THE ANALYTICAL CHEMISTRY
OF COPPER (III)

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THE ANALYTICAL CHEMISTRY OF COPPER (III)

By

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INTRODUCTION

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The early history of Cu(III) has been reviewed by Urtis (21). It was noted that in 1844 Kruger prepared a compound containing some trivalent copper by passing chlorine into an alkaline solution containing divalent copper. Crum subsequently showed the oxide prepared by Kruger had roughly the atomic ratio of 2Cu:3O. Kruss, Viatali, Moser, Brauner, and Picinni employing other oxidizing agents such as potassium perchlorate and bromine in alkaline solutions, and potassium nitrate fusions reported that a higher oxide of copper could be prepared.

While working on a separation of tellurium by means of persulfate oxidation of tellurite to tellurate, Kuzma (2) noted that a deep purple solution resulted if traces of copper were present. Brauner (21) suggested that the colored solution contained copper (III). Kuzma attempted to substantiate Brauner's postulation, and isolated materials for which he reported formulae such as $Cu_2O_3\cdot CuO\cdot 2TeO_3\cdot 2K_2OxH_2O$ and $2Cu_2O_3\cdot CuO\cdot 3TeO_3\cdot 2K_2OxH_2O$. In one preparation all of the copper was reported to be trivalent, and the formula was reported to be $2Cu_2O_3\cdot 3TeO_3\cdot 2K_2O\cdot 13H_2O$. This may be rewritten as $K_4Cu_4Te_3O_{17}\cdot 13H_2O$ for comparison with a formula reported by Malatesta (7), and substantiated by Lister (25), which is $K_5CuFe_2O_{12}\cdot 20H_2O$. Kuzma suggested these products were salts of a complex copper telluric acid (2).

Muller and Spitzer (24) oxidized alkaline solutions of copper (II), and reported results in terms of di, tri, and tetra-valent copper produced. A formula Cu_2O_3 was assigned to their copper oxide.

Urtis (21) investigated the role of the tellurate radical in the formation of copper (III). He reported the formula $KOH \cdot Cu(OH)_3 \cdot nK_2TeO_4 \cdot Te(OH)_6$ where n exceeds five. He noted that periodate may replace tellurate where "n" exceeds one in the formula. He suggested the copper (III) was present as the hydroxide and stated "this compound is peptized by tellurates (or periodates) yielding a collodial solution containing trivalent copper in the form of cuprites, $[Cu(OH)_4]^-$, which can form adsorption compounds with tellurates."

Urtis was unable to find agents other than tellurate and periodate to "peptize cuprites". Potassium and sodium hydroxide solutions were satisfactory alkaline media, but ammonium hydroxide, lithium hydroxide and tetraethylammonium hydroxide gave unstable solutions of copper (III).

Ninety eight per cent of the copper (II) was oxidized to copper (III) with potassium persulfate, but only 83-85 per cent conversion was achieved by anodic oxidation.

It is now known that tellurate ion and periodate ion form stable complexes with copper (III). Malaprade (19) has isolated the crystalline salt, $Na_7CuI_2O_{12} \cdot 6H_2O$, and Malatesta (7) isolated the corresponding potassium salt, $K_7Cu(IO_6)_2 \cdot 7H_2O$. Proof of the tripositive nature of the copper found in this complex is given by the magnetic susceptibility (7), at 18° $Xm = -30.2 \cdot 10^{-6}$ c.g.s., a value characteristic of diamagnetic compounds. Malatesta noted that solid potassium di-periodato cuprate (III) is dark brown and easily soluble in water, but that if the water is acidified the copper (III) compound decomposes with the liberation of oxygen.

Klemm and Hauss (23) have reported the preparation of K_3CuF_6 by the passage of fluorine over cuprous chloride at 250°C. The potassium percupri fluoride compound is unstable in aqueous solution, decomposing to give copper (II) fluoride, and gases which have not been identified.

Lister (25) has verified the formula reported by Malaprade for sodium di-periodato cuprate (III), and reports the formula $Na_3Cu(TeO_6)_2 \cdot 2H_2O$ for sodium di-tellurato cuprate (III). Lister eliminated the possibility of peroxide formation (27) which would give a pseudo oxidation state of copper (III) by using sodium hypochlorite to prepare his solution. This supplements the evidence for Cu(III) based on the magnetic susceptibility value (7).

According to Lister, when copper (II) chloride is treated with alkaline hypochlorite a brown precipitate of $Cu(OH)_3$ appears, which tends to dissolve in strong alkaline solutions giving $[Cu(OH)_4]^-$. In the presence of complexing agents nearly all the copper is complexed. Lister reports constants of dissociation for the following reactions:

$$[Cu(IO_6)_2]^{-7} + 4H_2O \longrightarrow [Cu(OH)_4]^- + 2[H_2IO_6]^{-3}$$

$$K_D = 8.0 \times 10^{-11} \quad \text{at } 40^\circ$$

$$[Cu(HTeO_6)_2]^{-7} + 2OH^- + 2H_2O \longrightarrow [Cu(OH)_4]^- + 2[H_2TeO_6]^{-4}$$

$$K_D = 1.1 \times 10^{-11} \quad \text{at } 40^\circ.$$

Lister states that complexes with a 1:1 ratio of copper to tellurium and with a 1:1 ratio of copper to iodine exist but that these complexes are unstable (25). Stannate ion, stibnate ion, and selenate ion did not complex trivalent copper. The heat of reaction for the di-tellurato cuprate (III) complex was twenty kilocalories per mole and for the di-periodato cuprate (III) complex was seven and one-half kilocalories per mole.

The first use of copper (III) solutions as titrants was reported by G. Beck in 1950 (9), and a series of papers have followed (10, 11, 12, 13, 14, 15). 31

Beck's work has been on a micro scale, and has been concerned largely with biochemical applications. Techniques have been reported for the determination of sugar in blood and urine (9). Several of the papers (11, 12, 13) deal with tests which enable one to draw conclusions about the amino acids and proteins present in albumins and various salts. Beck also worked with a number of inorganic materials. An attempt has been made to summarize Beck's findings in Tables I and II. For the inorganic reactions Beck has usually suggested products, but for the organic reactions reproducibility of titers is the only data reported.

On the basis of the titrations performed by Beck on a micro scale it was hoped that macro volumetric redox determinations could be developed, and that some oxidative selectivity among organic groups might be found.

This study was therefore begun to clarify the analytical work done, and to extend the usefulness of copper (III) as an analytical reagent.

TABLE I

INORGANIC OXIDATIONS WITH Cu(III) FROM BECK (10)

Substance Oxidized	Comments
As_2O_3	As^{+3} oxidized to As^{+5}
Sb_2O_3	Sb^{+3} oxidized to Sb^{+5}
$KCr(SO_4)_2$	End point is not sharp
NaCN	$NaCN + 2KOH + 5O = K_2CO_3 + NaNO_3 + H_2O$
$PbCl_2$	Slow rate
$Na_2S_2O_3$	$Na_2S_2O_3 + 4O + 2NaOH = 2Na_2SO_4 + H_2O$
As_2S_3	$As_2S_3 + 2O + 6OH^- = AsS_2O_2^{\equiv} + AsSO_3^{\equiv} + 3H_2O$
As_2S_3 (boiling hot)	$AsS_2O_2^{\equiv} + 4O + H_2O = AsSO_3^{\equiv} + H_2SO_4$

TABLE II

ORGANIC OXIDATIONS WITH Cu(III) FROM BECK (11)

Substance Oxidized	0.5 Ml Aliquots of Mg/50 Ml of .01 M KOH	Ml CuIII* Titer I	Titer II
Mannitol	91	0.48	0.48
Glycogen	162	0.30	0.28
Starch	81	0.40	0.40
Fumaric Acid	58	1.0	0.96
Glycerin	46	0.50	0.49
Mannose	45	0.75	0.75
Lactose	180	0.50	0.25 (Hot)
Formaldehyde	(0.02m)	0.99	0.99
Potassium Sodium tartrate**	141	0.66	0.66

* Cu III titer is 0.52 ml of arsenite (99 mg As_2O_3 per 50 ml of 0.01 m KOH solution).

** Six equivalents of Cu(III) per mole of tartrate.

EXPERIMENTAL

EXPERIMENTAL

A. Possible Copper (III) Reagents

An attempt was made to prepare salts of copper (III) using phosphate ion, periodate ion, perchlorate ion, selenate ion, tellurate ion, arsenate ion, chromate ion, plumbate ion, molybdate ion, antimonate ion, stannate ion and tungstate ion. In agreement with previous investigators (21, 25) only periodate ion and tellurate ion formed stable complexes with copper (III).

B. Preparation of the Reagents

Of the variety of methods available for preparing di-periodato cuprate (III) and di-tellurato cuprate (III), the simplest and most satisfactory technique was the oxidation of the divalent copper in the presence of the complexing ion in a potassium hydroxide solution with potassium persulfate.

Procedure for the Preparation of 0.05 M Potassium Di-periodato Cuprate (III)

Add to 175 ml of boiling distilled water 2.5 grams of copper sulfate penta hydrate, and completely dissolve. Then add 11.5 grams of KIO_4 (G. F. Smith Chemical Co.) and dissolve. A bright yellow-green precipitate appears. Add 13.5 grams of potassium hydroxide cautiously. The yellow-green precipitate dissolves completely and the clear solution remaining is deep green. Add to the boiling solution one gram portions of potassium persulfate at intervals of one minute until twelve grams have been added. The solution is boiled fifteen minutes to destroy the excess potassium persulfate. The solution is cooled, and the final volume is adjusted to 200 ml. The solution will be dark brown, free of insoluble matter, and it may be stored in polyethylene bottles for several months without signs of decomposition.

Procedure for the Preparation of 0.05 M Potassium Di-tellurato Cuprate (III)

Add to 175 ml of boiling distilled water 2.5 grams of copper sulfate penta hydrate, and completely dissolve. Add 8.8 grams of $K_2TeO_4 \cdot 2H_2O$ (Fisher Chemical Co.) and boil the solution fifteen minutes with mechanical agitation. Carefully add 10.4 grams of potassium hydroxide to the hot solution. The yellow-green copper tellurate precipitate partially dissolves in the potassium hydroxide, and a dark green slurry results. Add one gram increments of $K_2S_2O_8$ to the boiling solution until a total of 10 grams of potassium persulfate has been added. Boil the solution for fifteen minutes to destroy the excess persulfate. Cool and store in polyethylene bottles.

Solid potassium di-periodato cuprate (III) may be prepared by simple evaporation of the potassium copper (III) solution. This may be powdered and stored. It will redissolve in water to yield a clear dark brown solution with the properties of the solution from which it was prepared. This method of preparation gives a solid which is obviously a mixture of all of the salts in the mother liquor, and does not give pure $K_7Cu(IO_6)_2$.

