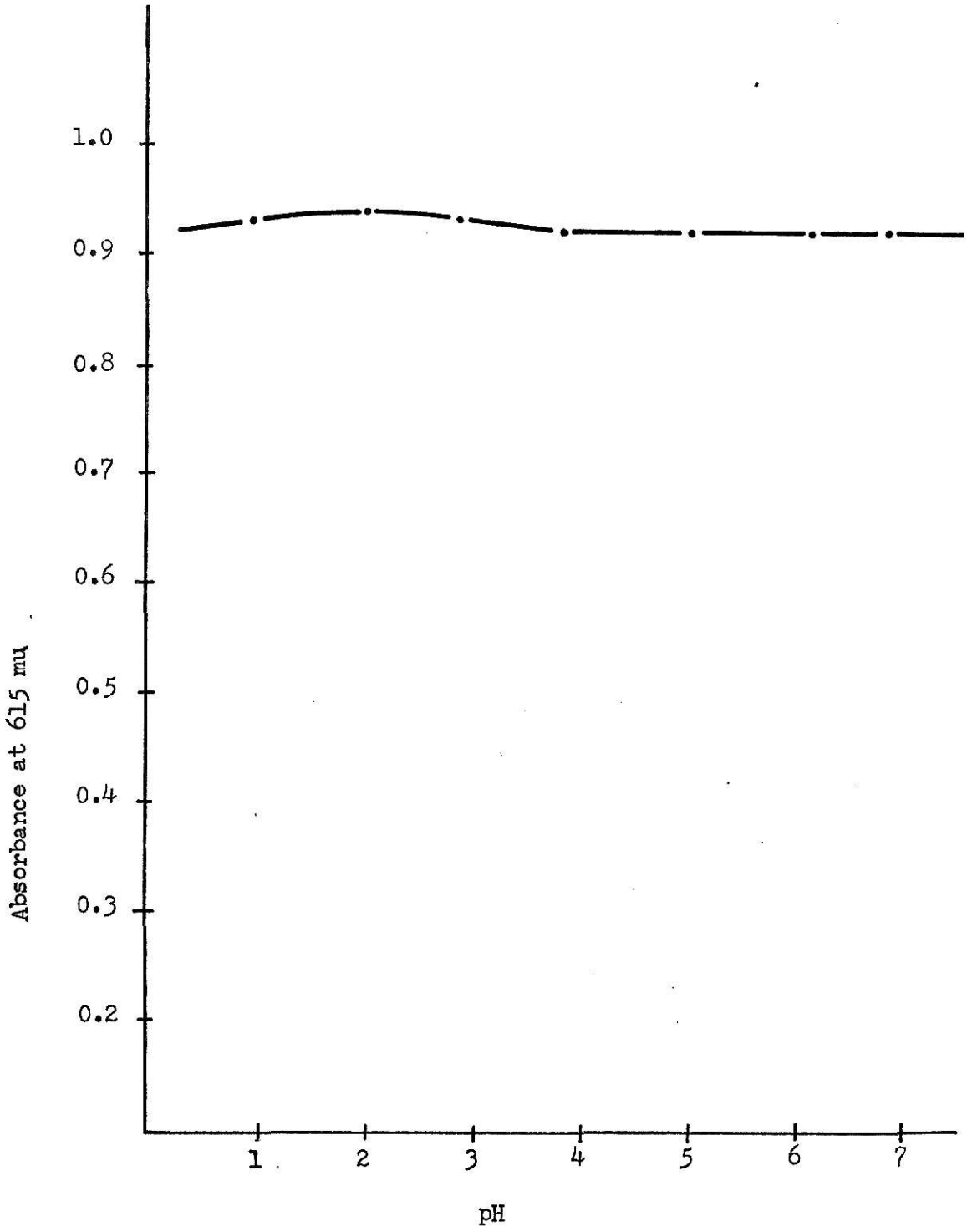

Fig. 3: pH affect upon the formation of I_3^--linear starch complex, with 6 ppm I_3^- and 3 ml of starch reagent in solution.

after formation of the complex excess iodide is not necessary nor does it affect the absorbance of the complex.

The complex formed between triiodide and linear starch is a large anion which precipitates from solution when sufficient amounts of a cation are in solution. Several different cations were allowed to interact with the starch complex until precipitation occurred. Three ml of CdI_2-linear starch reagent were added to 3.0 ml of 100 ppm I_2 and the solution was diluted to 100 ml with deionized water. The cations were added to the solution by titration of the solution with standard cation solutions until there was a visible turbidity. Table 1 shows the concentration of the cations necessary to cause precipitation. It can readily be seen that the larger the cation, the lower the concentration needed to cause formation of a precipitate and the more insoluble the complex-cation product. If a large cation is associated with the triiodide being determined by the formation of the blue starch complex, precipitation of the product would give erroneous results.

It was thought that perhaps tribromide would complex with linear starch in a manner similar to the triiodide complex. As shown in Fig. 4 the spectra of 100 ppm tribromide solution, both with and without starch added, are the same. Both exhibit only one maximum at 267 mμ. The spectra of 50 ppm tribromide yield similar results. Figure 5 shows that the plot of the absorbance versus concentration for tribromide does follow Beer's Law as would be expected if a complex did not form with the starch. Figure 6 shows that a complex does not form within a 48 hour period of time.

