VOL. XL. APRIL, 1918. No. 4.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[COMMUNICATION NO. 59 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

THE IODIDE TITRATION OF SILVER NITRATE WITH PALLADIOUS NITRATE AS THE INDICATOR.[1]

BY LOUIS SCHNEIDER.

Received October 17, 1917.

Introduction.

Of the rapid volumetric methods used for the silver titrations, the Volhard method is the most widely employed. The limitations of this method are many, as summarized by Dewey,[2] who makes the following statement:

> "When the Volhard method is applied to miscellaneous materials some objections appear. Mercury and palladium interfere. No objection is made to moderate amounts of copper and platinum. It is often said that 70% Cu may be present, but this is certainly a mistake. Nickel and cobalt obscure the end color. It has been suggested when Ni and Co are present to add excess of sulfocyanate and titrate back with silver. Chloride of silver must be absent since it gradually reacts with sulfocyanate in solution. Lower oxides of nitrogen must be absent. Ferrous iron, in presence of nitric acid, must not be used as the indicator since this would mean lower oxides of nitrogen. It should be noticed that ferric sulfate as an indicator may cause precipitation of lead sulfate when the bullion contains lead."

Further,

"for those cases in which the amount of silver is extremely small or the solution highly

---

[1] A paper read before the American Chemical Society, at the Boston meeting, September, 1917.

[2] F. P. Dewey, *J. Ind. Eng. Chem.*, **6**, 728 (1914).

dilute, it (the Volhard method) lacks the sensitiveness of the methods of Gay Lussac or Pisani."[1]

The palladium method is especially adapted for the determination of very small amounts of silver with a satisfactory accuracy and overcomes the effect of those metals that usually interfere with the Volhard method. This new method consists of the titration of silver nitrate with potassium iodide in the presence of a very small amount of palladious nitrate. The silver nitrate is precipitated by the potassium iodide and the slightest excess of potassium iodide is converted by the palladious nitrate to palladious iodide.

Standard Solutions.

The solutions required for the palladium method were very easily and rapidly prepared. The standard silver solution of tenth-normal strength was prepared by weighing fused silver nitrate[2] previously ground, heated to 160° for one-half hour and cooled in a desiccator. The hundredth- and the thousandth-normal silver solutions were prepared by the proper and careful dilution of this tenth-normal solution.

For this investigation, the potassium iodide (Kahlbaum) was ground and heated at 160° for one hour, then accurately weighed to make a tenth-normal solution. The hundredth- and the thousandth-normal solutions were prepared by the dilution of the tenth-normal solution. For ordinary practice it would not be necessary to exercise such care to prepare an approximately tenth-normal potassium iodide solution. However, if c. p. potassium iodide is properly dried and carefully weighed to make a tenth-normal solution, the potassium iodide solution would need no further standardization by silver nitrate, provided the recommended conditions for titration are followed and the constant error correction of 0.03 cc. applied when 0.1 *N* potassium iodide solution is employed. This latter procedure does not necessitate, for determinations of ordinary accuracy, the preparation of a standard silver nitrate solution.

Indicator.

The palladious nitrate indicator used in this investigation was a solution of palladious nitrate in 16% nitric acid (free from nitrous acid) with a metal content of 0.06%. The palladious nitrate solution may be prepared by dissolving the weighed palladium in nitric acid and evaporating to dryness, then dissolving the crystals in 15 to 20% nitric acid (free from nitrous acid) and filtering.

In applying the palladium indicator it was found advisable to employ

---

[1] L. W. Andrews, *Am. Chem. J.*, 24, 256 (1900).

[2] The silver nitrate used was that prepared by the Eastman Kodak Company and conformed to the requirements of acidity and permanganate number as specified for the silver voltameter. Rosa, Vinal and McDaniel, "The Silver Voltameter," *Bull. Bur. Stand.*, 9, 526.

a protective colloid to prevent the occlusion of silver nitrate or potassium iodide in tenth-normal titrations. Then, again, for very dilute solutions, the use of a protective colloid was necessary in order to obtain a precise colorimetric comparison in determining the end point. It was found most advantageous to use an addition of a 5% gum arabic solution to the silver nitrate solution to be titrated. This addition of gum arabic afforded very good precision and satisfactory accuracy.