A solution of divalent copper periodate was prepared using the procedure for the preparation of the trivalent copper periodate with the omission of the persulfate oxidation. Divalent copper periodate is a yellow-green insoluble material which dissolves in dilute potassium hydroxide to give a green soluble complex, and in strong potassium hydroxide to give a dark blue complex. It is known that periodic acid in aqueous solutions, has three replacable hydrogens, the first being replaced at a pH of about 5, the second at about 10 and the third in solutions in about tenth molar potassium hydroxide (28, 29, 4, 26). Because there are three apparent species of divalent copper, the following equilibria are suggested to account for these species:

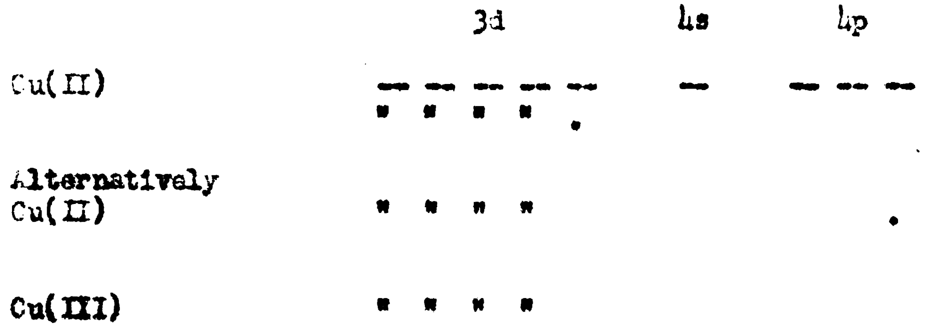
$$\begin{tikzcd}
\begin{array}{l} H_8Cu(IO_6)_2 \\ \text{yellow green} \\ \text{precipitate} \end{array} \arrow[r, shift left, "OH^-"] & \begin{array}{l} K_2H_6Cu(IO_6)_2 \\ \text{green solution} \end{array} \arrow[l, shift left, "H^+"] \arrow[r, shift left, "OH^-"] & {} \arrow[l, shift left, "H^+"] \\
\begin{array}{l} K_4H_4Cu(IO_6)_2 \\ \text{dark blue} \\ \text{solution} \end{array} \arrow[r, shift left, "\text{oxidation}"] & \begin{array}{l} K_3H_4Cu(IO_6)_2 \\ \text{dark brown} \\ \text{solution} \end{array} \arrow[l, shift left, "\text{reduction}"] \arrow[r, shift left, "\begin{array}{c}\text{Evaporation to dryness} \\ OH^-\end{array}"] & {} \arrow[l, shift left] \\
\begin{array}{l} K_7Cu(IO_6)_2 \\ \text{brown solid} \end{array} & &
\end{tikzcd}$$

The yellow-green precipitate $H_8Cu(IO_6)_2$ was shown to be potassium free by washing and applying a flame test.

A similar system of equilibria apparently exists for the copper tellurates, but the divalent copper tellurate requires very large concentrations of potassium hydroxide to keep the greenish yellow divalent copper tellurate in solution.

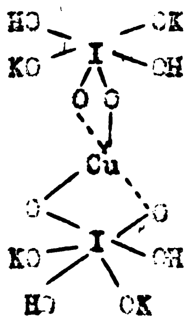
Structures of the di-periodato cuprate (II) and di-periodato cuprate (III) may be drawn and seem to be consistent with the known chemistry of the compounds.

Schematically the orbitals in copper (II) and three may be represented as follows:



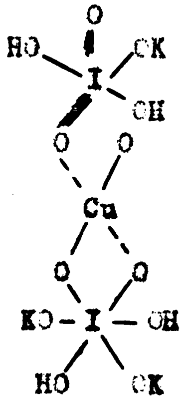
Therefore Cu(II) may have sp^3 type bonding or dsp^2 bonding. The former gives a tetrahedral structure, and the latter a planar structure. The dsp^2 bond is preferred since it is a stronger bond, and since most copper covalent compounds are planar. Both types of bonding give the usual coordination number of four. Therefore it is suggested that divalent copper periodate is best represented by structure I for the species $K_4H_4Cu(IO_6)_2$. Divalent copper compounds

Structure I

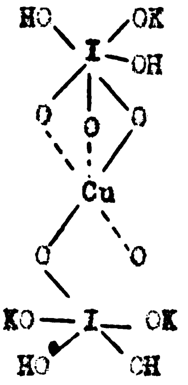


are paramagnetic with a magnetic susceptibility of about + 1200 x 10^{-6} c.g.s. with one unpaired 4p electron (32).

The di-periodato cuprate (III) resulting from the oxidation of the $K_4H_4Cu(IO_6)_2$ (blue species) to the $K_3H_4Cu(IO_6)_2$ may be written in two ways:



Structure I



Structure II

Structure I requires fourteen electrons in the iodine sphere and this is known to be possible since iodine forms a hepta flouride IF_7. Structure II is unsymmetrical and requires a dsp^3 bond which is available in the Cu(III) state of oxidation. Either structure has no unpaired electrons, required by the magnetic susceptibility of -30.2 x 10^{-6} c.g.s. It must be emphasized that the structures suggested are based upon knowledge of the behavior of the complexes and have not been absolutely proved by my experiments.

C. Determination of the Concentration of Copper (III) Reagents

Although the concentration of the reagents which were prepared as described on pages 7 and 8 is known from the fact that potassium persulfate oxidizes 98 per cent of the copper (II) to copper (III) (21), and because a rough check of the concentration of the solution was made from an indirect thiosulfate procedure, the first volumetric work was concerned with an attempt to develop a method for standardizing the reagents.

The indirect thiosulfate procedure for the approximate determination of concentration was as follows:

Two identical 1 ml samples of the 0.05 M Cu(III) solution were taken. The first was placed in an iodine flask with two ml of water and six to eight drops of six normal sulfuric acid were added. The copper (III) liberates oxygen, being reduced to copper (II). The oxygen was removed by boiling for two minutes. The solution was cooled to about 60°C. and 2-3 grams of KI were added. The stoppered flask was vigorously shaken for one minute. Dilute six normal sodium hydroxide was added through the lip until all the brown I_2 color had disappeared. Then 5-10 ml of glacial acetic acid was added and the iodine liberated was titrated with 0.1N $Na_2S_2O_3$.

The other 1 ml sample was placed in an iodine flask, diluted with 2 ml of water. Two to three grams of potassium iodide were added, the solution was warmed to 60°C. and then acidified with six to eight drops of six normal sulfuric acid. The stoppered flask was shaken for one minute, and 2-3 ml of six normal sodium hydroxide were added by filling the lip of the flask, and then removing the stopper so that no iodine escaped. Sodium hydroxide was added until all the iodine is dissolved, and then 5-10 ml. of glacial acetic acid were added. The iodine liberated was titrated with 0.1N sodium thiosulfate.

The difference in sodium thiosulfate consumed by samples I and II gave the iodine equivalent to the copper (III) in sample II. The data is summarized in Table III.

TABLE III

STANDARDIZATION OF Cu(III) SOLUTIONS BY THE INDIRECT THIOSULFATE METHOD

	Sample I (ml)	Sample II (ml)	Difference (ml)
1	19.70	20.20	0.50
2	19.73	20.18	0.45
3	19.68	20.20	0.52
Av.	19.70	20.19	0.49

The thiosulfate was 0.09920N and therefore the copper (III) solution was 0.049N. These data support the statement of Urtis that the persulfate oxidation achieves about 98% copper (II) to copper (III) conversion (21).

D. Titrations Suggested by Beck

Arsenious oxide as a Standard

Since Beck had already reported experimental work based on arsenious oxide titers of di-periodato cuprate (III), arsenious oxide was one of the first materials selected for the standardization of the copper (III) reagents. In the first set of titrations aliquots of potassium arsenite solution were titrated with di-periodato cuprate (III).

Ten ml of standard 0.1N arsenite solution were pipetted into seven 250 ml flasks each containing 50 ml of distilled water and two grams of potassium hydroxide, with the exception of the seventh, which contained only 0.2 grams of potassium hydroxide in the 50 ml of distilled water. Samples one and two were warmed, but the remainder were titrated cold. The end point taken was the brown color produced by the first excess of the Cu(III) reagent. The results of this titration are given in Table IV.

TABLE IV

TITRATION OF 10 ML. ALIQUOTS OF 0.1N POTASSIUM ARSENITE
USING POTASSIUM DI PERIODATO CUPRATE (III)

	Sample Number						
	1	2	3	4	5	6	7
Ml of Cu(III)	7.50	3.00	7.40	6.24	6.66	7.46	3.48

A variety of colored products appeared in the titration. Most of them were white, blue or green. It was difficult to see the first excess of copper (III). Lack of reproducibility in the titers renders this approach unsuitable.

Beck reported that the inverse titration (addition of arsenite solution to Cu(III) solution) gave a sharp end point and that the results were good (10). Therefore the inverse titration was attempted.

A fresh potassium arsenite solution was prepared and found to be 0.16N. This solution was used to titrate samples prepared by pipetting 25 ml aliquots of Cu(III) solution into 20 ml of water and adding 3.5 grams of potassium hydroxide. This approach gave a variety of colored products which made the end point difficult to see. Hence dead-stop end point detection was attempted. A 0.1 volt potential was applied using a sensitivity of 200X, and the sensitivity was increased to 50X near the end point. A drop from eleven to zero galvanometer units result when the last 0.03 ml of arsenite were added. The results are summarized in Table V.

TABLE V

TITRATION OF 25 ML ALIQUOTS OF DI-PERIODATO CUPRATE (III)
WITH 0.16N POTASSIUM ARSENITE

	Sample Number		
	1	2	3
Ml Arsenite	18.00	16.70	18.94

The same procedure was followed substituting di-tellurato cuprate (III) for di-periodato cuprate (III). In trial one no precipitate appeared, and the visual end point noted in Table VI was shown by a color change from brown-green to blue. In trial two a blue precipitate began to form quite early and the solution was so clouded by the precipitate that it was necessary to let the precipitate settle before the first excess di-tellurato cuprate (III) could be seen. The results are summarized in Table VI.

TABLE VI

TITRATION OF 25 ML ALIQUOTS OF DI-TELLURATO CUPRATE (III)
WITH 0.15N ARSENITE

Sample Number	Ml. of Arsenite to Visual End Point	Ml. of Arsenite to Dead-Stop End Point
1	11.55	11.55
2	11.69	10.79

The inverse arsenite titration was abandoned due to the lack of reproducibility.

The lack of reproducibility of the titers of the di-periodato cuprate (III) can be explained by a simple qualitative experiment. One can show that arsenite reacts with di-periodato cuprate (II) in an alkaline solution by mixing di-periodato cuprate (III) solution with alkaline arsenite. A precipitate forms immediately. The precipitate was separated by filtration and dissolved in hydrochloric acid. If potassium iodide is added free iodine is liberated. If the precipitate is dissolved in dilute nitric acid and silver nitrate is added, white silver iodate forms (34). Therefore di-periodato cuprate (II) is reduced by alkaline arsenite and the oxidation with di-periodate cuprate (III) is achieved in part by the copper (III) and in part by the periodate.

Glucose As a Standard

Beck has reported that the concentration of copper (III) solutions may be conveniently determined employing glucose as a standard. A 0.01M solution of glucose was prepared and used according to the directions of Beck (9).

When increments of one ml of 0.05M di-periodato cuprate (III) were added to the 0.01M glucose solution, the initial rate of reaction was slow, that is about thirty to forty seconds elapsed before consumption. Unfortunately the rate decreased so that finally it was impossible to tell visually in the highly colored solution produced if the copper (III) was still reacting or if an excess had been added.