The spectra of dibromoiodide shows results entirely different from the spectra of tribromide. Figure 7 shows the spectrum of pure dibromoiodide solution. Line A of Fig. 7 is the spectrum recorded immediately after

TABLE 1: CATION PRECIPITATION OF LINEAR STARCH I_3^- COMPLEX[a]

Cation	Grams Added	Moles	Molar Conc.
K^+	4.77×10^{-1}	6.42×10^{-3}	1.28×10^{-1}
Cs^+	7.91×10^{-1}	4.07×10^{-3}	8.14×10^{-2}
Rb^+	1.49×10^{-3}	1.02×10^{-5}	1.58×10^{-3}
$(CH_3)_4N^+$	3.46×10^{-1}	3.15×10^{-3}	6.30×10^{-2}
$(C_4H_9)_4N^+$	8.65×10^{-2}	3.12×10^{-4}	4.58×10^{-3}
$(C_4H_9)_4P^+$	8.00×10^{-3}	2.72×10^{-5}	5.23×10^{-4}
$(Ph)_3(PhCH_2)P^+$	1.40×10^{-3}	3.60×10^{-6}	7.01×10^{-5}

[a]Molar concentration of cation necessary to cause discernable turbidity in solution where the concentrations were as follows: starch, 1.5×10^{-6}M; iodide, 2.54×10^{-2}M; iodine, 1.18×10^{-5}M.

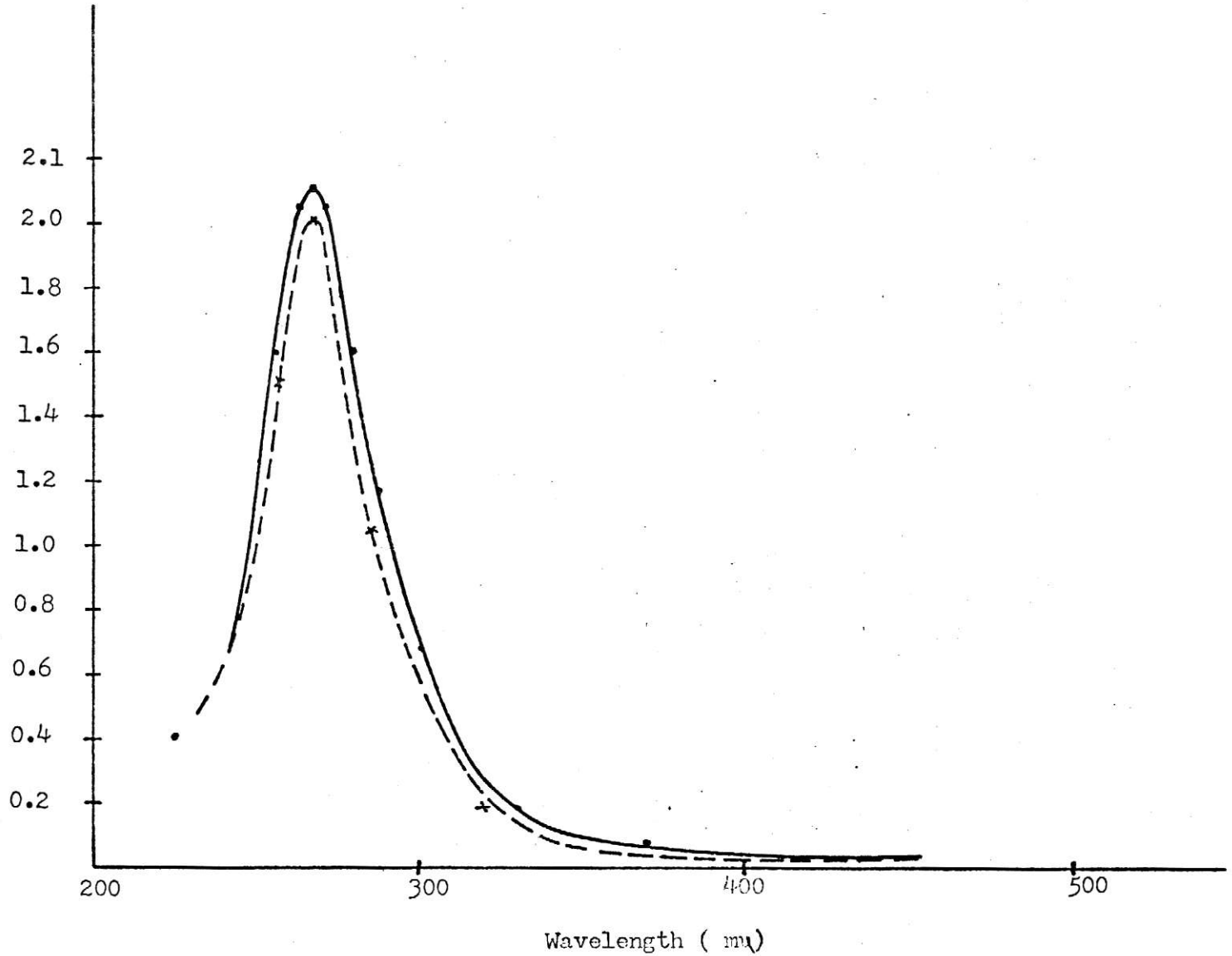

Fig. 4: Spectra of tribromide solutions. (———), no starch reagent added to the solution; (— — -), 3 ml of starch reagent added to the 100 ppm tribromide solution.

