THE ARGENTOMETRIC DETERMINATION OF THE HALIDES USING THE DEAD-STOP ENDPOINT

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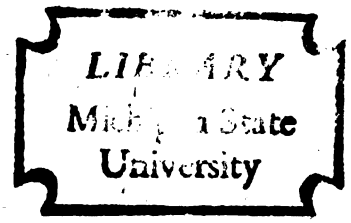

THE ARGENTOMETRIC DETERMINATION OF THE HALIDES USING THE DEAD-STOP ENDPOINT

By

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I. INTRODUCTION

Recent studies using the dead-stop endpoint technique have been primarily concerned with its application to oxidation-reduction systems. The polarization effect theory proposed by Foulk and Bawden (10) and Willard and Fenwick (32) has been further tested by Stone and Scholten (27) who showed that the applications of the dead-stop endpoint are much more numerous than those originally proposed. From their studies of different redox systems, Stone and Scholten suggested that the dead-stop phenomenon was not a polarization effect based on gas adsorption as suggested by Foulk and Bawden but concluded that the endpoint depended on electrolytic oxidation at the anode coupled with electrolytic reduction at the cathode. Stone and Scholten proposed that the dead-stop technique could be used when an electrolytic process was possible even if a redox system were not present.

The dead-stop technique is an electrometric method which is noted for its simple method of ascertaining the equivalence point by observing the current flow on a sensitive galvanometer. The endpoint is characterized, in general, by three possible ways in which the galvanometer may function; (a) the appearance of a small flow of current at the stoichiometric point; (b) the disappearance of a small flow of current at the stoichiometric point; or (c) the gradual disappearance of the current followed by a current increase after the endpoint. The functioning of the current in these endpoints may be explained as follows:

(a) an electrolytic cell begins to function as the stoichiometric point is reached and therefore, a current appears; (b) an electrolytic cell functions until the endpoint is reached causing a current to flow up to the stoichiometric point and then disappear; or (c) one electrolytic cell ceases to function as the endpoint is reached and a second electrolytic cell begins to function at the stoichiometric point. These endpoints are not a special case of the normal amperometric titration. In the dead-stop method, two half-cell reactions are involved and the current which flows between them is measured, while in the amperometric method, only one half-cell reaction is important with the amount of oxidation or reduction at the dropping mercury or rotating platinum electrode being the important factor.

The amperometric method differs from the dead-stop in that with the former the current is observed throughout the titration and the endpoint is determined graphically whereas only a sudden increase or sudden cessation of current is noted in the dead-stop method. The coulometric technique differs from the amperometric and dead-stop techniques in that it is based on the exact measurement of the quantity of electricity used in the determination. The quantity of electricity passed through the solution is measured and the amount of substance is calculated directly from Faraday's Law. A constant current method is best since time can be accurately measured. An indicator in the solution may be used to determine the approximate endpoint, or potentiometric methods are possible. An amperometric method for determining the endpoint has been applied to coulometric titrations which use electrolytically generated halogens.

Actually, this was a dead-stop technique since two indicator electrodes were used and the first large current increase due to an excess of the generated halogen marked the endpoint of the titration.

The endpoints noted in these cases are good examples of the first endpoint type in which a current appears or greatly increases at the stoichiometric point. Myers and Swift (20) used this method in the coulometric titration of arsenic by means of electrolytically generated bromine. An intermediate electrode reaction consisting of the anodic oxidation of bromide to bromine was used and the first excess bromine caused a current increase between a second pair of platinum electrodes. This current increase was easily noted on a sensitive galvanometer. The second pair of electrodes which were referred to as "indicator electrodes" had a small potential difference impressed across them as do the electrodes in the dead-stop method. Brown and Swift (3) applied the same method to the coulometric titration of antimony while Sease, Niemann, and Swift (26) used electrolytically generated bromine in the determination of thioglycol. Similarly, Meier, Myers, and Swift (19) applied it to the titration of chromate and vanadate using electrolytically generated cuprous copper. A method using electrolytically generated iodine for the titration of arsenic was developed by Ramsey, Farrington, and Swift (21) and an attempt to apply electrolytically generated chlorine to the determination of arsenic was made by Farrington and Swift (8). The indicator response was slower for chlorine than for bromine or iodine, making chlorine the least satisfactory of the three. In his coulometric method for the titration of 8-quinolonol with electrolytically generated

bromine, Carson (4) used an indicator system which he described as a hybrid of the amperometric indicator of Myers and Swift and the dead-stop indicator of Foulk and Bawden.

To determine the approximate endpoint in the above mentioned titrations, the indicator current was watched on a suitable galvanometer and the titration was stopped as soon as the current began to rise. Then small increments of the halogen were again generated into the system and galvanometer readings were taken. A plot of the indicator current versus the time of generation was constructed from the data obtained in this manner and the line was extrapolated to the time axis to give what is referred to by the authors as an "amperometric" endpoint.

The first endpoint type has also been applied by DuBois and Skoog (7) to the determination of bromine addition numbers. The flow of current at the equivalence point was detected by the opening of an electric eye of a cathode ray tube. Braae (2) used a similar method in the mercuric ion-catalyzed bromination of double bonds and found that it gave a good endpoint. Another application was that of Swinehart (29) who applied the dead-stop technique to the titration of stannous chloride with iodine and of zinc ions with ferrocyanide ions. The excess stannous chloride gave a small steady galvanometer deflection when 50 millivolts were applied across the platinum electrodes. Iodine was added and as the endpoint was approached the sensitive galvanometer showed small deflections which returned to the original steady readings. The endpoint was considered to be the first permanent deflection. The method for the determination of zinc was similar. A modified dead-stop method was used by Gale and

Mosher (11) in the determination of milligram quantities of vanadium in the presence of uranium. Wernimont and Hopkinson (30) applied the dead-stop method to the microtitration of selenium. They added an excess of thiosulfate and titrated this excess with the iodine liberated from an iodate-iodine solution. At the endpoint, as in the above cases, the galvanometer deflected away from zero. The attempt to reverse this titration and to titrate the liberated iodine was not successful. One of the most recent applications of the dead-stop technique was that by Scholten and Stone (24) and Ferrero and Brehain (9) to the determination of primary amines by diazotization.