Heating improved the rate, but varied combinations of temperature, alkalinity, and dilution failed to produce a rate rapid enough for a satisfactory visual end point.

Even if the rate were not prohibitive, the reaction is non-stoichiometric since some of the periodate is reduced to iodate. The supernatant of the titrations gives a white precipitate of silver iodate when treated with silver nitrate and nitric acid. An excellent discussion of the attack of polyhydroxy compounds in dilute potassium hydroxide by periodate has been published by Malaprede (35). He showed that periodate oxidizes the polyalcohols with the production of various organic acids, that the periodate goes to iodate, and that the rate and stoichiometry render the reaction unsuitable for volumetric use.

Di-tellurato cuprate (III) attacks glucose in an alkaline solution, but the end points are difficult to see, the rates are slow, and lack of reproducibility in the titers rendered the reaction unsuited to volumetric oxidimetry.

It was shown that di-tellurato cuprate (III) is reduced in a cold alkaline solution to a blue tellurato cuprate (II) complex. If excess glucose is available, and time is allowed, the blue tellurato cuprate (II) is reduced to red copper (II) tellurite precipitate. In a boiling solution glucose reduces di-tellurato cuprate (III) to free tellurium metal. One may test for tellurite in the presence of tellurate because sodium bisulfite rapidly reduces tellurite to tellurium metal in a six normal hydrochloric acid solution. Tellurate is not reduced under these conditions. The test was shown to be very sensitive to small amounts of tellurite by suitable blanks.

Sodium Tartrate as a Standard

Beck reported three identical check titers for the titration of tartrate with di-periodato cuprate (III), and that six equivalents of copper (III) were consumed for one mole of tartrate (11). On the basis of this report it was hoped that primary standard grade sodium tartrate dihydrate could be employed as a reference standard for the copper (III) reagents.

A 0.2M solution of the disodium tartrate dihydrate was prepared. Ten ml. aliquots were added to flasks containing 50 ml. of water and two grams of potassium hydroxide, and these solutions were titrated with di-periodato cuprate (III) solution. Occasionally a precipitate appeared. If it did, the precipitate was allowed to settle and the supernatant liquid was examined to see if an excess of di-periodato cuprate (III) had been added. If no precipitate appeared the color transition from blue to green was used as the end point. From Table VII it can be seen that the results were unsatisfactory.

TABLE VII

TITRATION OF 10 ML. ALIQUOTS OF 0.2M
$Na_2C_4H_4O_6 \cdot 2H_2O$ WITH $K_7Cu(IO_6)_2$

	Sample Number					
	1	2	3	4	5	6
Ml. of Cu(III)	41.60	41.65	40.25	45.70	41.42	37.68

Di-tellurato cuprate (III) is reduced by tartrate to a soluble blue tellurato cuprate (II) complex if the alkalinity is high, but to a yellow green tellurato cuprate (II) precipitate in weakly alkaline solutions. Due to a lack of reproducibility of titers, and to great difficulty in determining the end point visually because of the highly colored medium, tartrate was found unsuited to the standardization of di-tellurato cuprate (III) by visual end point technique.

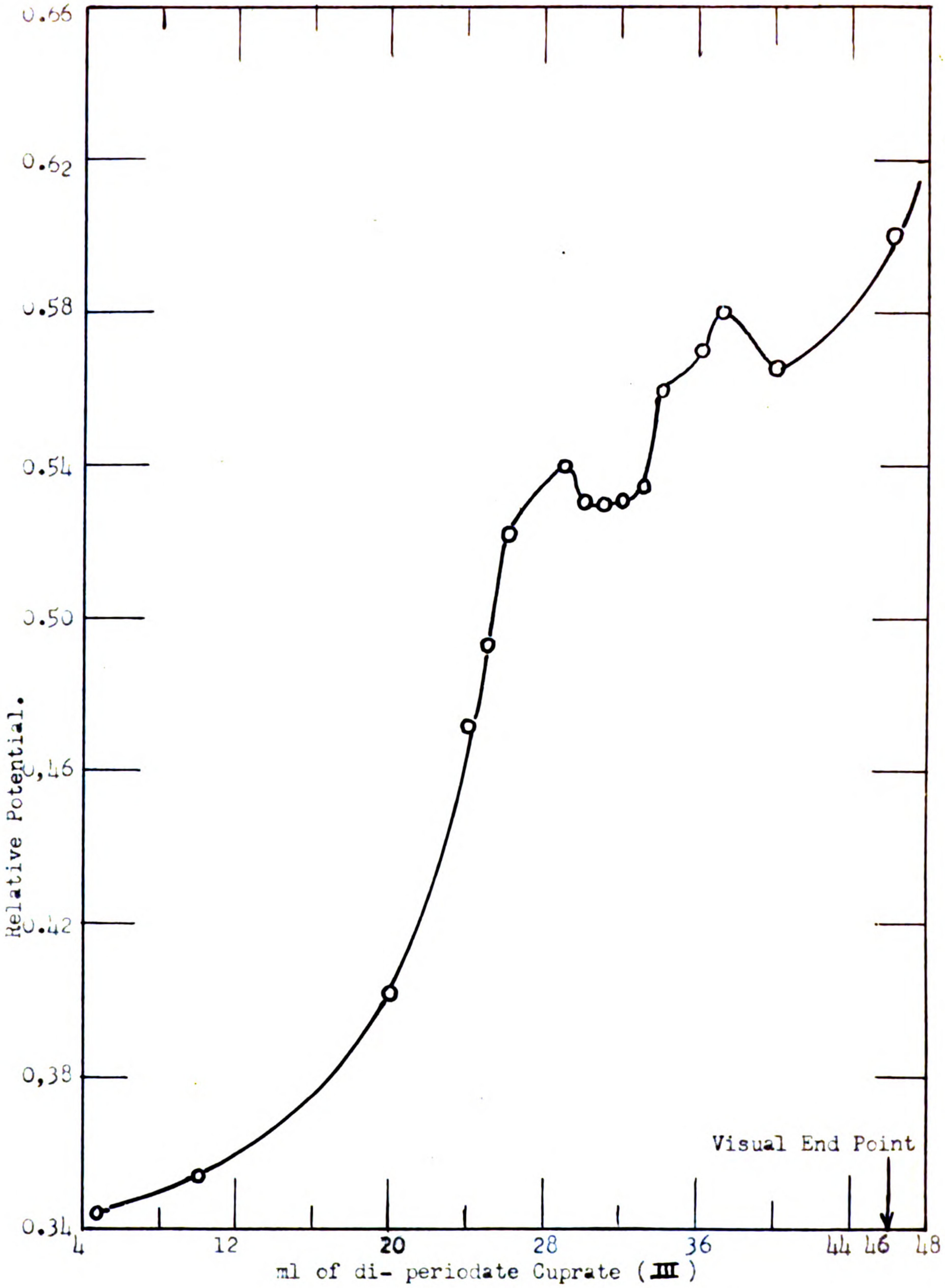


Fig.1. Potentiometric Titration of $Na_2C_4H_4O_6.H_2O$.

It was hoped that a potentiometric determination of the end point might improve the reproducibility of titrations. A Fisher Titrimeter was employed. A platinum-calomel electrode system was used. A ten ml. aliquot of 0.2M tartrate solution was added to 150 ml of H_2O containing 1.2 grams of potassium hydroxide. The 0.05M di-periodato cuprate (III) was consumed slowly, the first 0.5 ml requiring two minutes, and seven minutes passed before the titrimeter came to equilibrium when only 2.20 ml had been added. At 4.60 ml the solution contained a bluish white precipitation and 15 minutes were required for reduction of the di-periodato cuprate (III). The titration required about three hours to complete and the end point based on visual excess of the copper (III) was about 46 ml. Figure I shows the plot of the titration, and it can be seen that although there are several steep rises, there is no steep rise for a small volume increment characteristic of a potentiometric titration curve end point. Although visually the end point was about 46 ml, it is seen from Figure I that the potentiometric plot has not improved the end point.

The tartrate system was selected as representative of the redox systems encountered in copper (III) titrations suggested by Beck, and was studied by means of qualitative tests in an attempt to account for the variety of colors produced, and to explain the lack of reproducibility of titers.

Four samples were prepared to represent the initial reduction products, the products encountered later in the titration, the state of the copper and the iodine near the "end point", and the state of the copper and the iodine when an excess of copper (III) had been added. To each of four flasks 10 ml. of 0.172M sodium tartrate solution 50 ml. of distilled water, and 0.5 grams of potassium hydroxide were added. Five ml. of di-periodato cuprate (III) was added to the first 25 ml. to the second, 50 ml. to the third, and 75 ml. to the last. The four mixtures were filtered on Gooch crucibles with asbestos mats and washed well.

Sample I Filtrate (F_I) colorless; precipitate (P_I) pale blue.

Test	Conclusion
(1) $F_I + HCl \rightarrow$ clear soln $\xrightarrow{NH_3}$ no color	Cu absent
(2) $F_I + HCl + KI \rightarrow I_2$	IO_3^- and/or IO_4^- present
(3) F_I + solid KI $\rightarrow$ no I_2 on crystals	IO_4^- absent or in small quantities
(4) F_I + flame test for K^+	K^+ present
(5) $F_I + HNO_3 + AgNO_3 \rightarrow AgIO_3$ (white) Ref 34	IO_3^- present
(6) $F_I + HCl \rightarrow$ no I_2	I^- absent (since IO_3^- present)
(7) F_I alkaline to litmus	OH^- present

F_I contains KOH, KIO_3 and possibly small amounts of KIO_4, but no copper.

(8) $P_I + HCl + KI \rightarrow I_2 + Cu_2I_2$	Cu^{++} present
(9) $P_I + KOH \rightarrow$ blue copper periodate complex	IO_4^- present
(10) $P_I + HNO_3 + AgNO_3 \rightarrow$ no ppt	IO_3^- absent
(11) $P_I + HNO_3$ + flame test	No K^+

P_I contains only Cu^{++} and IO_4^- and probably partly as $H_6Cu(IO_6)_2$ since the material is K^+ free.

Samples II, III and IV were examined qualitatively with the tests employed in sample I. F_{II} was colorless and contained K^+, IO_3^-, and OH^-, but no copper, P_{II} was pale blue and contained copper (II) periodate. F_{III} was green and contained KIO_3, KOH, Cu^{+2}, and IO_4^- as the green complex of diperiodato cuprate (II), $H_2Cu(IO_6)_2^=$. P_{III} was copper (II) periodate. F_{IV} was brown and contained IO_3^-, Cu^{+3}, Cu^{+2}, IO_4^-, OH^-, K^+ and probably largely as $HCu(IO_6)_2^{-6}$ (brown), $H_2Cu(IO_6)_2$ (green), KIO_3 and KOH. P_{IV} was copper (II) periodate.