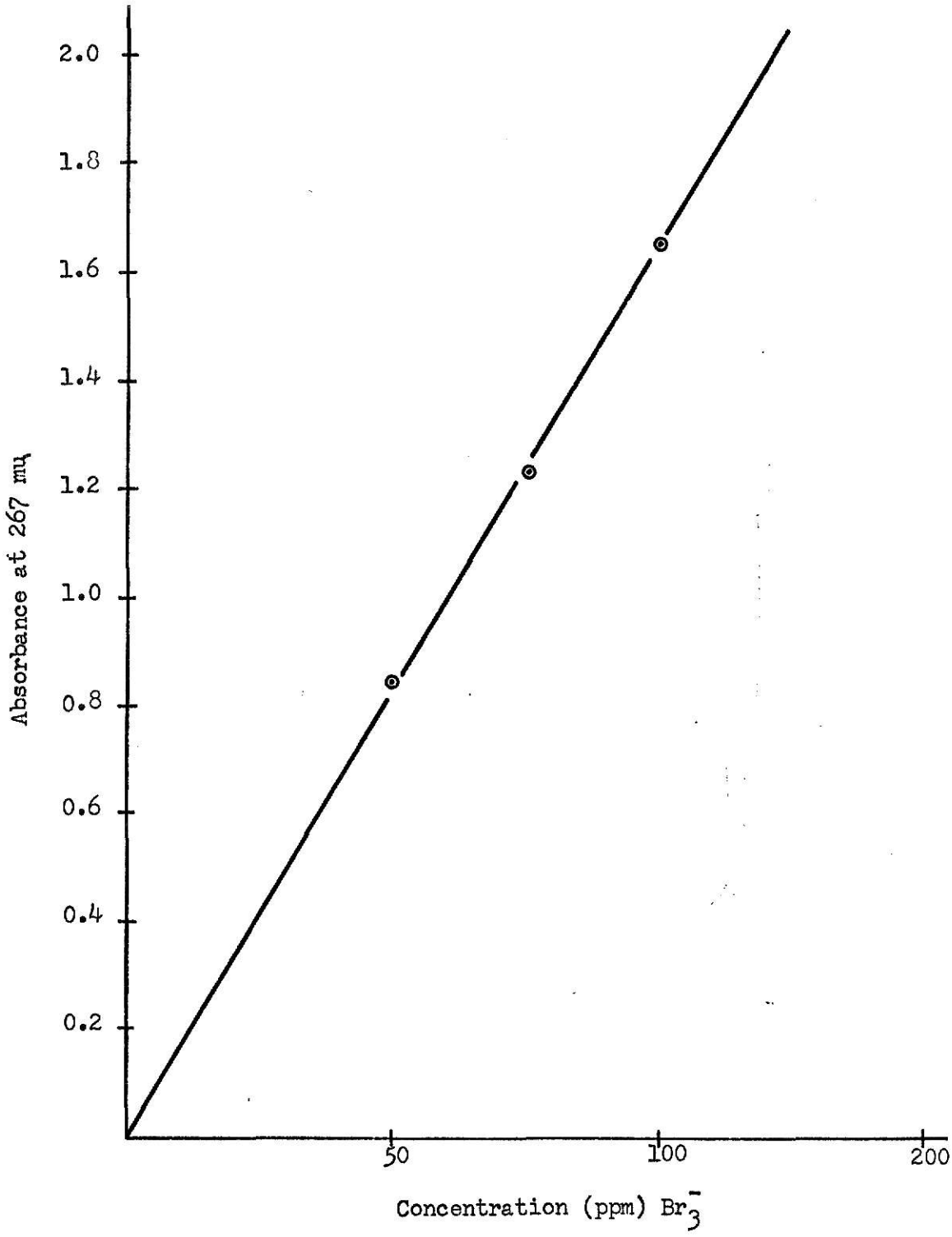

Fig. 5: Concentration versus Absorbance of Br_3^- solutions. Absorbance values were the same with or without starch reagent added to the solution.