As mentioned before, the above cited titrations are examples of the first dead-stop endpoint type in which a current begins to flow at the endpoint. This type is probably the most common of the three. It has been pointed out by Reilley, Cooke, and Furman (22) that in a reversible system, the current initially and at the endpoint should approach zero but that the dead-stop method is applied mostly to irreversible systems. The scope of this first endpoint type was widened by Clippinger and Foulk's (6) application of "electrometric indicators" so that the dead-stop technique might be used in neutralization and precipitation methods. Clippinger and Foulk used the iodide-iodate system as the anodic depolarizer in the neutralization reactions and sodium nitrite in the precipitation reactions.

The second endpoint type in which the current ceases to flow at the endpoint is exemplified by the original work of Foulk and Bawden (10) in which the dead-stop method was accidentally discovered. In their experiment,

Foulk and Bawden titrated iodine with thiosulfate and the light spot remained off the galvanometer scale and was deflected back to zero at the endpoint. This is in agreement with the theory of the second endpoint type as the thiosulfate-tetrathionate system is irreversible and no current would be expected to flow at the endpoint. Another example of this type comes from the work of Schroeder, Kay, and Mills, (25) who applied the dead-stop technique to the determination of amino acids by the iodometric titration of their copper salts. Probably one of the most useful adaptations of the dead-stop technique is that devised by Wernimont and Hopkinson (31) for the Karl Fischer method of determining water. In their work, Wernimont and Hopkinson found that 10-15 millivolts applied potential was enough to deflect the pointer off the scale where it remained during the addition of the standard water in methyl alcohol solution. The pointer returned to zero at the endpoint. The reverse titration was attempted but the endpoint was not as good.

The third endpoint type can only occur in redox work when two reversible systems are present, one preceding and one following the endpoint of the titration. An example of this is found in Wooster, Farrington, and Swift's (33) work with the coulometric titration of iodide with electrolytically generated bromine. The galvanometer registered an initial indicator current believed to be due to the iodine resulting from air oxidation. This current increased to a broad maximum corresponding to the oxidation of iodate to iodine, followed by a minimum near the equivalence point corresponding to the oxidation of the iodine to the

monovalent positive ion, and finally followed by a current increase due to the excess bromine. Often in these titrations it was found necessary to plot the current versus the time of generation and extrapolate to get the accurate endpoint.

II. THE TITRATION OF HALIDES

There have been several studies of the application of electrometric methods to the titration of the halides with a standard silver solution. The "galvanometric endpoint" developed by Salomon (22) is very similar to the work carried out in this experiment. Salomon's method was developed from an attempt to determine the normality of a silver nitrate solution using a 0.01 N potassium chloride solution. The solution to be titrated was prepared by accurately measuring about twenty milliliters of the potassium chloride solution into a beaker and diluting with water. Silver electrodes clamped to a sensitive galvanometer were immersed in this solution and an e.m.f. of 100 millivolts was impressed across them. The silver nitrate solution, whose normality was to be determined, was added slowly from a buret and the galvanometer deflection was observed. The first drop of silver solution established a current which was noted on the galvanometer. Every drop of silver nitrate added caused a slight rise in the flow of current. The first excess drop of the silver nitrate after the stoichiometric point caused a rapid increase in the current flow. This jump was described by Salomon as being unusually sharp on a sensitive galvanometer. The Volhard method was used as the control and the results of the two methods agreed within one part per thousand. The advantage of the sharp endpoint and the possibility of overtitrating and still determining the endpoint was pointed out by Salomon. This was the only attempt in the silver halide system, however, which Salomon made.

The method used in this experiment is similar to Salomon's in that the standard silver ion solution is added to the halide solution and the current flow is observed. A much smaller e.m.f. of about 10 mv. is applied across the silver electrodes and a different type of endpoint is observed. This will be described in detail in the experimental section.

Potentiometric titrations using a silver electrode as the indicator electrode were applied by Behrend (1) to the titration of halides with silver nitrate. Behrend found that it was possible to titrate halide pairs by adding ammonium hydroxide to increase the solubility of the more soluble silver halide. The first drop in potential when working in ammoniacal solution was equivalent to the amount of the less soluble halide. Then, nitric acid was added and the second potential drop corresponded to the total halide present. Behrend could not titrate bromide in the presence of chloride in this manner. Clark (5), who was primarily interested in photographic emulsions, did further work in which he measured the e.m.f. of a silver electrode connected to a normal electrode after adding silver nitrate in small increments. This method was quite successful for single halides, but the first endpoints were late in the titration of bromide-chloride and iodide-bromide combinations in water solution while the iodide-chloride mixtures were only in slight error. A 5% barium nitrate medium gave better results for both halide pairs and the combination of the three halides in photographic emulsions. Clark's paper also contains a good bibliography of previous work in this field.

It has been found that the potentiometric method can be applied to the determination of alkali halides in concentrations as low as 0.001 N

but that the silver electrodes were slow in attaining equilibrium. However, in Sutton's book (28), Glasstone states that although mixtures of halides can be analyzed in this manner, the results are not always accurate and the inflections on the potential curves are not always distinct.

The coulometric technique has been applied to the determination of the halides by Lingane and Small (18). The method was based on the measurement of the quantity of electricity required to achieve a quantitative reaction of the halide ions according to the reaction

$$Ag + X^- \longrightarrow AgX + e.$$

The halide solution was electrolyzed with a silver anode whose potential was controlled very carefully and a platinum cathode was used. Lingane and Small's results for the separate determinations of 0.5-100 mg. of the halide ions compared favorably with the classical methods. Iodide-bromide and iodide-chloride mixtures were analyzed with better accuracy than the argentometric titration but the bromide-chloride combination was poor since silver chloride coprecipitated with the silver bromide. During the titration the current decreased exponentially with time and finally dropped to virtually zero when the electrolysis was complete. The quantity of electricity passed through the solution was measured by a coulometer and the amount of halide present was calculated using Faraday's Law.