Other protective colloids were tried, such as soluble starch, gelatine, agar-agar, gum tragacanth and white dextrine. The order of their usefulness as protective colloids is, respectively, (1) gum arabic, (2) gelatine and agar-agar, (3) gum tragacanth, (4) dextrine, and (5) soluble starch.

For tenth-normal concentrations of silver nitrate, 5 cc. of a 5% gum arabic solution were used, whereas for thousandth-normal solutions, 1 cc. was sufficient because of the dilution of the electrolytes. To prevent decomposition of the gum arabic solution, a small amount of thymol (less than 0.1 g. per 100 cc. of solution) was added to the filtered gum arabic solution which then kept for months without any signs of decomposition or mould growth.

Containers.

The titration may be made in various containers such as porcelain crucibles, casseroles, evaporating dishes or in square bottles.[1] Although fairly good precision can be obtained with porcelain ware, the square wide-mouthed bottles of colorless glass are preferred and recommended. When these bottles are placed on an evenly illuminated sheet of opal glass or white paper, they enable one to make a precise comparison, whenever necessary, of the colors of the supernatant liquids by transmitted light viewed against a white background. Three sizes of the square bottles were employed; the smallest had a diameter of 46 mm. and 60 cc. capacity, another a diameter of 55 mm. and 130 cc. capacity, and the largest a diameter of 70 mm. and 250 cc. capacity.

Sensitiveness of Indicator.

The visibility of palladious iodide, as determined by adding 0.2 cc. of 0.0002 *N* potassium iodide to 10 cc. water containing 0.25 cc. palladious nitrate indicator, was 1 part in 1,400,000 parts of solution.[2] The coloration of the liquid was reddish brown and easily discernable, comparison with a blank being unnecessary. Of course, under these conditions, the optimum sensibility was reached since no silver iodide was present to interfere with the coloration of the liquid. However, under working conditions as for example the titration of silver nitrate with tenth-normal potassium

---

[1] W. M. Dehn, This Journal, **39**, 1392 (1917).

[2] R. Kersting, *Ann.*, **87**, 19 (1853), in the estimation of potassium iodide with palladious chloride, obtained a faint brown coloration with an iodine content of 1 part in 1,000,000.

iodide, a sensibility of 1 part in 500,000 parts of solution was obtained without any difficulty.

Series of experiments were made to determine (1) the minimum amount of indicator required to produce a definite end point for various concentrations of silver nitrate with and without gum arabic present, (2) the influence of the dilution of tenth-normal silver nitrate solutions upon the sensitiveness of a fixed quantity of the indicator, and (3) the influence of various concentrations of palladium upon a fixed concentration of silver.

I. Effect of Dilution on Sensitiveness of Indicator.

A series of experiments similar to that given in Table I was conducted with the use of 1 cc. 0.1 *N* silver nitrate instead of 5 cc. The results were practically the same since only 0.03 to 0.04 cc. of 0.1 *N* potassium iodide was required to produce the brown coloration at the end point. The color of the end point obtained in Expt. 5 was reddish brown, which was considerably less intense than the color in the other experiments, and proved to be at the limit of easy discernability of the end point, without the use of a blank or comparison standard. Therefore, it may be concluded from the experiments in Table I, that dilutions of 0 to 200 cc. of water are without any appreciable influence upon the determination of the end point under the specified conditions.

TABLE I.—EFFECT OF DILUTION ON SENSITIVENESS OF INDICATOR.