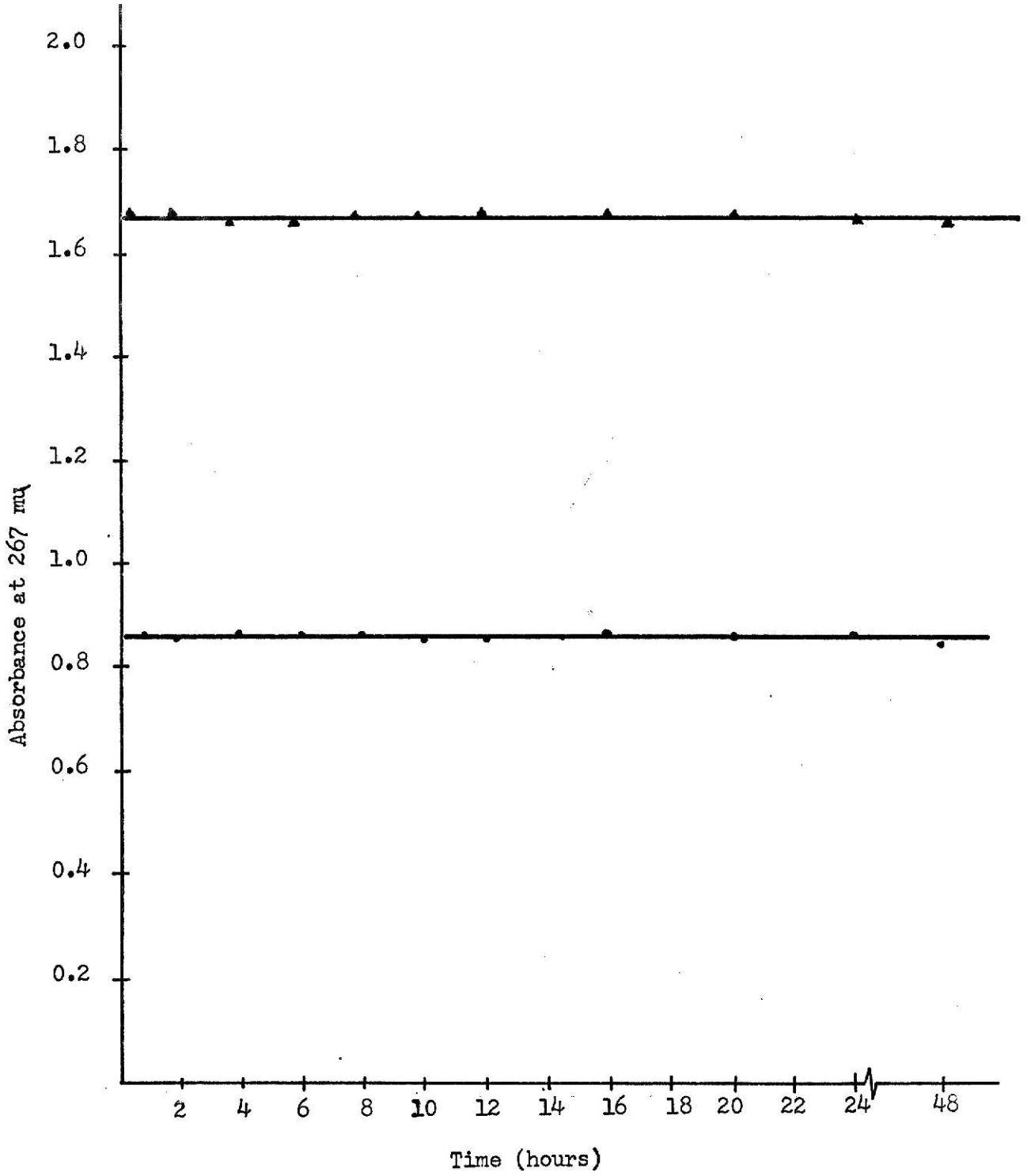

Figure 6: Time after 3 ml of starch reagent was added to a tribromide solution, versus absorbance of the solution. Tribromide concentrations were 50 (—●—) and 100 (—▲—) ppm.

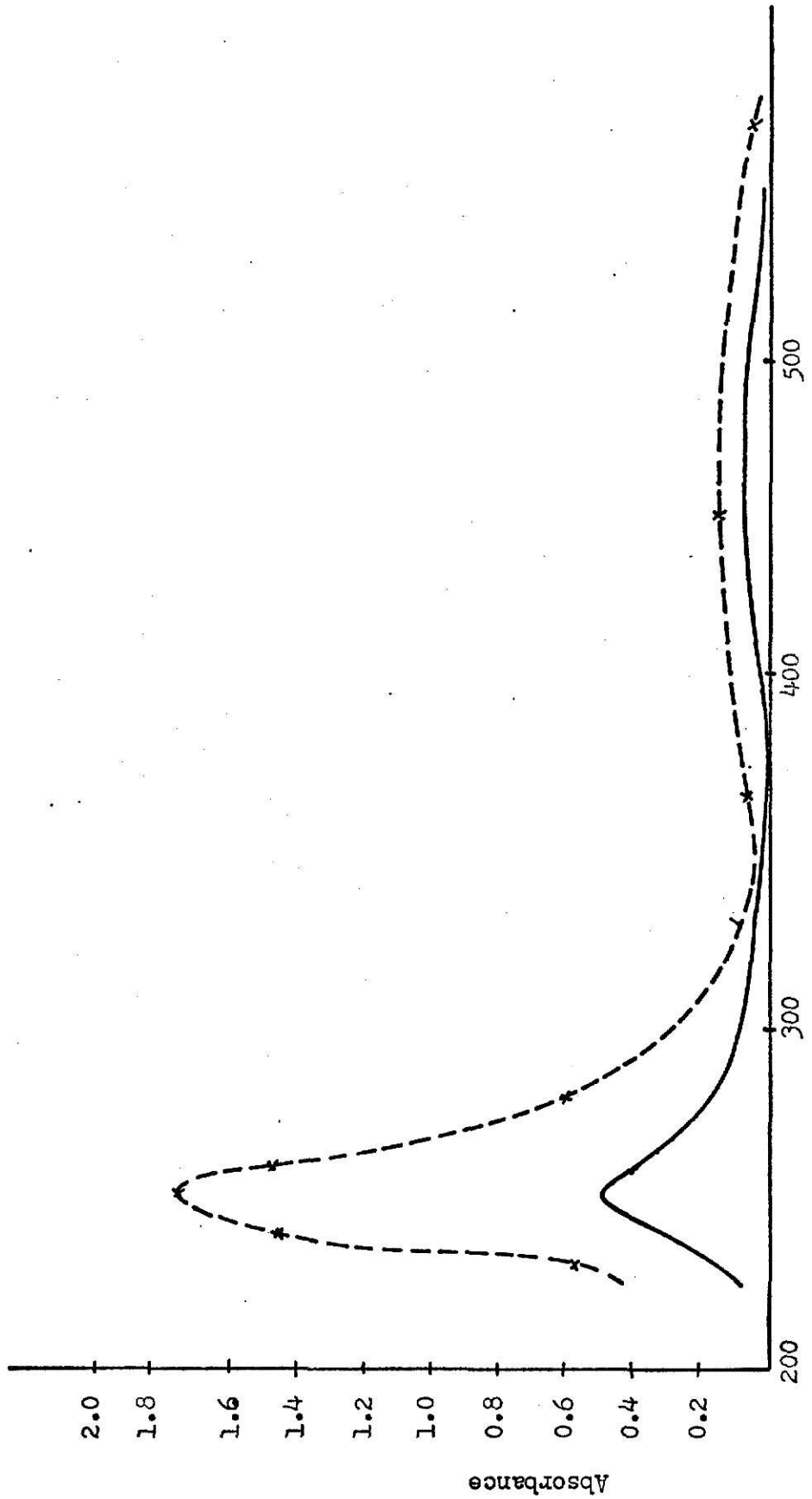

Fig. 7: Spectra of Br_2I^-. Concentrations of dibromoiodide were 100 (——) and 200 (— — —) ppm.