The use of the dead-stop endpoint in titrations using electrolytically generated halogens has been mentioned previously. An amperometric titration using rotating platinum electrodes has been applied to

the titration of the halides with a standard silver solution. Laitinen and Kolthoff (17) first attempted this in the titration of silver, which has a diffusion current, with potassium chloride, which has no diffusion current. Laitinen and Kolthoff noted that the current decreased proportionally with the decreasing silver ion concentration and reached a very small residual current with the presence of a large excess of potassium chloride. This endpoint might be compared to the third dead-stop type in which the current decreases and reaches zero at the stoichiometric point and then increases again upon the addition of excess titrant. The stoichiometric point corresponded to the intersection of these two straight lines. Very large currents comparable to the original diffusion current were found at a potential of 50 mv. versus the S.C.E. even after the equivalence point had been passed. These observations were attributed to the reduction of silver ions from particles of the silver chloride precipitate in suspension and colloidal solution.

Kolthoff and Harris (13) used silver nitrate and the amperometric method in the titration of mercaptans. When working in an ammoniacal medium to prevent the interference of chloride and bromide, the current was found to be small or zero when the silver was not in excess. The deflection after the endpoint corresponded to the diffusion current of the excess silver.

Soon after this, Laitinen, Jennings, and Park (15) attempted to reverse the earlier work with the halides by using the standard silver solution as the titrant. The amperometric endpoint with rotating platinum electrodes was again used. The determination of chloride was found to be

most successful in a solution 0.8 N with nitric acid and containing 0.1% gelatin. In solutions less than 0.002 N in chloride, a 50-75% acetone solution was used to decrease the solubility of the precipitate. Similar attempts with the bromide showed that gelatin was unnecessary in aqueous solution and acetone was again used for low concentrations. To prevent interference, a 0.01-0.02 N ammoniacal solution was used. The titration of iodide in a nitric acid, neutral, or dilute ammoniacal solution was found to be successful. A solution 0.1-0.3 N in ammonium hydroxide was used to prevent the interference of chloride and bromide. Laitinen, Jennings, and Parks (16) followed their earlier work with the application of the same method to the determination of halide mixtures. Included in this paper is an extensive bibliography of previous electrometric methods used in halide determinations. With this and their own previous work as a background, Laitinen, Jennings, and Parks found the best method to be one in which the solution was made 0.1 N in ammonia for the iodide, 0.8 N in nitric acid for the bromide, and 0.1% in gelatin for the chloride determinations. In comparing their method to the potentiometric technique, they stated that the amperometric method was more rapid but not too accurate, especially in dilute solutions.

The dead-stop method using platinum electrodes has been applied to the determination of the halides by Clippinger and Foulk (6) who proposed the use of "electrometric indicators" in precipitation and neutralization determinations. They used sodium nitrite as the anodic depolarizer during the titration of all the halides but the iodide which is an anodic depolarizer itself. A sharp reproducible endpoint was claimed and the

authors theorized that the first excess silver ion depolarized the cathode.

The dead-stop procedure used in this work replaces the platinum electrodes of the previous amperometric and dead-stop experiments with the silver electrodes of the potentiometric titrations. However, the current rather than the potential is observed in order to ascertain the equivalence point of the titration. Actually, the dead-stop endpoint using silver electrodes as applied to volumetric precipitations and the "galvanometric titration" of Salomon are identical except that Salomon used the halide rather than the silver solution as the standard solution and observed a current increase rather than a decrease in current at the endpoint. His work, however, could be considered to be a preliminary experiment in the application of the then unknown dead-stop technique to volumetric precipitation.

In order to test the newly proposed method, a study was made of its application in different media to the quantitative determination of single halides, one halide in the presence of another, and the combination of the three halides.

III. EXPERIMENTAL

1. Apparatus

A convenient system for applying the potential to the electrodes and measuring the current that flows is described by Wernimont and Hopkinson (31). The Fisher Scientific Company Electropode was found to be very convenient for this work. The dropping mercury electrode was removed from the Electropode and the leads from the two silver electrodes were inserted in its place. It was then used to apply the potential to the electrodes and the enclosed sensitive galvanometer was used to measure the flow of current. The actual current was not known but could be ascertained by the calibration of the galvanometer. However, only the relative current was necessary in this case.

The silver electrodes were prepared by joining silver and copper with silver solder. This was then sealed to glass tubing with De Khotinsky cement allowing approximately one cm. of silver wire to protrude from the end of the seal. The cement seal was then coated with glyptal to increase its water resistance. The copper wire extending from the other end of the tubing was clamped into the leads of the Electropode.

In later work, silver foil electrodes were used which were prepared by joining a piece of silver foil about 2.5 by 4 cm. to silver wire which was, in turn, soldered to copper wire and sealed in glass tubing in the same manner.

2. Reagents

The standard 0.1 N silver nitrate solution used in this experiment was prepared from Baker's Analyzed silver nitrate in one liter quantities. The approximate amount necessary for one liter of tenth normal solution was weighed out and dried in an oven for one hour at 110° C. It was then weighed on an analytical balance and the solution was prepared by diluting to one liter in a retested volumetric flask from which it was transferred to an amber bottle for storage and use.

Baker's Analyzed sodium chloride was dried in the oven at 110° for one hour before use. The potassium bromide used was of U.S.P. purity and therefore, its purity was checked gravimetrically as silver bromide. The results of the analysis are tabulated in Table I. The potassium bromide was found to be 99.9% pure or better. It was dried in the oven for one hour at 110° C before being weighed out for use. Potassium iodide

TABLE I

THE ANALYSIS OF U.S.P. POTASSIUM BROMIDE

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.4638	0.4634
2	0.5129	0.5128
3	0.4566	0.4558

(Fisher's A.C.S.) was dried in the oven in the same manner before being weighed out.

The 2% dextrin solution was prepared by weighing out approximately 20 grams of dextrin and dissolving it in one liter of distilled water. The ammonium carbonate solution was prepared by weighing one mole of reagent-grade ammonium carbonate and diluting it to one liter with distilled water.

3. General Procedure

The sample which was to be analyzed was weighed into a 250 ml. beaker with the sample size being limited so as to require between 15 and 60 ml. of 0.1000 N silver nitrate solution. One hundred milliliters of distilled water were added along with 5 ml. of the 2% dextrin solution to prevent the adherence of the halide precipitate to the silver electrodes. The electrodes were then immersed with only a short length of the protruding silver wire actually being in the solution. The stirrer was started and the galvanometer was set at zero. Then a potential of 10 mv. was applied across the electrodes.