The reduction of di-periodato cuprate by tartrate does not proceed in a simple manner. It is obvious that copper (III) as $HCu(IO_6)_2^{-6}$ cannot be going to $H_6Cu(IO_6)_2$ and IO_3^- too, without the appearance of copper (II) in some new species. Note the copper (III) periodate ratio is one to two, and in the reduced form the copper (II) periodate ratio is also one to two. The iodate ion produced must come from the periodate ion and this indicates that the blue precipitate must be a mixture of a copper (II) periodates. Copper (II) periodates with the formulae $Cu_5(IO_6)_2$ and $HCu_4(IO_6)_2$ have been isolated by Bahl, Singh and Bali (30, 26). In addition to these complications the green $H_6Cu(IO_6)_2^=$ complex, or the blue $H_4Cu(IO_6)_2^{\equiv}$ may appear if the alkalinity is high. It is seen that the tartrate is oxidized by both periodate and copper (III). One might predict on the basis of the great variety of colored species which are produced, and the periodate attack, that the end point would be uncertain, and the reaction non-stoichiometric in the titration of tartrate with di-periodato cuprate (III). The titrations in Table VII and the potentiometric curve in Figure I clearly demonstrate the validity of such a prediction.

E. Potentiometric Titrations With the Fisher Titrimeter

The second section of the volumetric studies was directed toward finding a simple system capable of being oxidized in an alkaline medium by copper (III). Among the materials considered were hydrogen peroxide, potassium iodide, sodium thiosulfate, potassium iodate, sodium bisulfite and potassium cyanide. The hydrogen peroxide was eliminated because of a tendency of the peroxide to decompose spontaneously in the presence of the copper compounds, the potassium iodide, potassium iodate, and sodium bisulfite were oxidized too slowly, and among the remaining reagents, all of which had fair rates the potassium ferrocyanide was believed to be most promising because ferrocyanide should be oxidized directly to ferricyanide.

The first titrations were carried out visually employing ten ml. aliquots of 0.01M potassium ferrocyanide and the titers ranged from 33.5 ml. to 35.0 ml. of 0.005M potassium percupri periodate. A number of redox indicators were employed unsuccessfully in an attempt to improve the end point, so that the Fisher Titrimeter was again employed to improve the end point. Figures 2 and 3 show titration curves for two 10 ml. aliquots of 0.004M $K_4Fe(CN)_6$ with 0.005M copper (III) periodate. About 0.5 gram of potassium hydroxide was added, and distilled water was added to make the volume about 150 ml. The titration in Figure 2 was done at room temperature and titration in Figure 3 was done at 70°C. Figure 2 shows no inflection point improving the visual end point of 32.50 ml., but the curve in Figure 3 gave a good inflection point and potentiometrically the end point was shown to be 22.70 ml.

The visual end point was 29.00 ml. A fresh 0.003362M potassium ferrocyanide solution was prepared to check the work, and Figure 4 shows a titration carried out in an attempt to duplicate the results of Figure 3. Figures 5 and 6 show titrations of 20 ml. aliquots of 0.003362M potassium ferrocyanide titrated at 70°C. with 0.005M di-periodato cuprate (III). An inflection point was obtained in only one out of five potentiometric titrations, and this inflection point differed from the end point obtained by visual means by 6.30 ml. Potentiometric end point determinations of potassium ferrocyanide using di-periodato cuprate (III), employing the platinum calomel electrode couple with the Fisher Titrimeter, are not satisfactory because of the absence of suitable inflection points in the titration curves.

The ferrocyanide-ferricyanide, and di-periodato cuprate (II)-di-periodato cuprate (III) systems, represent couples which should be ideally suited to dead-stop end point detection. A new 0.139M solution of potassium ferrocyanide was prepared, and 20 ml. aliquots of this solution were titrated with di-periodato cuprate (III). The Fisher Electropode was used with platinum electrodes. Figures 7 and 8 show plots of the galvanometer deflection and ml. of 0.05M copper (III) periodate added. The end points obtained by graphical extrapolation are seen to be 12.70 ml. and 12.00 ml.

Calculations based on the visual end point titration show that about four equivalents of copper (III) per mole of potassium ferrocyanide were consumed. Based on the dead-stop titrations the calculations indicate about 4.5 equivalents of copper (III) per mole of potassium

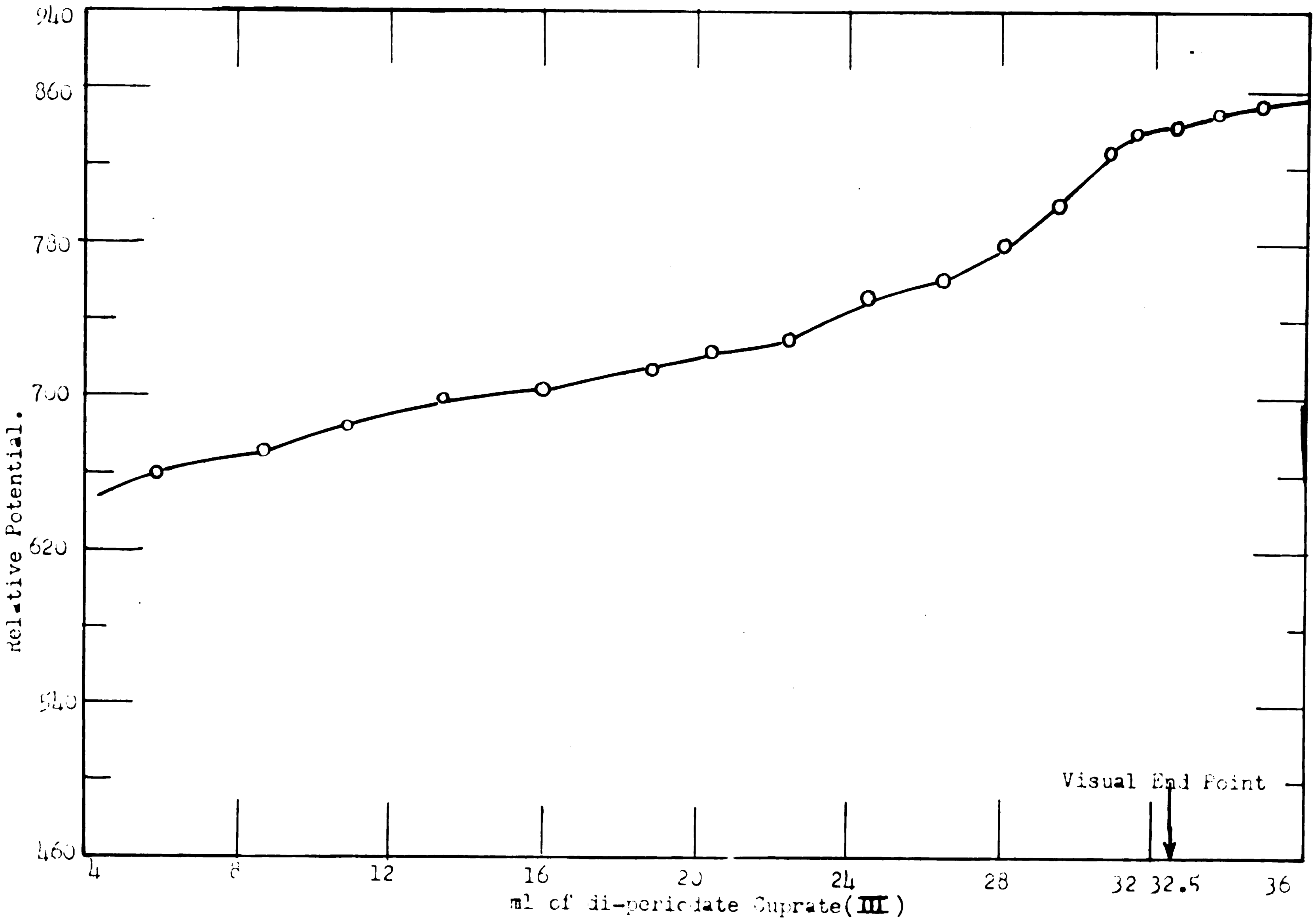


Fig.2. Potentiometric Titration of $K_4Fe(CN)_6$ at 40°C.