NOTE.—In each of the following experiments, 0.5 cc. of the palladious nitrate indicator and 5 cc. of a 5% gum arabic solution were used:

Expt.	Cc. water added.	Cc. 0.1 *N* $AgNO_3$.	Cc. 0.1 *N* KI.
1	0	5.00	5.02[1]
2	25	5.00	5.02
3	50	5.00	5.05
4	100	5.00	5.05
5	200	5.00	5.03

II. Influence of Concentration of Palladious Nitrate.

The series of experiments in Table II shows that the concentration of the palladium is without any influence upon the determination of the silver content. With 0.25, 0.5 and 1 cc. of the palladious nitrate indicator approximately eight minutes were consumed for the completion of the titration, but with 2 and 5 cc. of the indicator the time required was 24 and 32 minutes, respectively. This considerable increase of time was necessitated by the slow conversion of the large amount of palladious iodide, formed near the real end point, over to silver iodide. In Expts. 9 and 10, the values of 0.1 *N* potassium iodide marked "initial" were obtained at the

---

[1] The smallest divisions on the burets were 0.05 cc. The readings were estimated to 0.01 cc. The burets were certified and the corrections on the certificates were given to 0.01 cc.

end of seven minutes, when a deep dark brown coloration first persisted throughout the whole liquid. Constant agitation caused the palladious iodide to be quickly converted over to silver iodide whereas the further addition of a drop of potassium iodide solution again caused a dark brown coloration of the liquid. This procedure of slow addition and constant stirring finally gave a coloration which persisted at the end of 5 minutes' agitation. In all cases where the color remained after 5 minutes' agitation, the end point proved to be the real and not the apparent one because the coloration persisted even overnight and was permanent.

TABLE II.—INFLUENCE OF CONCENTRATION OF PALLADIOUS NITRATE.

NOTE.—In each of the following experiments, 50 cc. of water and 5 cc. of a 5% gum arabic solution were used:

Expt.	Cc. indicator added.	Cc. 0.1 *N* $AgNO_3$.	Cc. 0.1 *N* KI required.	Time required for complete titration. Minutes.
6	0.25	5.00	5.03	8
7	0.5	5.00	5.05	6
8	1.0	5.00	5.03	7
9	2.0	5.00	4.97 Initial 5.04 Final	24
10	5.0	5.00	4.78 Initial 5.02 Final	32

III. The Optimum Quantity of Indicator for Various Dilutions.

The volumes of indicator that were used in this series of experiments were 0.25, 0.5 and 1 cc., since with these volumes the true end point was obtained within a reasonable length of time (see Table II). From the several experiments that were carried out, the following conclusions were drawn:

(1) For titrations of 0.1 *N* silver nitrate with 0.1 *N* potassium iodide in the presence of gum arabic, either 0.5 or 1 cc. of the indicator may be used with equally good effect for total volumes up to 125 cc. For volumes from 125 to 225 cc., the amount of indicator necessary for the easy determination of the end point is 1 cc.

(2) For titration of 0.1 *N* silver nitrate with 0.1 *N* potassium iodide without gum arabic, at least 1 cc. of the indicator is required for all volumes ranging up to 225 cc.

Permanency of End Point.

The permanency of the end point as obtained with palladious nitrate is very satisfactory. This is due to the stability of palladious iodide, and its inappreciable absorption to silver iodide. It is well known that the color (ferric sulfocyanate) obtained at the end point in a Volhard titration gradually fades in the presence of silver sulfocyanate, especially at high temperatures. On the other hand, with the palladious iodide end point neither temperature nor long standing affects its stability. For instance, when a check titration of thousandth-normal silver nitrate with thousandth-normal potassium iodide was carried out in the presence of gum arabic, the brown color of the suspended palladious iodide persisted for over a week without any appreciable change in the intensity of the color.

Limits of Accuracy of the Method.