The amount of applied potential is very important as the fundamental requirement for the production of the dead-stop endpoint is the use of the highest potential possible between the electrodes which still causes little current to flow. This potential can best be ascertained experimentally by preparing a solution of the water and dextrin and adding one drop of the silver ion solution. The electrodes are immersed, the stirrer started, and the potential is applied in approximately 5 mv. increments while noting the galvanometer deflection. The potential at which a rather large current increase is noted approximates that which should be applied

in the determination. Sometimes this method does not give too sharp a break and the only way to ascertain the correct potential is through the "trial and error" method. The largest potential possible should be impressed across the electrodes in order to obtain the sharpest endpoint. In working with the silver-silver ion system it was found that a current jump occurred when 5 mv. were applied but a sluggish endpoint was obtained. The system gave a much sharper endpoint when 10 mv. were applied although the increase in potential had little effect on the original current registered on the galvanometer. Since the highest sensitivity possible was required in these titrations, the galvanometer of the Electropode was operated at the full sensitivity of 0.011 microamperes per mm. at all times.

After the preparation of the sample as outlined above and the application of the potential, the 0.1 N silver solution was added from a 50 ml. buret in such a manner that rapid drops rather than a stream of titrant entered the solution. The approach of the endpoint was usually indicated by fluctuations in current followed by a gradual decrease in current flow. When this occurred the titrant was added dropwise allowing time for equilibration before the addition of the next drop. At this point in some titrations, the current decrease was very slow and one to two milliliters of silver solution had to be added in this manner while in other cases less than 0.5 of a milliliter was added to reach the final endpoint.

Also of utmost importance was the sensitivity of the electrodes. In order to remove all adhering precipitate and impurities from them following a titration, the electrodes were immersed in a concentrated

sodium thiosulfate solution and washed with distilled water before being used again. Electrodes which had been exposed to air for some time appeared to be sluggish when used in a titration. They seemed to be coated with a dulling film which was thought to be an oxide. In such cases the electrodes were scraped with a sharp object and then immersed in a thiosulfate solution before using.

4. Determination of the Single Halide

a. Chloride

The first attempts using this method were in the determination of the chloride. A sample of sodium chloride was prepared as described above and the titration was carried out in a solution containing five drops of concentrated nitric acid per 100 ml. The endpoint in this case was not too sharp, probably due to the fact that the silver chloride is the most soluble of the three silver halide salts. When the potential was first applied to the solution the current surged upward and then dropped slowly to a constant reading near zero. Upon the addition of the silver solution the current began to rise quite rapidly and then a bit more slowly, finally reaching a maximum at which a current reversal occurred. The endpoint was not marked by a sharp current decrease but rather the current dropped to a low at the endpoint upon the dropwise addition of the silver solution and finally the addition of one drop caused a gradual current increase. The decrease in current as the endpoint was approached was very gradual and at this point a short time was allowed for equilibration after each drop was added. A few excess drops of the silver solution, on the other hand, caused a rather large increase in current. In Table II are

recorded the results of some titrations of chloride in the nitric acid medium. These titrations were carried out very slowly in the region of

TABLE II

THE TITRATION OF CHLORIDE IN NITRIC ACID MEDIUM

Sample No.	Weight NaCl, g.	
	Taken	Found
1	0.1780	0.1787
2	0.2553	0.2548
3	0.2648	0.2643
4	0.2295	0.2293
5	0.2321	0.2317
6	0.2330	0.2329
7	0.2642	0.2649
8	0.1881	0.1878
9	0.2530	0.2534

the endpoint so the electrodes could equilibrate and more accurate results could be obtained.

The chloride was also titrated in acetic acid medium. Ten drops of glacial acetic acid were added to 100 ml. of the solution. The endpoint was quite similar to that found in the nitric acid medium but was a bit easier to ascertain. Table III lists the results of these titrations.

TABLE III

THE TITRATION OF CHLORIDE IN ACETIC ACID MEDIUM

Sample No.	Weight NaCl, g.	
	Taken	Found
1	0.2367	0.2367
2	0.2546	0.2545
3	0.2337	0.2343
4	0.2074	0.2071
5	0.2486	0.2482

An attempt to increase the sensitivity of the chloride determination was made by using the larger silver foil electrodes. These did give a slightly more rapid and larger galvanometer deflection at the endpoint in acetic acid medium making it a bit easier to follow the titration. The foil electrodes did serve to improve the chloride endpoint.

b. Bromide

The nitric acid medium was the first one tried for the titration of bromide. The current behaved much as it had during the chloride determinations. It approached a maximum about half-way through the titration and near the endpoint the current reversal was indicated by the needle shifting about the center of the galvanometer, finally going right rapidly and then left. Again, the endpoint occurred at the lowest galvanometer reading which was found by adding the silver solution dropwise when the approach of the endpoint was indicated and allowing equilibration with each drop. The final endpoint required approximately 0.10-0.15 ml. of titrant after the first large current reversal. However, it was easier to ascertain than the chloride endpoint. Table IV gives the results of these titrations. It should be stressed that the operator must be familiar with the endpoint before reproducible results can be obtained.

TABLE IV

THE TITRATION OF BROMIDE IN NITRIC ACID MEDIUM

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.3408	0.3408
2	0.3595	0.3598
3	0.4556	0.4547
4	0.3335	0.3326

In order to study the behavior of bromide in ammoniacal solution, titrations were attempted after adding 5 ml. of ammonium carbonate solution rather than nitric acid to the prepared sample solution. The titration proceeded much as the previous one but the galvanometer deflection was slightly less sharp in the ammoniacal solution as would be expected due to the slight solubility of silver bromide in ammonium hydroxide. The endpoint was again taken at the lowest current flow indicated by the lowest galvanometer reading and more rapid titrations resulted in larger errors. Table V lists the results of the titrations of bromide in ammonium carbonate solution. It will be noted that the last determinations in this sequence gave the best results. This further substantiates the statement that these titrations should be done by an experienced operator.