preparation of the 100 ppm solution. Line B is the spectrum of 200 ppm dibromoiodide solution. Both curves show a maximum at 254 mμ and a small shoulder around 450 mμ. With addition of 3 ml of linear starch solution (without CdI_2) maxima at 400 and 500 mμ appear as shown in Fig. 8. The 254 mμ maximum is also present in the starch solution spectra. Line B of Fig. 8 illustrates that the 254 mμ maximum begins to decrease after 30 minutes of development time. Line C shows even more distinctly the decrease after 24 hours of development time. At this time the absorbance has decreased to 0.72 at 254 mμ and the other two peaks have increased in intensity and have shifted to higher wavelengths. Line D shows the spectrum at 48 hours after preparation after which time it remained constant. Solutions of 50, 100, 200, and 300 ppm show corresponding changes, indicating that there is a change in composition of the species producing the color, and also indicating the formation of a complex with the linear starch similar to the complex formed by triiodide. It can be seen from Figs. 8-10 that the original 254 mμ peak disappears over a period of time and that the other two peaks steadily increase with a time of development for the 430 mμ peak of approximately 2.5 hours and for the 540 mμ peak up to 24 hours with a constant shift to higher wavelengths.

Figure 11 illustrates the fact that dibromoiodide shows a threshold concentration for both the 430 and the 540 mμ maximum and consequently does not follow Beer's Law. Calculation of the extinction coefficient yields a value of 15,800 when $\varepsilon = \frac{D - D_o}{L(C - C_o)}$, $D = 1.22$, $D_o = 0$, $C = 1.04 \times 10^{-3}$M, $C_o = 2.72 \times 10^{-4}$M, and $L = 0.996$ cm. This would make the equation of the line plotted in Fig. 11 to be Abs. = 15,800 moles^{-1} cm^{-1} l (concentration Br_2I) - 0.35.

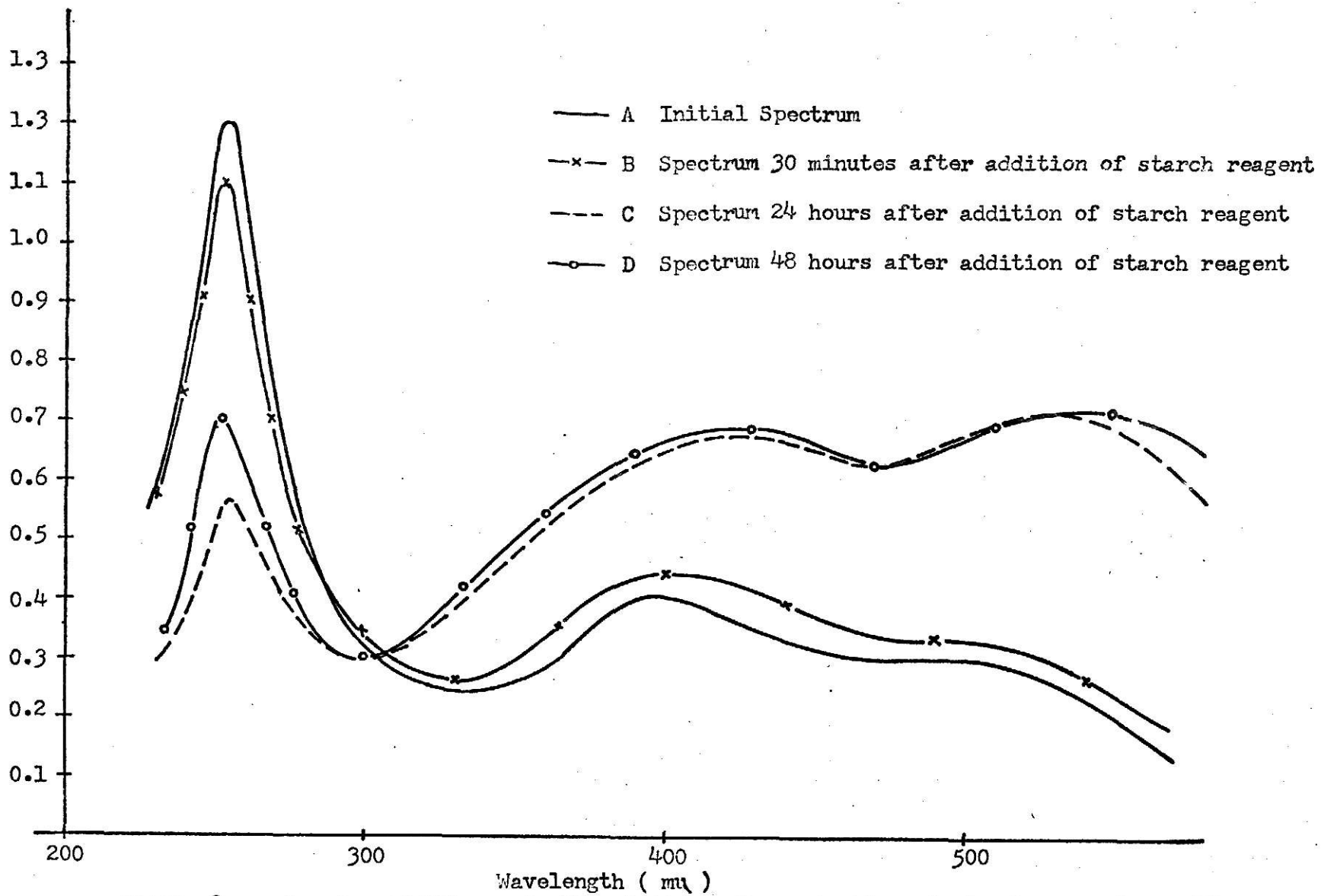

Figure 8. Spectra of 200 ppm Br_2I^- solution. Concentration of starch reagent was 3%