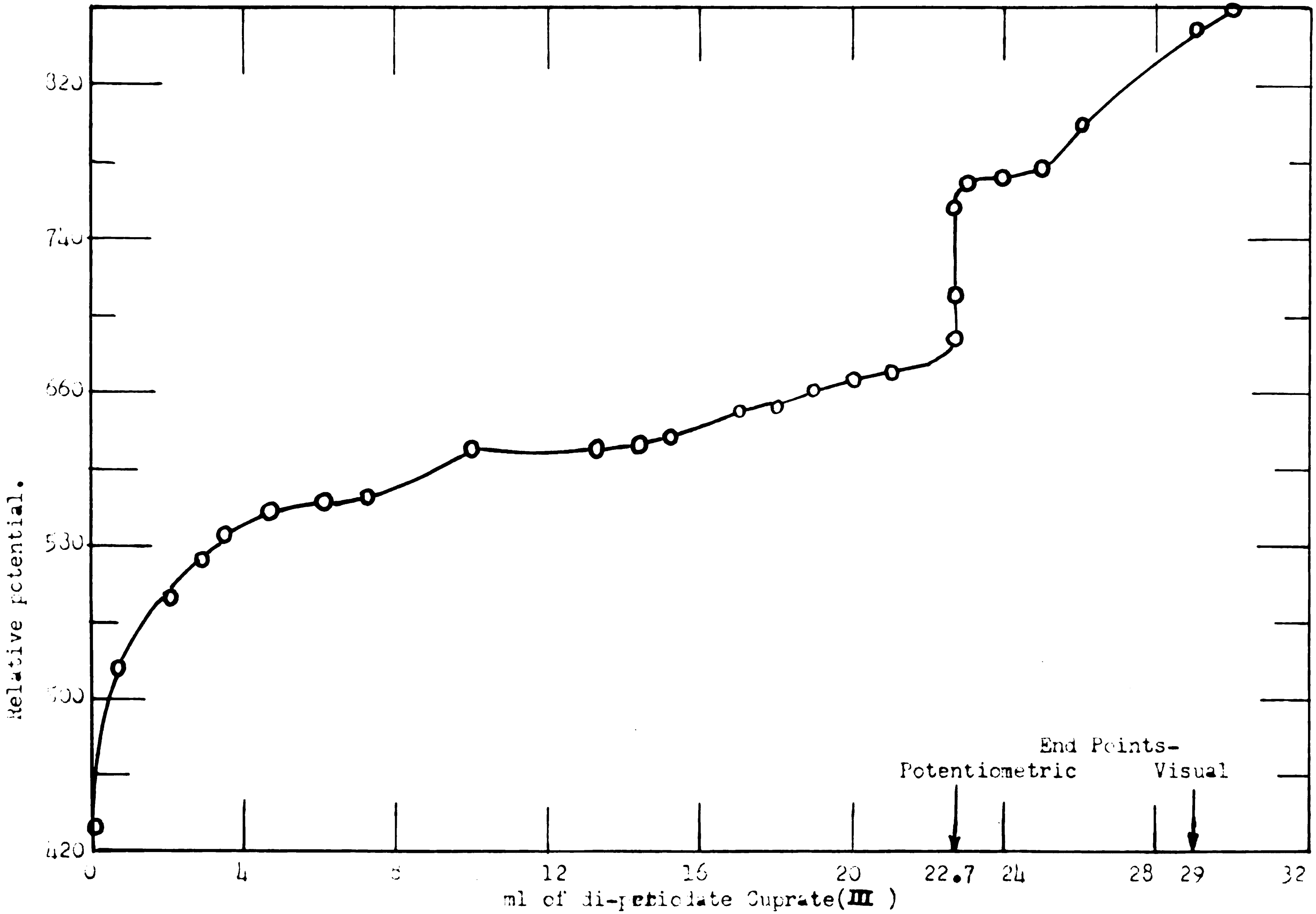


Fig.3. Potentiometric Titration of $K_4Fe(CN)_6$ at 70°C

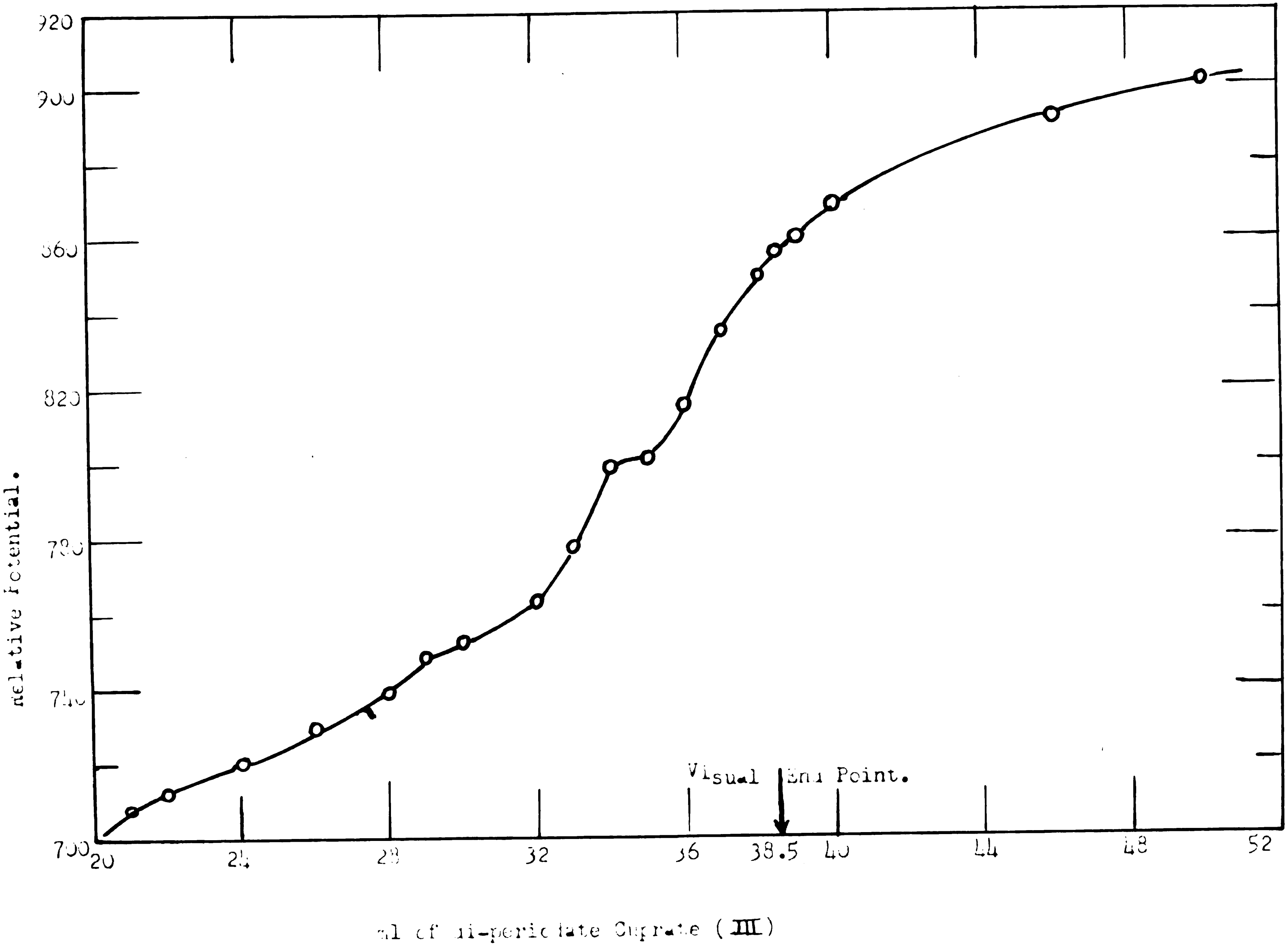


Fig.4. Potentiometric Titration of $K_4Fe(CN)_6$ at 70°C.

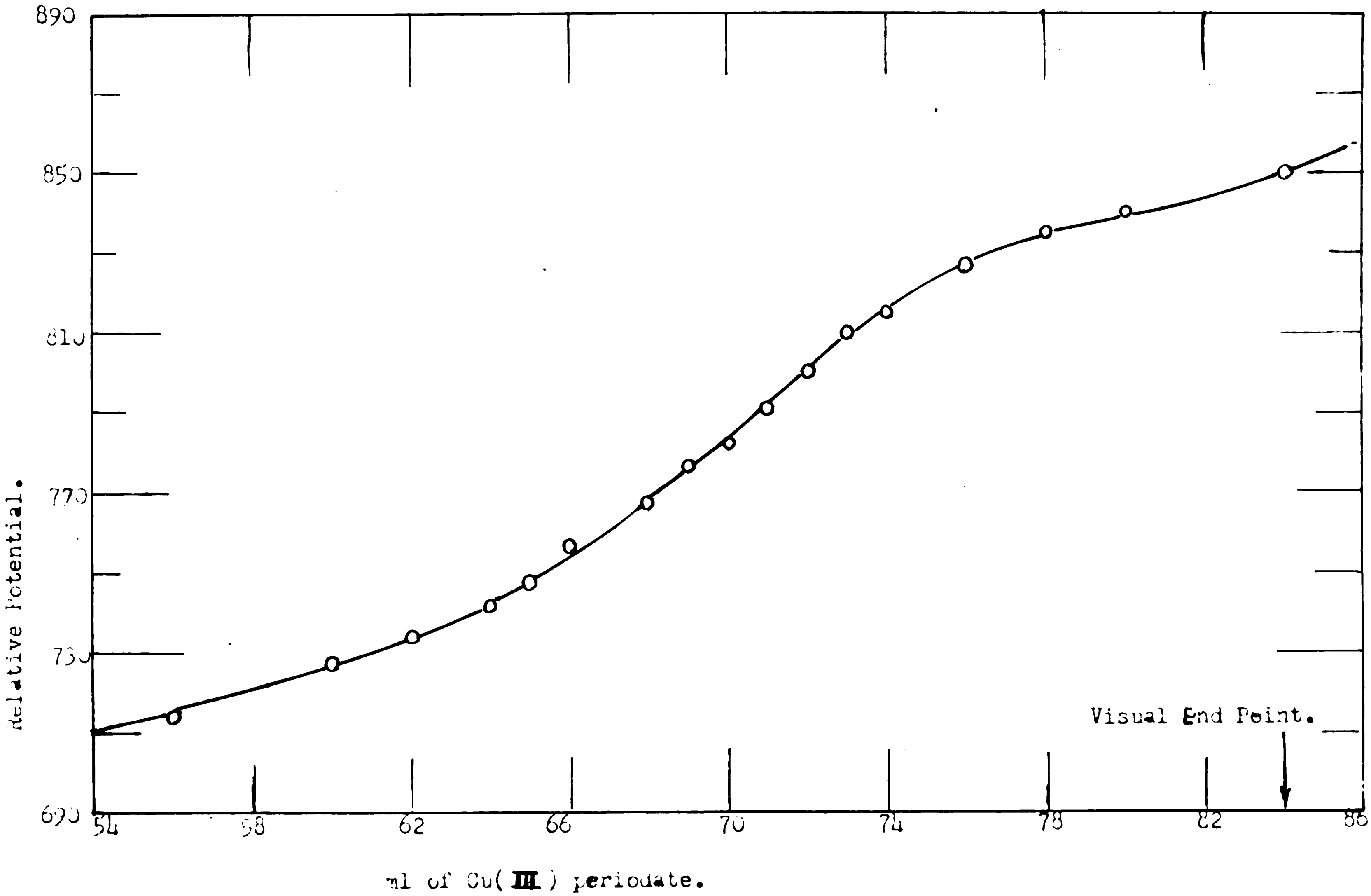


Fig.5. Potentiometric Titration of $K_4Fe(CN)_6$ at 70°C.

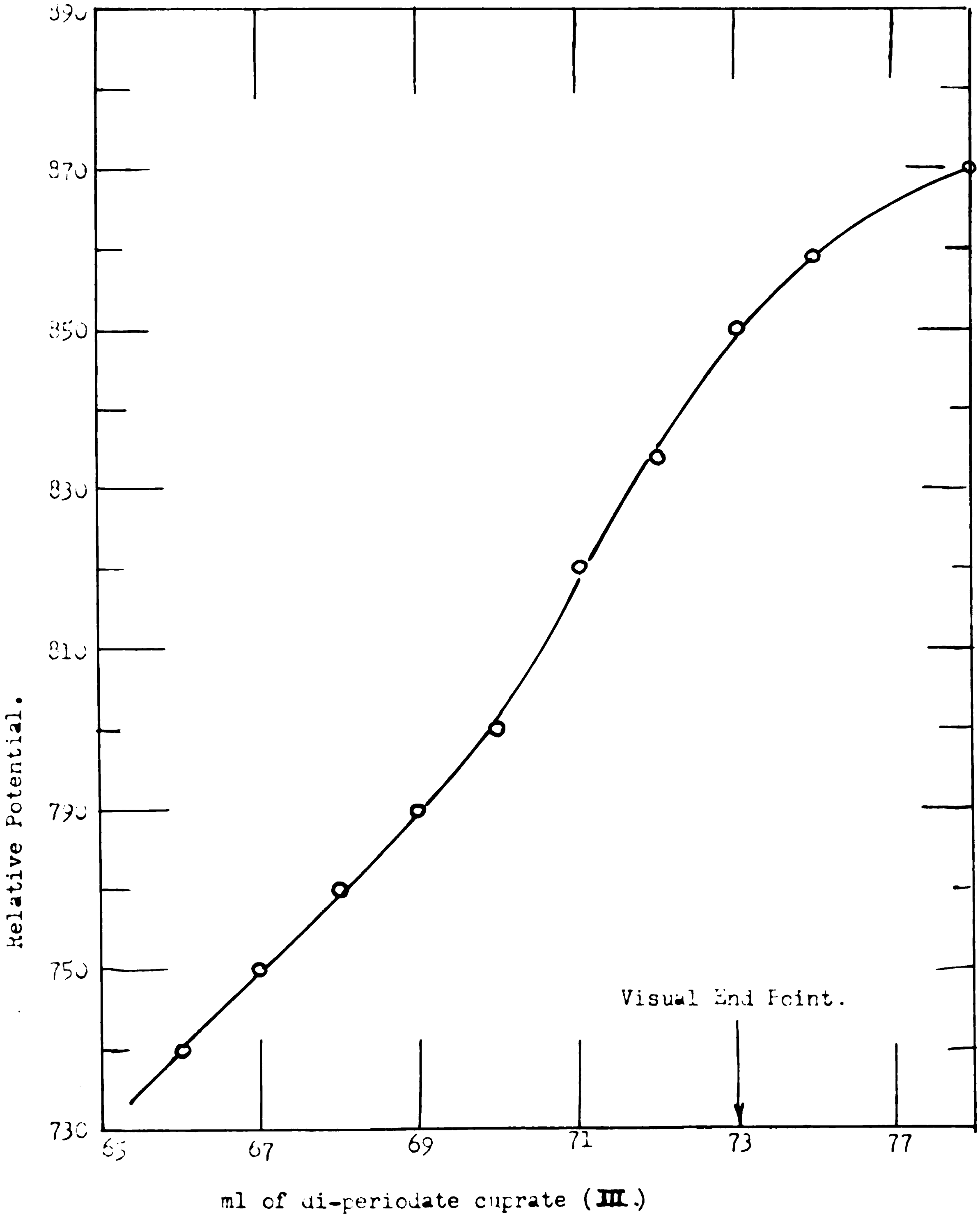


Fig.6. Potentiometric Titration of $K_4Fe(CN)_6$ at 70°C.