TABLE V

THE TITRATION OF BROMIDE IN AMMONIUM CARBONATE MEDIUM

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.2896	0.2883
2	0.3351	0.3330
3	0.3218	0.3208
4	0.2889	0.2856
5	0.2934	0.2939
6	0.4744	0.4744

The third medium in which the bromide was titrated was one in which ten drops of glacial acetic acid were added to the original bromide solution. The course taken by this titration was similar to the others.

As the endpoint was approached the current decreased quite rapidly and the galvanometer light shot off the left side. This sharp deflection was caused by the addition of only one drop of the silver solution and the light returned after a short equilibration time. The stoichiometric point in this case still coincided with the lowest reading obtained after allowing a short equilibration and an excess of silver again caused the current to rise. The results of these titrations are tabulated in Table VI.

TABLE VI

THE TITRATION OF BROMIDE IN ACETIC ACID MEDIUM

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.5666	0.5663
2	0.5308	0.5307
3	0.4636	0.4634
4	0.4399	0.4396
5	0.4167	0.4162
6	0.5707	0.5703
7	0.4788	0.4779
8	0.4625	0.4617
9	0.3832	0.3830
10	0.3664	0.3669

In general, the bromide endpoints in acid media were easier to ascertain than the chloride endpoints. The lower solubility of the silver bromide would indicate this.

c. Iodide

The titration of iodide alone was not attempted in nitric acid medium as even a very small amount of the acid had a tendency to release

iodine and gave incorrect results. Because of this, the first iodide titrations were carried out in a neutral, aqueous solution. The endpoint was a bit more obvious in these titrations. The current increased upon the addition of silver solution and the first clue of the approaching endpoint was given by a sudden current reversal indicated by a shift of the galvanometer off the left side of the scale. The silver solution was stopped at this point and the galvanometer light returned slowly. It was noted that coagulation of the precipitate usually occurred at this time. After this, the silver solution was added dropwise allowing time for equilibration and the galvanometer usually repeated these fluctuations until one drop caused a rapid and large current increase noted by a shift of the light completely off the right side of the galvanometer scale where it remained. This was taken as the final endpoint and corresponded closely to the true stoichiometric point. The results are shown in Table VII.

TABLE VII

THE TITRATION OF IODIDE IN NEUTRAL MEDIUM

Sample No.	Weight KI, g.	
	Taken	Found
1	0.6595	0.6571
2	0.7714	0.7714
3	0.5557	0.5576
4	0.4873	0.4870
5	0.6113	0.6121
6	0.6337	0.6343
7	0.6182	0.6184
8	0.8061	0.8054
9	0.6412	0.6409

The next attempt was the titration of iodide in ammoniacal solution prepared by the addition of 5 ml. of concentrated ammonium hydroxide to the sample solution. It was very difficult to find any galvanometer behavior which could actually be called an endpoint in these titrations. A rather rapid current increase indicated by a rapid shift to the right usually occurred in the general region of the endpoint. The coagulation of the colloidal silver iodide precipitate occurred at the same time as the shift. Further dropwise addition of the silver solution after this shift had little effect on the current and the ammonium hydroxide solution seemed to cause both a late endpoint and a late coagulation as will be noted from the data in Table VIII.

TABLE VIII

THE TITRATION OF IODIDE IN AMMONIUM HYDROXIDE MEDIUM

Sample No.	Weight KI, g.	
	Taken	Found
1	0.3717	0.3898
2	0.5041	0.5161
3	0.4729	0.4797
4	0.5230	0.5373
5	0.7443	0.7454
6	0.5104	0.5241
7	0.8133	0.8171
8	0.5258	0.5356
9	0.5163	0.5285
10	0.5948	0.6017

Since concentrated ammonium hydroxide gave such poor results and the success of the titration of iodide in ammoniacal solution was thought to be of some importance, the next attempts were with the titration of iodide

in ammonium carbonate medium. In these titrations, 5 ml. of the ammonium carbonate solution were added to the prepared sample and the titrations were carried out in the usual manner. The endpoint was much like that found in the neutral solution. Near the endpoint, one drop of the silver solution caused the occurrence of a rapid current reversal with the needle shifting to the left, sometimes going past zero and completely off the galvanometer scale. After a short equilibration, the galvanometer light returned to the previous reading. The next drop of titrant usually caused a large increase in current. In the first attempts this endpoint was difficult to find and both high and low results were obtained. After observing a number of titrations, however, the endpoint became more obvious. As will be noted by the data in Table IX, all of these endpoints occurred slightly early.

TABLE IX

THE TITRATION OF IODIDE IN AMMONIUM CARBONATE MEDIUM

Sample No.	Weight KI, g.	
	Taken	Found
1	0.5132	0.5116
2	0.5158	0.5149
3	0.7043	0.7024
4	0.5052	0.5034
5	0.4142	0.4123
6	0.4906	0.4884
7	0.5481	0.5480
8	0.4263	0.4249
9	0.5355	0.5342
10	0.3672	0.3661

Acetic acid was the third medium attempted for the iodide titration. Ten drops of glacial acetic acid were added to the sample before titrating. The endpoint in this case was less definite than before but gave the same general type of current fluctuations. The actual endpoint occurred at the point where the current greatly increased and the galvanometer light shot rapidly off the right side and did not return following a short equilibration. This usually coincided almost exactly with the coagulation of the precipitate. Some data from these titrations are given in Table X.

TABLE X

THE TITRATION OF IODIDE IN ACETIC ACID MEDIUM

Sample No.	Weight KI, g.	
	Taken	Found
1	0.5020	0.5017
2	0.4225	0.4213
3	0.5556	0.5552
4	0.5191	0.5199
5	0.4817	0.4813

5. Determination of One Halide in the Presence of Another

The first attempts to determine one halide in the presence of another were made with the iodide-chloride system. This titration would be expected to be successful because of the lower solubility of the silver iodide. Since Kolthoff (12) had been successful using ammonium carbonate in his work with adsorption indicators and the halide determinations, the first attempts were made in this medium. The solution containing known iodide was prepared in the usual manner except that approximately one gram

of the Baker's Analyzed sodium chloride was added. It was observed that 5 ml. of the ammonium carbonate solution were not enough to give a sharp endpoint so 10 ml. were used and the endpoint was improved. Again the endpoint coincided with the lowest current reading registered on the galvanometer during the final dropwise addition of the silver solution. A small current flow was registered on the galvanometer even at the endpoint. Further silver ion addition caused a rapid deflection to the right due to a large current increase. As will be noted from the results in Table XI, the endpoint in all the titrations was slightly late. In his work with adsorption indicators, Kolthoff found 40 milligrams of potassium iodide could be determined in the presence of one gram of potassium chloride with 1% accuracy. The similar analysis by the dead-stop method gave an average error of less than three parts per thousand for the sample range of 0.4 to 0.8 grams of potassium iodide in the presence of approximately one gram of sodium chloride.