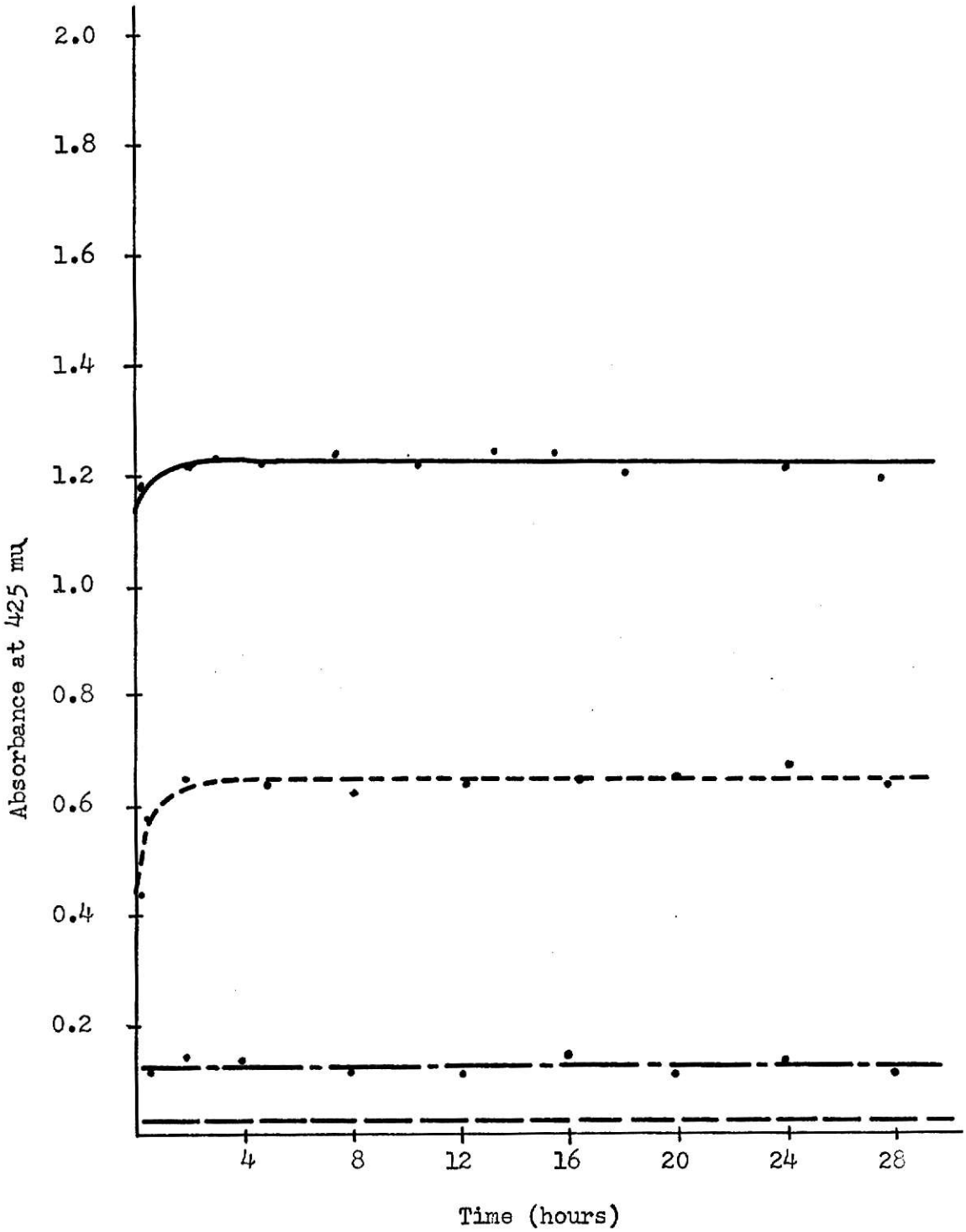

Fig. 9: Time elapsed after addition of 3 ml of starch reagent to Br_2I^- solutions versus the absorbance of the solutions. Concentrations of Br_2I^- were 50 (—), 100 (— - —), 200 (– – –), and 300 (———) ppm.