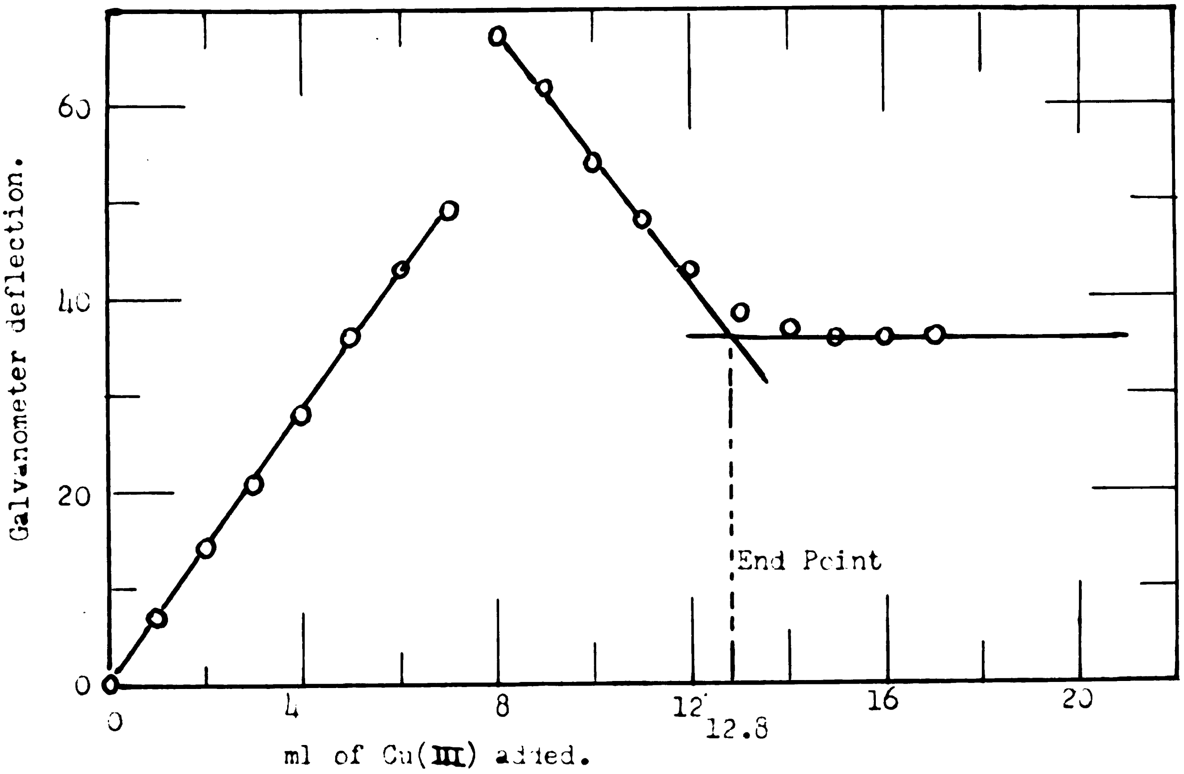
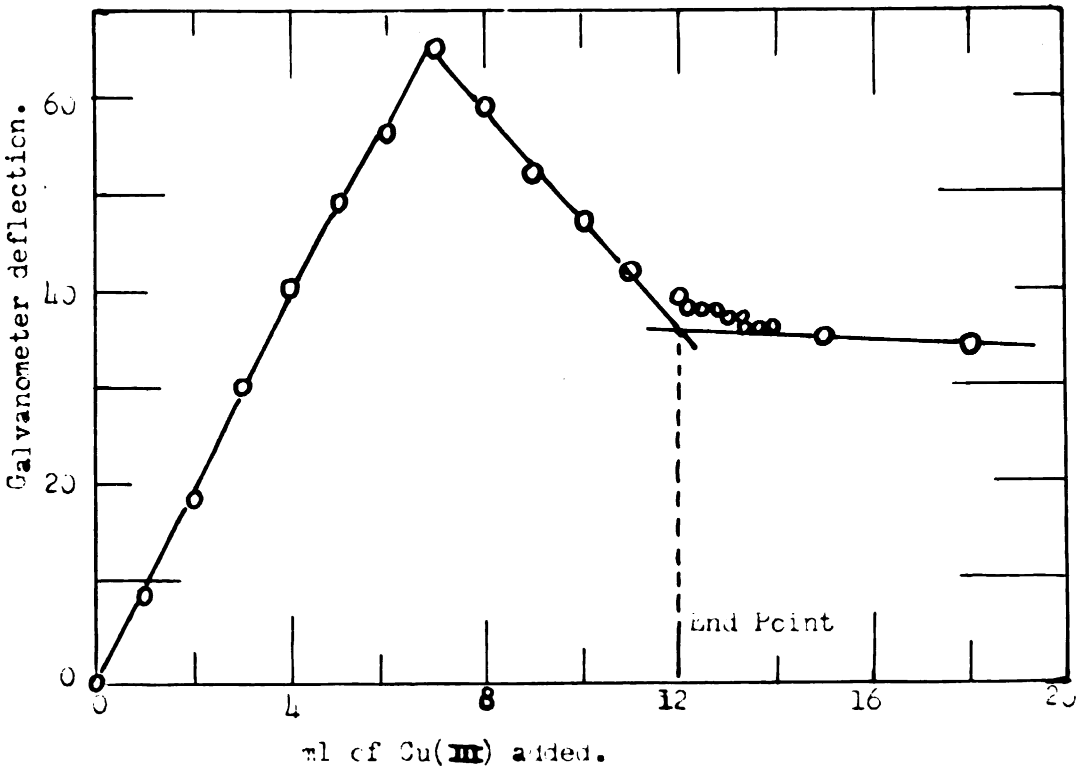


Fig. 7. Dead stop titration of $K_4Fe(CN)_6$ with di-periodate cuprate



Dead stop titration of $K\ Fe(CN)_6$

ferrocyanide were consumed. This differs greatly from the one equivalent consumption expected and therefore the ferrocyanide is not simply oxidized to ferricyanide, but oxidation of the ferricyanide itself must occur. Potassium ferrocyanide was found to be unsuitable for the standardization of potassium di-periodato cuprate (III) because no good end point detection devise could be found, and because the reaction does not represent a simple oxidation with clear stoichiometry.

F. Dead-Stop Applied to Copper III Titrations

It has been mentioned in the second section of volumetric experiments that potassium cyanide and sodium thiosulfate reduced copper (III) reagents rapidly. The fourth section in the volumetric experiments considers the application of dead-stop end point detection in the titrations of potassium cyanide and sodium thiosulfate with copper (III) reagents.

Potassium Cyanide

The results obtained when 10 ml. aliquots of approximately 0.13M potassium cyanide are titrated visually in solutions containing 1.5 grams of potassium hydroxide and 10 ml. of water with an approximately 0.05M solution of di-periodato cuprate (III), and with an approximately 0.05M solution of di-tellurato cuprate (III) are summarized in Table VIII.

The reproducibility of the titrations has been greatly improved by application of dead-stop end point detection. Figure 9 shows that the end point is marked by a large change in galvanometer reading. The

TABLE VIII

VISUAL TITRATION OF POTASSIUM CYANIDE WITH COPPER (III) REAGENTS

	Ml. Copper (III) Periodate	Ml. Copper (III) Tellurate
1	4.40	5.16
2	4.15	5.00
3	4.00	5.10

Fisher Electropode was used with platinum electrodes. It was found that 50 ml. aliquots of 0.01M potassium cyanide diluted with distilled water to 125 ml., and containing 2 grams of potassium hydroxide were titrated to 21.80 ± 0.02 ml., and calculations show that two equivalents of di-tellurato cuprate (III) for each mole of potassium cyanide are consumed.

TABLE IX

DEAD-STOP TITRATION OF POTASSIUM CYANIDE WITH POTASSIUM DI-TELLURATO CUPRATE (III)

	Sample Number			
	1	2	3	4
Ml. CuIII Consumed	21.80	21.78	21.82	21.82

Since two equivalents of the copper (III) are consumed it is reasonable to write the following reaction for the cyanide oxidation:

$$KCN + [O] \longrightarrow KCNO$$

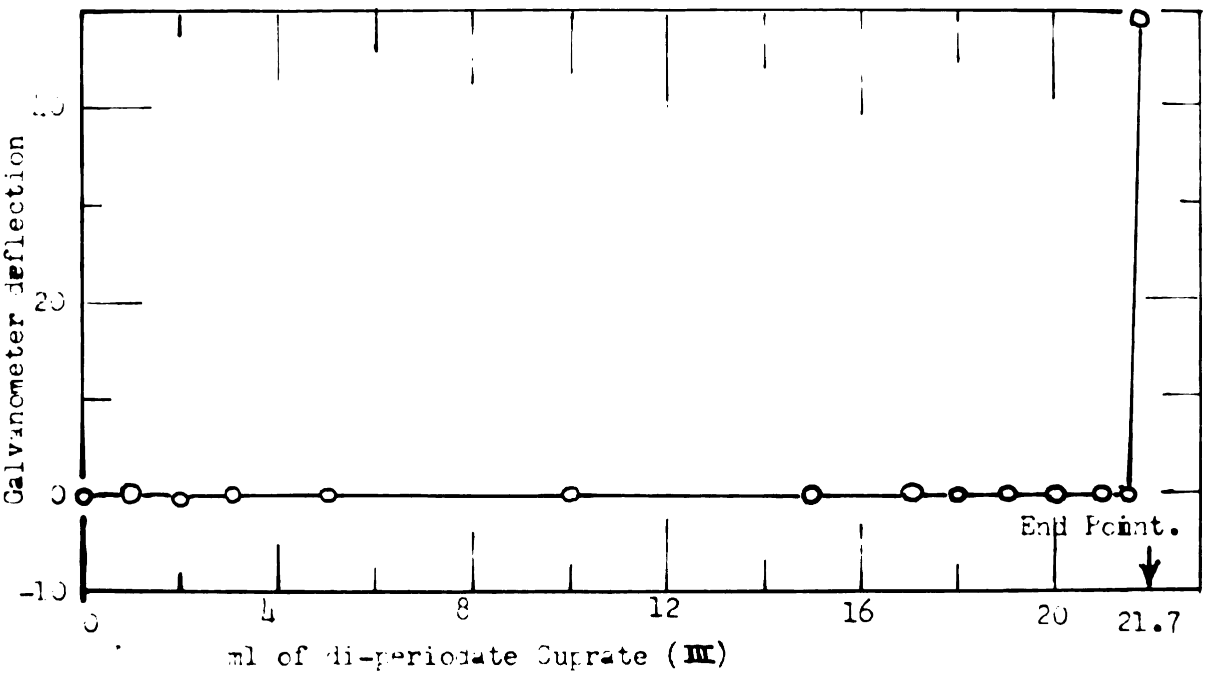


Fig. 9. Dead stop titration of KCN.