The next attempts were with the determination of iodide in the presence of bromide. The sample was prepared in the same manner with approximately one gram of U.S.P. pure potassium bromide being added to the sample of potassium iodide. The endpoint was not definite in this titration. The current began to drop within about one milliliter of the calculated stoichiometric point and from that time the silver solution was added dropwise allowing time for equilibration. However, each drop caused only a slight lowering of the current and no definite endpoint was observed long after the calculated one had been passed.

TABLE XI

THE TITRATION OF IODIDE IN THE PRESENCE OF CHLORIDE IN AMMONIUM CARBONATE MEDIUM

Sample No.	Weight KI, g. Taken	Found
1	0.4319	0.4323
2	0.4562	0.4554
3	0.4817	0.4827
4	0.5952	0.5955
5	0.7847	0.7864
6	0.6115	0.6136
7	0.5775	0.5807
8	0.6356	0.6380
9	0.5618	0.5630
10	0.6002	0.6025

Table XII gives the results of some of these titrations in which the endpoint could only be approximated.

TABLE XII

THE TITRATION OF IODIDE IN THE PRESENCE OF BROMIDE IN AMMONIUM CARBONATE MEDIUM

Sample No.	Weight KI, g. Taken	Found
1	0.6010	0.6863
2	0.5672	0.5996
3	0.6827	0.7387
4	0.5747	0.6872
5	0.2671	0.2964

A several milliliter excess of silver caused the current to rise. It was obvious that the endpoint had been overstepped as a colloidal precipitate which did not resemble the silver iodide was beginning to form

in the supernatant solution. This precipitate darkened rapidly upon standing in the sunlight. An attempt was made to increase the sensitivity by using the larger foil electrodes. These electrodes appeared to be more sensitive in the titration but still did not give an endpoint which could be definitely observed through the galvanometer behavior. In his work with the determination of iodide in the presence of bromide, Kolthoff (12) also found that the endpoint came much too late when adsorption indicators were used. Since silver iodide and silver bromide are similar in their solubilities, a definite endpoint would not be anticipated.

The final attempts were applied to determining bromide in the presence of chloride. As would be expected from their solubilities, the bromide endpoint was not sharp and came much too late in ammonium carbonate medium as will be noticed in table XIII, and further work in this medium was

TABLE XIII

THE TITRATION OF BROMIDE IN THE PRESENCE OF CHLORIDE IN AMMONIUM CARBONATE MEDIUM

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.4678	0.4839
2	0.3587	0.3652
3	0.5735	0.5886
4	0.4555	0.4607

abandoned. Kolthoff also found the endpoint was too late and too indefinite.

Attempts were also made to determine bromide in the presence of chloride in acetic acid medium. The endpoints in these determinations were much sharper and the results are recorded in Table XIV.

TABLE XIV

TITRATION OF BROMIDE IN THE PRESENCE OF CHLORIDE IN ACETIC ACID MEDIUM

Sample No.	Weight KBr, g.	
	Taken	Found
1	0.5666	0.5671
2	0.5308	0.5309
3	0.4636	0.4642
4	0.4399	0.4397
5	0.4167	0.4171
6	0.5707	0.5710

No more work was done in this group although the application of a more strongly ammoniacal solution might serve to improve the endpoint.

6. The Titration of Three Halides in a Mixture

The titration of halide mixtures was originally only an attempt to determine total halides. Samples containing chloride, bromide, and iodide, which would require twenty-five to fifty milliliters of tenth normal silver nitrate solution, were weighed out. Five drops of dilute nitric acid were added to the first prepared sample and a visible amount of iodine was liberated. The next samples were titrated in the presence of ten and twenty drops of glacial acetic acid, respectively. The larger amount of acid did not improve the endpoint. At the beginning of the titration, the current behaved in the usual manner. After some silver

solution had been added, the current increased rapidly and the pointer was deflected completely off the right hand side of the scale. However, the galvanometer light did return to the scale and leave again at least once during the titration and a fair current reversal followed by the reaching of the lowest current flow occurred very close to the true equivalence point corresponding to the total halides. Upon further study of the significance of the first return of the galvanometer light to the scale during the course of the titration, it was found that the milliliters added at that point corresponded approximately to the number of milli-equivalents of iodide plus bromide in the sample.

Another sample was titrated with dropwise addition of the silver solution when the galvanometer pointer first returned to the scale. The current dropped slowly to a low point where it remained while an excess of about one milliliter of silver solution was added before the current again increased. At the endpoint equivalent to the total halides, the galvanometer light again returned to the scale and a low point in current was reached by dropwise addition of the titrant. Coagulation was observed shortly before the endpoint was reached. Further work with these combinations showed on close observation that another drop in current occurred between the beginning of the titration and the endpoint due to the chloride plus bromide present. It was thought that this could be equivalent to the number of milliequivalents of iodide in the sample and in another sample, the silver solution was again added dropwise at this point. This first endpoint had a tendency to arrive a bit late and to lag even more than the iodide-bromide endpoint as one and one-half to two milliliters of excess

silver solution were needed to cause a new increase in current after the current low was reached. The next drop in current corresponding to the iodide-bromide endpoint in the sample was quite accurate. The approach of the final endpoint was characterized by a rapid current reversal due to the addition of one drop of the silver solution. Further slow dropwise addition of the solution caused a decrease in current to the lowest reading followed by a slight current increase. The first excess drop of silver caused a new decrease in current which did not go quite as low as the preceding one followed by a rapid increase in current. A larger excess of silver ion caused the galvanometer needle to make a definite shift to the right. It was only after several such titrations were carried out that the operator could be sure of the three endpoints. Table XV gives the results of some consecutive titrations made in the above described manner. Since only the number of milliequivalents of the three halides had been recorded, the table states only the milliliters required for the three separate endpoints along with the number of milliliters actually used.