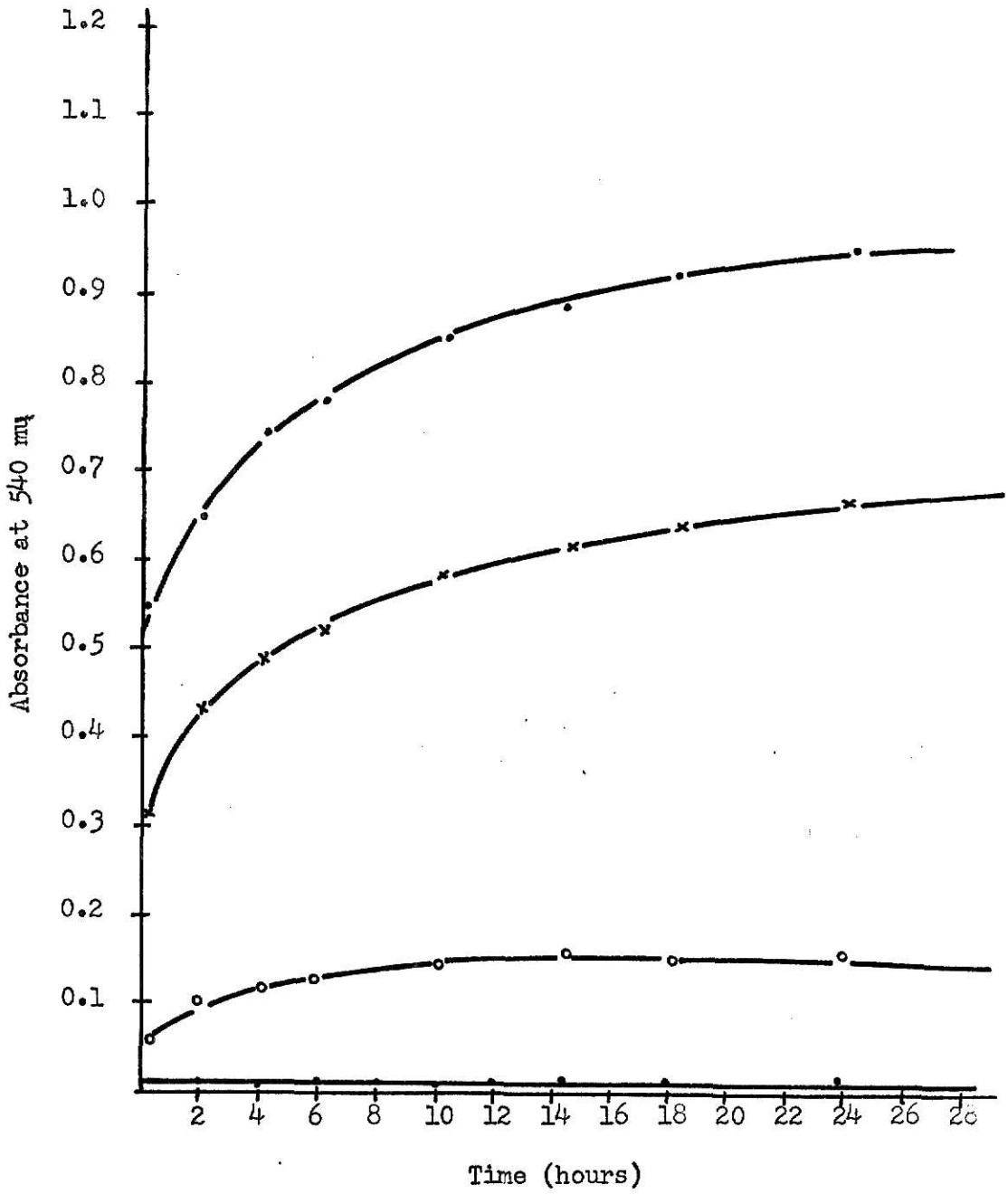

Fig. 10: Time elapsed after the addition of 3 ml starch reagent to Br_2I^- solutions versus the absorbance at 540 mμ. Concentrations of Br_2I^- used were 50 (—•—), 100 (—o—), 200 (—×—), and 300 (—·—) ppm.