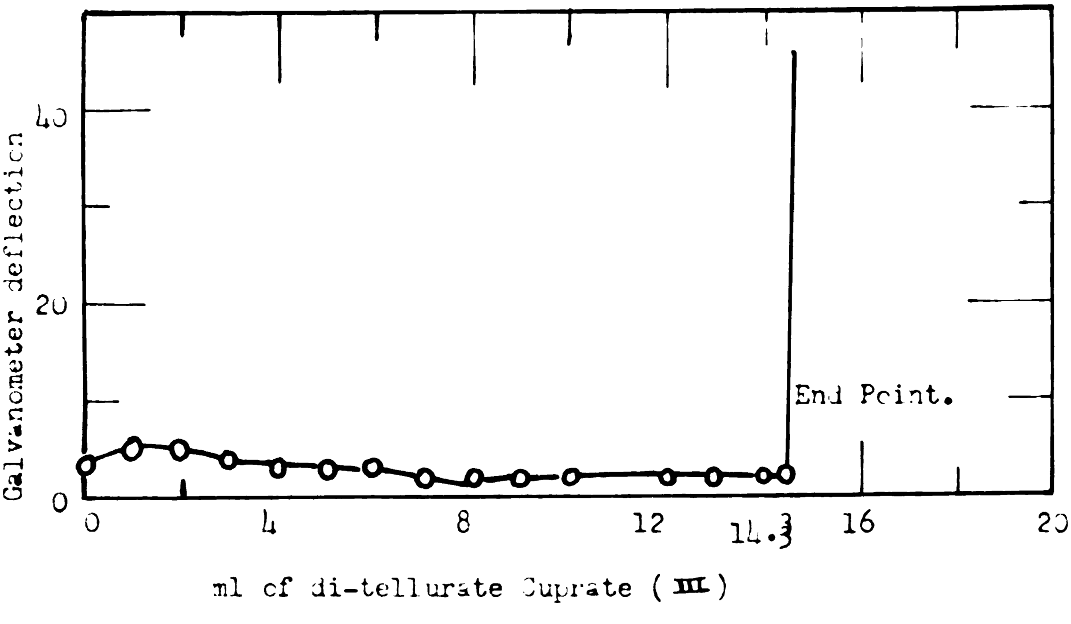


Fig. 10. Dead stop titration of $Na_2S_2O_3$

According to Treadwell and Hall (31) potassium cyanate rearranges in potassium hydroxide solution

$$KCNO + 2H_2O \xrightarrow{KOH} NH_4KCO_3$$

Ammonia is liberated from ammonium salts in alkaline solutions.

$$NH_4KCO_3 + KOH \longrightarrow K_2CO_3 + NH_3\uparrow + H_2O$$

If potassium cyanide is oxidized to potassium cyanate, ammonia should be evolved as a result of the rearrangement indicated.

It was shown that when the oxidation of potassium cyanide by di-tellurato cuprate (III) in a dilute potassium hydroxide solution is carried out in a Kirk micro diffusion cell, which has Nessler's reagent in the diffusion cup, ammonia is liberated, as indicated by a very positive Nessler test. The postulated oxidation of potassium cyanide to potassium cyanate has therefore experimental support. It was observed in the introduction that Beck had suggested that the reaction was

$$NaCN + 2KOH + 5O = K_2CO_3 + NaNO_3 + H_2O$$

with the consumption of ten equivalents of copper (III) reagent for each mole of sodium cyanide. My experimental evidence indicates Beck's conclusions about the cyanide oxidation are erroneous.

Sodium Thiosulfate

Sodium thiosulfate may be titrated visually in a saturated bicarbonate solution with di-tellurato cuprate (III). The oxidation is slow in potassium hydroxide, and the reproducibility is not good if di-periodato cuprate (III) is used in place of copper (III) tellurate due to periodate attack of the thiosulfate. The excess white bicarbonate and the green-yellow tellurato cuprate (II) precipitate produced in the titration tend to make it difficult to see the first excess of the di-tellurato cuprate (III). The reproducibility of titration values is greatly improved by using dead-stop end point detection.

Tables X and XI summarize the results of the dead-stop titration of 5 ml. aliquots of 0.145M sodium thiosulfate in 75 ml. of water containing two grams of solid sodium bicarbonate with di-periodato cuprate (III), and di-tellurato cuprate (III) using the Fisher Electropode with a 0.2V potential and a sensitivity of 5X.

TABLE X

DEAD-STOP TITRATION OF SODIUM THIOSULFATE WITH
DI-PERIODATO CUPRATE (III)

	Sample Number				
	1	2	3	4	5
Ml. of Cu(III)	25.70	28.65	23.39	17.70	16.40

TABLE XI

DEAD-STOP TITRATION OF SODIUM THIOSULFATE WITH
DI-TELLURATO CUPRATE (III)

	Sample Number				
	1	2	3	4	Av.
Ml. of Cu(III)	14.51	14.18	14.30	14.30	14.30

A heavy green precipitate appears during the titration. Figures 10 and 11 show the galvanometer readings during the titration. If the end point is taken as the first galvanometer reading of thirty or more which persists for thirty seconds when the last five milliliters are added dropwise precision of ± 0.05 ml. may be obtained. The reduction of di-tellurato cuprate (III) is slow near the end point.

According to the data in Table XI one mole of sodium thiosulfate consumes one equivalent of di-tellurato cuprate (III). Oxidation of thiosulfate to tetrathionate properly accounts for the data collected.

C. Copper (III) Applied to the Determination of Organic Compounds

The fourth section of the volumetric studies consisted of experiments designed to investigate possible applications of copper (III) volumetric oxidimetry in organic compound analysis.

Tartrate and glucose have already been considered. It was shown that benzene and cyclohexane are not oxidized even when refluxed with copper (III) for several hours. Cinnamic acid, malonic acid, acetone, and benzoic acid are all attacked, but the rate is very slow. When 0.05 gram of benzoic acid was added to dilute potassium hydroxide with only 0.5 ml. of 0.05 M di-periodato cuprate (III) the copper (III) was not reduced after five minutes of boiling, but the copper (III) was reduced after boiling for ten minutes. When 0.5 ml. of 0.05 M di-periodato cuprate (III) is added to a refluxing solution of ethyl alcohol the reduction of the copper (III) is instantaneous. The rate of reduction of di-periodato cuprate (III) in cold dilute ethyl alcohol is slow.

Ten milliliters of 0.05M di-periodato cuprate (III) were added to 10 ml. of 0.05M ethyl alcohol containing 1.0 grams of potassium hydroxide and the solution was refluxed. After thirty minutes the copper (III) had been reduced and ten ml. more of copper (III) were added. After six hours of increment additions the solution had become very dark blue, and it was not possible to determine whether there was an excess of copper (III).

Five more partial titrations of ethyl alcohol with potassium di-periodate cuprate (III) were performed and the results of these experiments are summarized in Table XII. The aliquots of ethyl alcohol should have required 20 ml. of the 0.05M copper (III) reagent to convert the alcohol to acetaldehyde, 40 ml. for conversion of the alcohol to acetic acid, and 120 ml. to convert the alcohol to carbon dioxide and water. Both the slow rate of oxidation, and the lack of suitable end point indicated this titration is unsatisfactory. All of the organic compound titrations considered had prohibitive rates in the ordinary sense of a volumetric titration.

H. Colorimetric Work

Absorption spectra were determined for 0.0002M and 0.0005M di-periodato cuprate (III) employing the Beckman DU Quartz Spectrophotometer. A solvent blank of dilute potassium hydroxide was employed, and the cells were matched to a precision of 0.001 cm. Although di-periodato

TABLE XII

RATES OF CONSUMPTION OF 0.05M COPPER (III) PERIODATE BY 10 ML. ALIQUOTS OF 0.05M ETHYL ALCOHOL

Grams of KOH	Milliliters of Cu(III)	Fraction For Conversion to Acetaldehyde	Time Required to Reduce Cu(III)	Temperature	Comments
0.2	0.5	0.025	more than 1 hr	room	No apparent reduction of Cu(III)
0.2	0.5	0.025	more than 1 hr	reflux	Some reduction of Cu (III) reagent to a light precipitate of Cu(II) periodate
2.0	0.5	0.025	45 seconds	reflux	Initial rate "fast" possibly due to impurities.
4.0	2.0	0.1	15 minutes	reflux	dark green divalent copper periodate: no precipitate appeared
2.0	4.0	0.2	2 hours	reflux	Color of solution too intense to be sure when the brown first disappeared

cuprate (III) absorbs somewhat in the ultraviolet region no absorption peaks were present. Suitable solutions of di-periodato cuprate (III), stabilized by dilute potassium hydroxide were prepared, and the behavior from 0% to 100% transmittancy for $\lambda = 410$ was investigated. This range was rechecked with fresh solutions, and both sets of solutions showed marked deviation from Beer's Law. The second set of solutions did not reproduce the values obtained by the first set, and both sets of solutions faded upon standing. Set I was measured after standing 2.5 hours, and Set II was measured immediately after preparation. The concentration range of 0.0005M to 0.05M copper (III) periodate was investigated using a Cenco Photolometer with a yellow glass filter. It was found that Beer's Law is approximately obeyed in this range, and that comparisons of solution strengths is possible to a precision of 10%.

TABLE XIII

TRANSMITTANCY RELATIONSHIP TO CONCENTRATION EMPLOYING THE CENCO PHOTOLOMETER TO INVESTIGATE DI-PERIODATO CUPRATE (III)

Conc M/L	Density/Concentration
0.0500	0.34
0.0200	0.39
0.0100	0.40
0.0050	0.40
0.0020	0.34
0.0005	0.34