The reproducibility is fair when titrations are carried on in porcelain ware but a better precision is obtained with square bottles of clear glass. It has been found that especially with thousandth-normal solutions a very satisfactory precision can be obtained by the addition of a 5% solution of gum arabic to the solution to be titrated. The gum arabic prevents precipitation of the silver iodide and keeps the palladious iodide formed at the end of the reaction uniformly suspended throughout the liquid. It also prevents the formation of a scum of silver iodide on the surface of the liquid, as is the case when gum arabic is absent. This scum seriously interferes with the determination of the end point for thousandth-normal titrations when the intensity of the coloration of the liquid is observed from above. On account of this even distribution of the suspended palladious iodide, checks can be made easily and a single blank can be used for the day without fearing alteration of the intensity of the color. The intensity remains unaltered even for fairly high temperatures provided the concentration of the nitric acid is not too great. Other factors to be considered and observed are the sufficient dilution of tenth-normal silver nitrate solutions in the absence of gum arabic, the constant agitation of the liquid to be titrated and the slow addition of the titration solution.

Finally, for thousandth-normal titrations care was exercised in the selection of the intensity of the color to be employed for comparison. A fairly intense reddish brown coloration was selected for the comparison standard, usually 3.0 cc. of 0.001 potassium iodide developed this coloration. This amount corresponds to the 0.03 cc. of 0.1 potassium iodide which was necessary to produce a satisfactory coloration at the end point in tenth-normal titrations. The necessity for the selection of a good coloration for thousandth-normal solutions is due to the color effect of the silver iodide formed in the titration. If all these factors are considered there should be no difficulty in securing a very satisfactory precision under various conditions.

When the necessary precautions and conditions as previously stated are observed for titrations of silver solutions with tenth- or hundredth-normal potassium iodide solution, the uncorrected error ranges from 0.1% to 0.5%; whereas after a constant error correction of 0.03 cc. of 0.1 N or 0.01 N potassium iodide solution is applied, an accuracy of 0.1% is easily obtained. For thousandth-normal titrations, the error ranges from ± 0 to 1.0%, which must be regarded as being satisfactory on account of the low silver content. In Expt. 17 (Table IV) the silver content was slightly more than 0.1 mg. and this amount was determined within 1%, which is very satisfactory for such a small amount of silver. In the presence of other metallic salts, the silver, which was titrated with 0.1 *N* potassium iodide solution, was determined with a corrected error of approximately 0.1%; for thousandth-normal titrations with colored metallic salts present, a silver content of a milligram was determined with an accuracy of 0.6% and less. The accuracy therefore for various concentrations of silver under various conditions seems, therefore, to be quite satisfactory.

TABLE III.—TITRATIONS WITH 0.1 *N* AND 0.01 *N* POTASSIUM IODIDE SOLUTIONS.

NOTE.—In these experiments, no blanks or comparison standards were employed. The constant error correction applied to 0.1 *N* titrations was 0.03 cc. of 0.1 *N* KI, likewise the correction was 0.03 cc. 0.01 KI for 0.01 *N* titrations when the end point was a faint reddish brown. A darker coloration caused by the further addition of a drop of 0.01 *N* KI would require a correction of 0.08 cc. 0.01 *N* KI.

Expt.	Cc. indicator.	Cc. water added.	Cc. 5% gum arabic solution.	Cc. $AgNO_3$. 0.1 *N*.	Cc. KI. 0.1 *N*.	G. Ag taken.	G. Ag found.	Error. %.	Corrected error. %.
11	0.25	50	5	5.00	5.03	0.0539	0.0542	+0.55	±0
12	0.5	25	5	20.00	20.05	0.2157	0.2162	+0.23	+0.1
13[1]	0.5	..	..	20.00	20.05	0.2157	0.2162	+0.23	+0.1
14	0.5	25	5	25.00	25.04	0.2697	0.2701	+0.14	+0.04
				0.01 *N*.	0.01 *N*.				
15	0.5	..	1	10.00	10.04	0.01078	0.01082	+0.37	+0.1
16	0.5	20	1	10.00	10.04	0.01078	0.01082	+0.37	+0.1

TABLE IV.—TITRATIONS WITH 0.001 *N* POTASSIUM IODIDE SOLUTION.

NOTE.—Five cc. of a 5% gum arabic solution were used in all of the following experiments. The "blank correction" was obtained by determining the number of cc. of 0.001 *N* KI solution required under similar conditions to produce a definite intensity of the coloration at the end point.