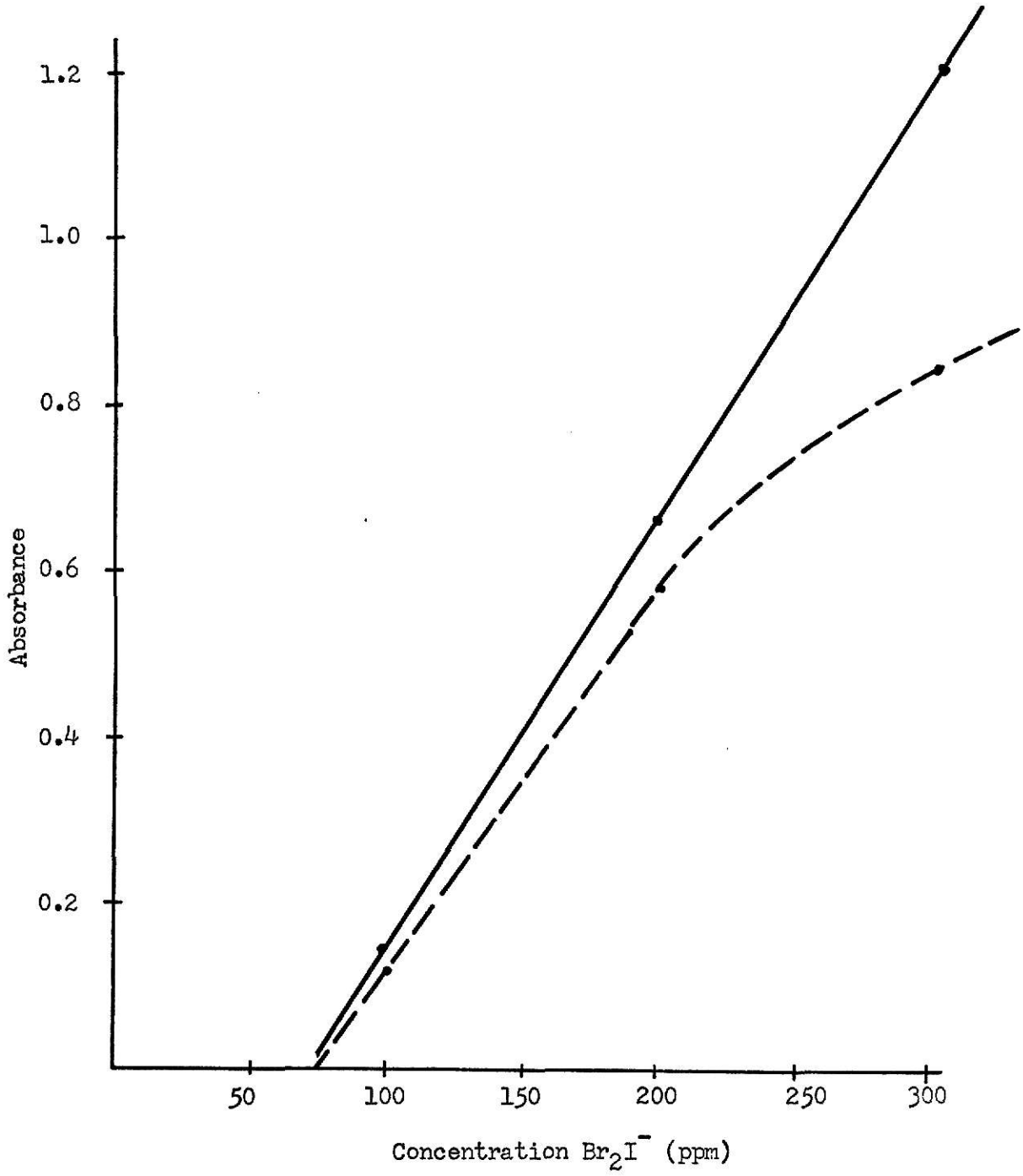

Fig. 11: Concentration Br_2I^--starch solution versus absorbance at 430 mμ (———) and 540 mμ (-----).

SUMMARY

The linear starch-cadmium iodide reagent used to detect iodine was found to be sensitive to 0.2 ppm I_2. The reagent is essentially pH independent below 7 when initially prepared, but the starch hydrolysizes after standing a few minutes below pH 2.5. Above pH 7 $Cd(OH)_2$ precipitates from solution yielding an unstable reagent. When sufficient iodide is present to give the triiodide ion with iodine, the concentration of iodide does not affect the formation of the complex with starch. The combining ratio of iodine to linear starch necessary to form the complex was found to be one triiodide per helical coil. The addition of large univalent cations of sufficient concentration to a solution of linear starch-triiodide complex causes precipitation of the complex from solution.

Dibromoiodide was found to produce an orange complex similar to the triiodide-starch complex. It has overlapping maxima at 430 and 540 mμ of which the first has a development time of 2.5 hours and the other a development time of 24 hours. Tribromide does not form a complex with linear starch and appears to be unaffected by the addition of starch.

PROJECTIONS AND CONTINUATIONS

The linear starch used in this study was prepared by precipitation of amylose from solution with n-amyl alcohol. There should be a study made as to the effect of n-amyl alcohol upon the formation and stability of the triiodide complex. Perhaps the presence of the alcohol in solution helps to fashion a helix in the amylose, keeping it intact, hence less I_2 is required to produce the blue color. This could give a reason for the low combining ratio obtained in this study.

A natural extension of the starch system would be to use the starch reagent as a colorimetric reagent or a trap for oxidizing substances. Ozone has been of particular interest in air pollution. In the present study some work was done on developing a solid support for linear starch cadmium iodide reagent. If such a system were developed it could be used to absorb oxidizing materials which pass over the surface. The reagent could then be removed from the support and diluted to give a colorimetric determination of the oxidant. This method should be reliable and sensitive but work has not been completed in this area. Several solid supports for starch were tried. Silica gel and porcelin chips do not release the complex completely into solution after it has been formed on the surface. Solid $MgSO_4$ readily hydrates and is soluble in water and would not interfere with the formation of the complex. A small amount of cadmium iodide and dry linear starch were powdered with magnesium sulfate and allowed to stand over water. The powder solidified and upon exposure to the atmosphere turned blue indicating the sensitivity of the reagent to oxidizing materials. This shows promise as an analytical tool, but needs to be more extensively studied.

The possibility of continuous analysis with cadmium iodide starch reagent as the indicator has been studied also. Recently Taylor et al. (30) found that strongly basic anion exchange resin saturated with triiodide is a strong disinfectant. The captured triiodide on the resin was not displaced by Cl^-, SO_4^-, HCO_3^- or NO_3^-. In this current sutdy, strongly basic quanternary ammonium anion resin in the iodide form was prepared and a solution of starch complexed with I_2 was passed through the column. The eluent did not have the blue color of the complex, but when a small amount of iodine was added to the eluent it turned blue immediately. This would indicate that the resin takes the I_2 from the starch complex but does not affect the cadmium, the iodide, or the starch. This suggested to us a continuously monitoring system for oxidants. It would be a self contained system. The triiodide could be stripped from the starch reagent and the reagent recycled to be used again.

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INVESTIGATIONS OF LINEAR STARCH-HALIDE COMPLEXES

by

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AN ABSTRACT TO A THESIS

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A B S T R A C T

Linear starch complexation with triiodide was studied to determine various characteristics of the reaction and the complex formed. The reaction was found to be pH independent. The iodide concentration, when increased above the level of iodide ion in the cadmium iodide reagent, was not found to affect the formation or the stability of the complex. The sensitivity of linear starch was found to be 0.2 ppm I_2.

Linear starch was found to form a complex with dibromoiodide similar to the complex with triiodide. The development time for it is about 2.5 hours and it has absorption maximum at 430 and 540 mμ. Tribromide did not form a complex with linear starch and was unaffected by its presence in solution.