CONCLUSIONS

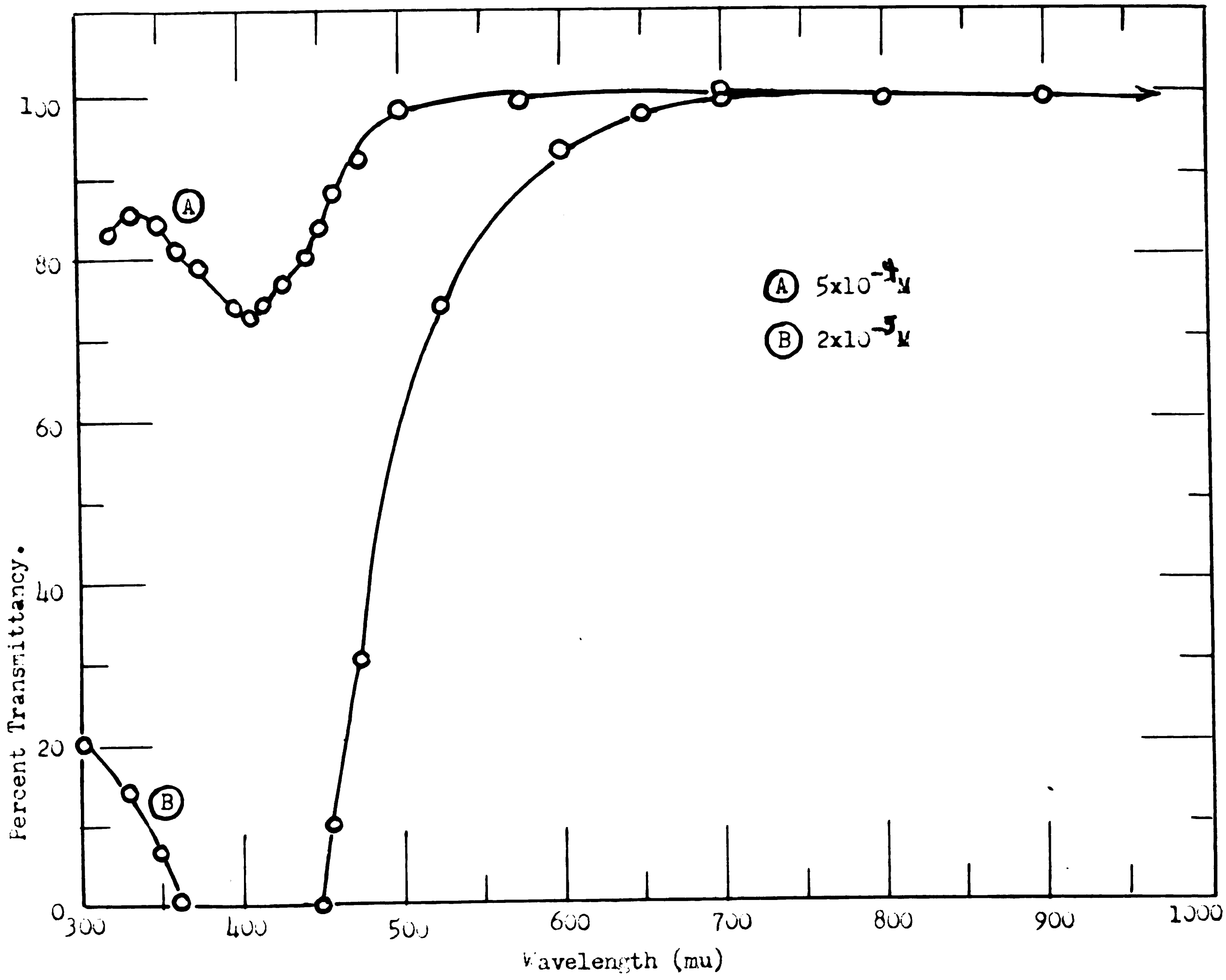


Fig. 11. Spectral transmittancy of di-periodate Cuprate (III)

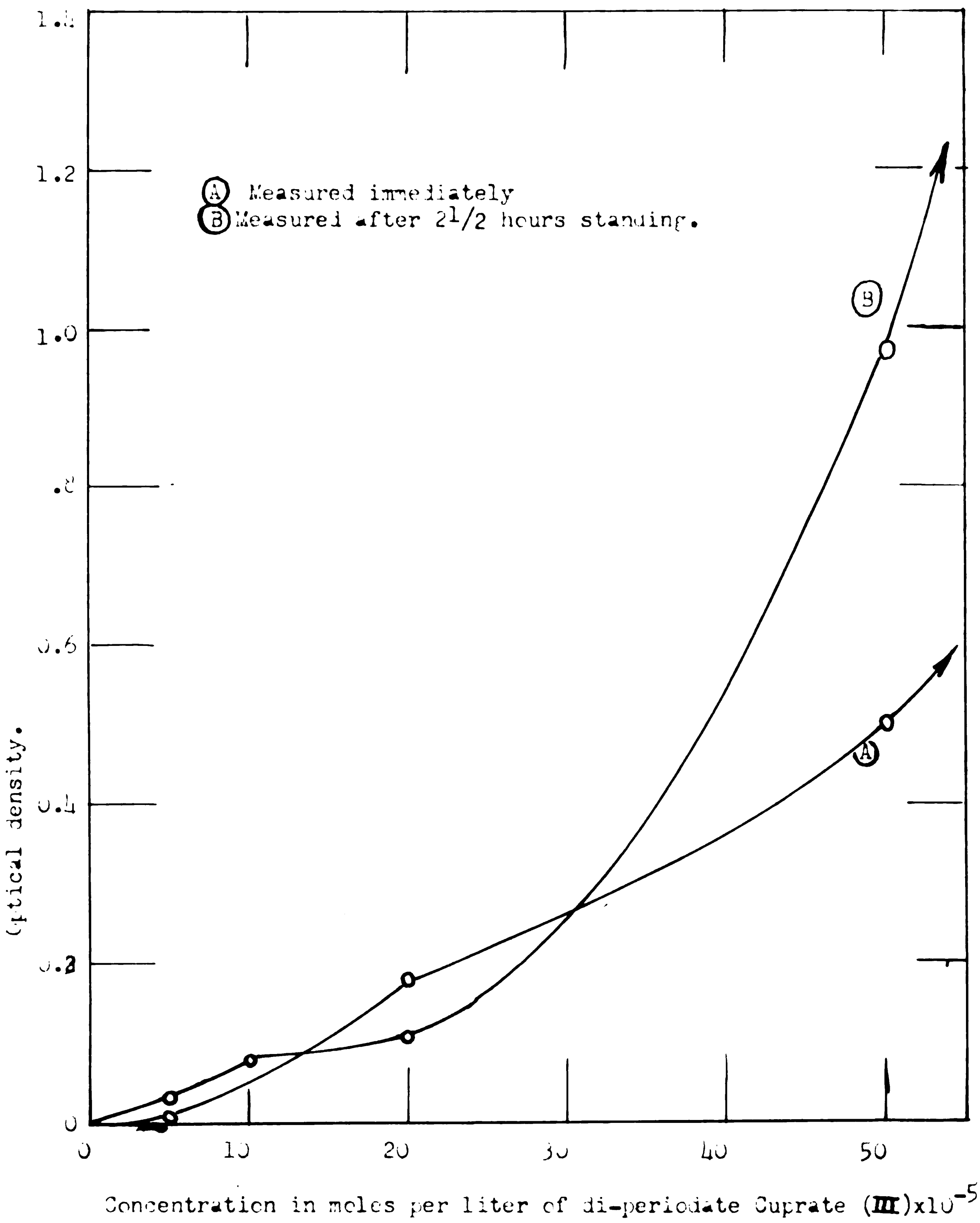


Fig.12. Beckman Du Spectrophotometer calibration curve (λ = 410)

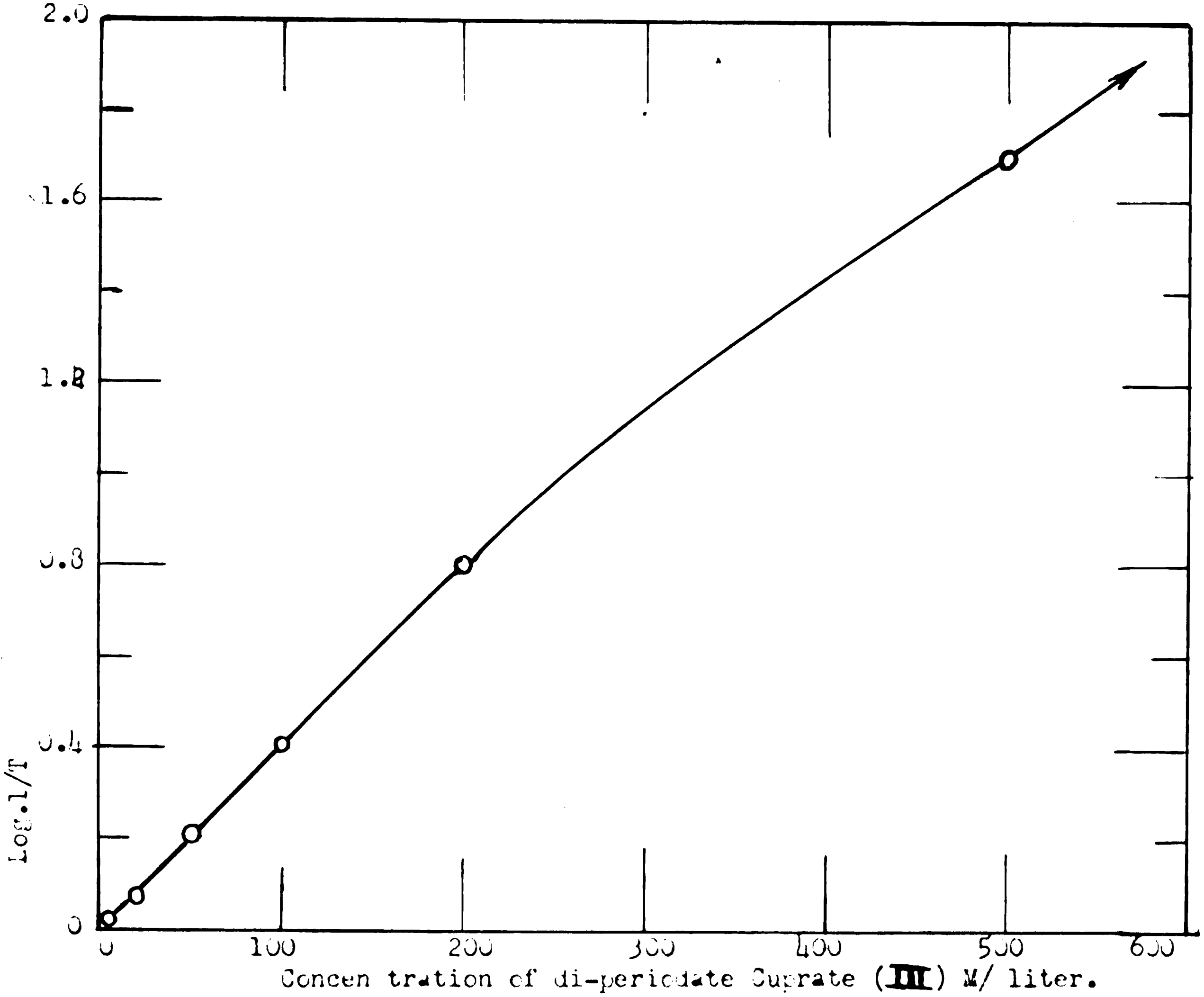


Fig. 13. Cenco Photometer Calibration Curve.

CONCLUSIONS

Only two stable complexes of trivalent copper, di-periodato cuprate (III) and di-tellurato cuprate (III) were found. The use of trivalent copper solutions in volumetric oxidimetry is limited by slow reaction rates, uncertain end points and non-stoichiometry of many reactions resulting in non-reproducible titers. Some of the non-stoichiometric reactions have been explained by showing that divalent copper periodate, and to a lesser extent divalent copper tellurate are partially reduced. In general, organic compounds are unsuited to volumetric determination by copper (III) reagents as a result of prohibitive rates. Potassium cyanide, and with less precision sodium thiosulfate, and potassium ferrocyanide may be empirically titrated with copper (III) reagents, and the nature of the oxidations of these compounds has been elucidated. Colorimetric determinations of di-periodato cuprate (III) are limited by the absence of an absorption peak, but empirical colorimetric comparisons may be made in the concentration range of 0.0005 to 0.05M copper (III) periodate.

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