Expt.	Cc. indicator.	Cc. 0.001 *N* $AgNO_3$.	Cc. 0.001 *N* KI.	Blank correction. Cc. 0.001 *N* KI.	Mg. Ag taken.	Mg. Ag found.	Error. %.
17[2]	0.25	1.00	3.26	2.27	0.107	0.106	—0.93
18	0.25	10.00	12.72	2.75	1.078	1.075	—0.27
19	0.25	10.00	12.75	2.75	1.078	1.078	±0
20	0.25	10.00	12.76	2.75	1.078	1.079	+0.09
21	0.25	20.00	22.77	2.75	2.156	2.159	+0.13
22	0.50	25.00	28.15	3.20	2.695	2.690	—0.18
23	0.50	25.00	28.16	3.20	2.695	2.691	—0.14
24	0.50	50.00	53.80	3.90	5.394	5.376	—0.33

Effect of Metallic Salts.

A few experiments were tried with the addition of a metallic salt in order to determine the effect of the colored metallic salts or of the metal itself. In all cases with the colored metallic nitrates, such as the nitrates of copper, nickel and cobalt, no difficulty was encountered in easily observing the end point. With the tenth-normal titrations, the end point was obtained

---

[1] Temperature = 72°.

[2] 15 cc. H_2O were added to the silver nitrate solution before titration.

by observing the supernatant liquid by transmitted light against a white background until the black precipitate of the palladious iodide presisted after vigorous stirring for 5 minutes. The end point with the thousandth-normal solution in these particular experiments recorded was determined by comparison, by reflected light, of the upper surface of the liquid against a similar blank.

TABLE V.—EFFECT OF METALLIC SALTS (0.1 *N* TITRATION).

NOTE.—In the following experiments the metals were added as the nitrates. The end point was obtained without the use of a blank or comparison standard, except in the case of the mercury experiment. The percentages listed under the column headed "Corrected Error" were obtained by applying a constant error correction of 0.03 cc. 0.1 *N* KI.

Expt.	Cc. indicator.	Cc. substances added.	G. metal added.	Cc. 0.1 *N* $AgNO_3$.	Cc. 0.1 *N* KI.	G. Ag taken	G. Ag found.	Error. %.	Corrected error. %.
25	0.5	45 H_2O	0.0655 Cu	10.00	10.05	0.1078	0.1083	+0.48	+0.15
26	0.5	45 H_2O	0.262 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
27	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.262 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
28	0.5	45 H_2O	0.393 Cu	20.00	20.03	0.2157	0.2160	+0.13	±0
29	0.5	45 H_2O	0.065 Co	10.00	10.02	0.1078	0.1080	+0.15	−0.09
30	0.5	45 H_2O	0.260 Co	20.00	20.05	0.2157	0.2162	+0.23	+0.09
31	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.260 Co	20.00	20.04	0.2157	0.2161	+0.18	+0.04
32	0.5	25 H_2O	0.096 Ni	10.00	10.05	0.1078	0.1083	+0.46	+0.15
33	0.5	45 H_2O	0.384 Ni	20.00	20.05	0.2157	0.2162	+0.23	+0.09
34	0.5	(45 H_2O + 5 cc. 5% G. A.)	0.384 Ni	20.00	20.08	0.2157	0.2166	+0.41	+0.23
35	0.5	50 H_2O	0.162 Hg	10.00	10.05	0.1078	0.1083	+0.46	+0.15
36	0.5	25 H_2O	0.117 Cd	10.00	10.04	0.1078	0.1082	+0.37	+0.09
37	1.0	30 H_2O	0.702 Cd	20.00	20.09[1]	0.2157	0.2167	+0.46	+0.27

TABLE VI.—EFFECT OF METALLIC SALTS (0.001 *N* TITRATION).

NOTE.—In the following experiments the metallic salts were added as the nitrates. The "blank correction" was obtained by running a parallel experiment and determining the number of cc. of 0.001 *N* KI that were necessary to produce the definite hue required.