It will be noted that the intermediate endpoints usually came slightly late due to the lag which occurred when the less soluble halide was nearly all precipitated and the next less soluble halide was beginning to precipitate. Because of this overlapping, one must work with these titrations for some time before the intermediate endpoints are recognized.

A general titration curve plotting the current versus the milliliters of silver solution added is shown in Figure I. This shows the lag found to be present in these titrations. The first minimum corresponds to the

TABLE XV

THE TITRATION OF HALIDE MIXTURES IN ACETIC ACID MEDIUM

Sample No.	Iodide		Iodide+Bromide		Total Halides	
	Ml. Req.	Ml. Used	Ml. Req.	Ml. Used	Ml. Req.	Ml. Used
1	12.00	12.09	28.28	28.51	42.69	43.30
2	7.41	7.43	21.76	22.05	39.64	39.90
3	5.29	5.32	11.09	11.15	43.96	44.10
4	7.98	8.00	18.82	19.10	46.83	46.78
5	8.44	8.42	24.40	24.75	41.13	41.18
6	6.92	6.92	20.18	20.13	55.07	54.92
7	9.20	9.15	22.28	22.22	53.94	53.90
8	8.97	9.00	21.06	21.10	35.10	35.04
9	6.34	6.38	18.10	18.10	45.87	46.02
10	12.13	12.11	34.97	34.86	53.54	53.41

amount of iodide present, the second to the bromide plus iodide, and the third to the total amount of halides as would be expected due to the increasing solubility of silver salts in this order.

Since the intermediate endpoints were not too sharp, a titration was made using the larger silver foil electrodes. These electrodes did not greatly improve the first two endpoints but did make the total halide endpoint appear to be a little more definite. A titration was also attempted in dilute nitric acid solution but the endpoints were not nearly as sharp.

Since Laitinen, Jennings, and Parks (16) in their amperometric work suggested a hange in media to increase the sensitivity of the three different endpoints, similar media were tried in this experiment. In the first attempt, ten milliliters of the ammonium carbonate solution rather than pure ammonium hydroxide were added but the endpoint was no more

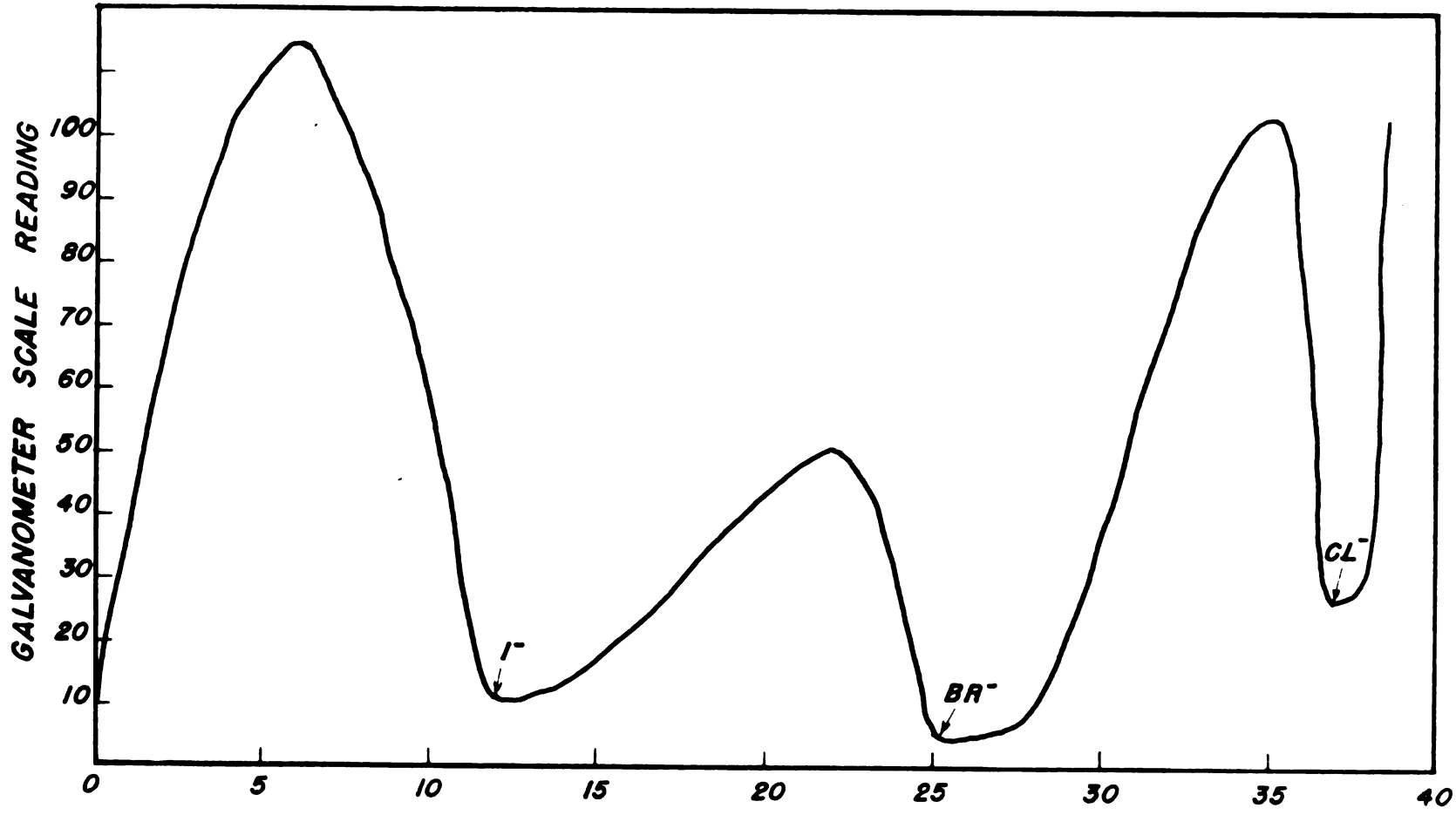

FIGURE 1

TYPICAL TITRATION OF A HALIDE MIXTURE WITH SILVER NITRATE IN ACETIC ACID MEDIUM

definite. Five drops of concentrated nitric acid were added for the bromide endpoint which also lagged. The addition of five milliliters of the dextrin solution gave the usual chloride endpoint and the use of five drops of concentrated ammonium hydroxide for the iodide determination did improve the endpoint slightly. However, the endpoint was not sharp in any of the titrations in which ammonium hydroxide was used. Amounts varying from ten to twenty drops of both concentrated nitric and glacial acetic acid were tried for the bromide endpoint and the twenty drops of concentrated nitric acid seemed to give the best endpoint. The titration using twenty drops of the glacial acetic acid on the other hand was not too successful. The sensitivity of the total halide determination was increased by the use of ten rather than five milliliters of the 2% dextrin solution. As a whole, the media suggested by Laitinen, Jennings, and Parks in their work were not found to be too successful in this experiment. Much more work should be done in studying media which might improve the sensitivity of the triple endpoint titration.

IV. CONCLUSIONS

It is evident from the above experiments that the dead-stop technique can be applied to some volumetric precipitation reactions without the use of anodic depolarizers when electrodes of the same metal as the titrant are used. This method cannot be applied to all metallic systems due to the tendency of many metal electrodes to be sluggish in reaching equilibrium in a solution. The application of the dead-stop method in this determination suggests the need of a theory to explain the phenomenon which would also be in agreement with previous theories concerning the dead-stop endpoint. Part of the dead-stop theory is based on oxidation taking place at the anode accompanied by a reduction process at the cathode. Here, the two silver electrodes assume the identity of an anode and cathode when a potential is applied across them in solution. Before the titration is actually begun, the electrodes will be surrounded by an excess of negative halide ions and the current registered on the galvanometer when the small potential is applied will be equal to or near zero when equilibrium is attained between the electrodes and the solution. When the silver solution is added, a silver halide precipitate is formed at once and some of this precipitate will come in contact with both electrodes. At the anode, which has attracted a large number of the negative halide ions, oxidation is taking place and some of the silver metal of the anode is being oxidized to silver ions which react with the halide ions in solution to precipitate out as a silver halide. At

the cathode, only a small amount of the halide ions are present and the reduction of the silver halide to free silver plus a negative halide ion is taking place. As the large excess of halide ions is decreased by their precipitation with the added silver ions, the current increases quite rapidly as indicated by the fast rise of the galvanometer pointer. But as the amount of silver ions added to the solution and the halide ions which have precipitated out with the silver ions become more nearly equal, an equilibrium between the reactions taking place at the two electrodes is reached. This

$$AgX + e \rightleftharpoons Ag + X^-$$

equilibrium accounts for the maximum in the titration curve and as more silver ions are added, precipitation continues to occur causing a shift in the equilibrium. Because of this, the current decreases quite rapidly at first and then more slowly as the last bit of the halide ion is precipitated. At the stoichiometric point the current should again be at the original zero point but due to the sluggishness of the metallic electrodes it only reaches a low point. The first excess silver ions cause another rapid increase in current by the electrolytic couple, $Ag = Ag^+ + e$. This theory, along with the knowledge of the solubility of the silver halide salts, would account for the maxima and plateaus seen in Figure I. It also would allow for the application of such a determination to other heavy metal systems. An attempt was made to use the lead-lead ion system in the titration of chromate. However, the method was found to be unsatisfactory due to the sluggishness of the lead electrodes as well as to the high oxidation potential of the chromic-chromate system in the medium used.

The accuracy of the single halide determinations carried out by one familiar with the endpoint is comparable to that of the amperometric and potentiometric methods. Since the coulometric method was carried out with much smaller concentrations, the results are not comparable. The dead-stop method is more rapid than the potentiometric titration and requires a very simple apparatus as well as not requiring the plotting of a graph to determine the exact endpoint. This method has the advantage that dark-colored substances would not interfere with the endpoint as they do in the Mohr, Fajans, and Volhard methods. Also, it is a direct determination and a less rigorous control of pH is required.

The accuracy of one halide determination in the presence of large amounts of another has already been compared to Kolthoff's work with adsorption indicators. A true comparison cannot be made as Kolthoff stated his accuracy for a more dilute solution than was used in these experiments. No results or accuracies were stated by many of the former workers in this field so that no actual comparisons can be made. The method outlined in this paper for the determination of the three halides is a rapid one with a fair degree of accuracy. The potentiometric technique is not too good since only small potential breaks of about 0.1 volt are found for the different halides.

Much more experimentation should be done before the study of the silver-silver ion system will be complete. Other media should be tried with the single halides. In the determination of one halide in the presence of another, different concentrations of ammonium hydroxide might be tried as well as Clark's (5) barium nitrate media. These methods

should also be tried with lower halide concentrations. In the mixture of the three, more study of media should be made in order to induce a sharper endpoint.

Also, there are many determinations in which the silver electrode-silver ion system could be attempted. An amperometric method has already been developed for the titration of mercaptans with silver nitrate (13) and adsorption indicators have been used in the titration of mercaptobenzothiazole (14). Other applications might be made in the determination of thiocyanate, selenocyanate, cyanate, cyanide, carbonate, iodate, oxalate, phosphate, arsenate, chromate, and succinate ions, higher fatty acids and barbituric acid derivatives. Attempts have been made to apply the Volhard method in these determinations and many of the suggested procedures are outlined by Kolthoff and Stenger (14). Of course, the success of the determination would depend on the conditions necessary for the stoichiometry of the reaction, the solubility of the silver salts, and the reactions taking place at the anode and cathode in the titration.

The dead-stop endpoint technique is a simple, rapid, and accurate method of determining the halides. This application to volumetric precipitation only further proves that the applications of the dead-stop endpoint are definitely more numerous than those proposed by Foulk and Bawden and do depend on the ingenuity of the analytical chemist as Stone and Scholten (27) have stated.

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