Expt.	Cc. indicator.	Substances added.	Mg. metal added.	Cc. 0.001 *N* $AgNO_3$.	Cc. 0.001 *N* KI.	Blank correction. Cc. 0.01 *N* KI.	Mg. Ag taken.	Mg. Ag found.	Error. %.
38	0.25	10 cc. H_2O + 5 cc. 5% G. A.	13.1 Cu	10.00	13.46	3.40	1.078	1.085	+0.63
39	0.25	10 cc. H_2O + 5 cc. 5% G. A.	13.0 Co	10.00	13.24	3.20	1.078	1.083	+0.46

In the particular case of mercury nitrate, sufficient time (5–10 mins.) and constant agitation must be given for the yellow mercuric iodide formed at the end point to go into solution again in order to distinguish the coloration due to palladious iodide. This coloration increases with time until

---

[1] Coloration at end point grew darked upon long standing. G. A. = gum arabic.

all the mercuric iodide is converted over to palladious iodide. The end point was obtained in this experiment by matching against a similar precipitation with indicator absent.

No attempt was made to determine the limit of the amount of each metal that may be present without interfering with the accuracy of the determination of the silver. Nevertheless the results show that the amount of metal or metals that may be present is a large percentage of the total metal content in the solution.

Errors.

There are present both the plus and minus errors, usually inherent in nearly all analytical work. The plus error, particularly for tenth-normal solutions, is the occlusion of potassium iodide[1] in the precipitated silver iodide. This occlusion consequently causes an increased addition of the tenth-normal potassium iodide solution in order to obtain a coloration of the liquid. The error can be overcome for the most part by good stirring of the liquid together with the slow addition of the titration liquid, also either by dilution or by the addition of a gum arabic solution. Another source of the plus error is nitrous acid present in the nitric acid. The nitrous acid readily liberates iodine from the palladious iodide formed at the end of the reaction. The free iodine after being partly dissolved by the precipitated silver iodide, colors the liquid a light yellowish brown tint which is not to be confused with deep reddish brown color of the palladious iodide. This nitrous acid can easily be removed by boiling the silver solution before titration.

On the other hand, the minus error is due to the occlusion of silver nitrate[2] in the precipitated silver iodide. There are several methods for correcting this source of error. Sufficient dilution of the silver nitrate solution will do this, also good stirring and the slow addition of the potassium iodide solution. The method that proved to be the most effective was the addition of a 5% gum arabic solution to the solution to be titrated. The specific effect of the gum arabic is the prevention of a curdy precipitate of silver iodide, which is caused by local concentration, thus entrapping the mother liquor containing silver nitrate. Unless these precautions are observed, balanced errors are likely to occur. This is due to the fact that in the titration of the more concentrated solutions the silver iodide first precipitated will occlude silver nitrate (minus error); whereas near the end of the titration, the precipitate will occlude potassium iodide (plus error). The effect of the gum arabic is really equivalent to a very rapid stirring of the silver nitrate solution with a very slow addition of the titrating liquid. Finally it was thought possible to overcome this occlusion of

---

[1] Lottermoser and Rother, *Z. phys. Chem.*, **62**, 359–383 (1908).

[2] Kothner and Aeuer, *Ann.*, **337**, 123 (1904); Baxter, *Pub. Carnegie Inst.*, **135**, 107 (1910).

silver nitrate by heating the liquid to be titrated to a fairly high temperature (75°). Although this heat treatment reduced the time required for the titration, it was not so good as the use of the gum arabic.

Recommended Conditions.

To obtain good precision and satisfactory accuracy, it is necessary to observe the following conditions: First of all the usual precautions that are customarily practiced with any titration that involves precipitation should be observed, especially in reference to the slow addition of the titrating liquor as well as the constant agitation of the liquid. The titration should be effected preferably in square bottles of clear, colorless glass. As to the temperature of the liquid, room temperature is recommended although considerably higher temperatures do not affect the results provided the concentration of the nitric acid is sufficiently diluted not to dissolve palladious iodide or decompose silver iodide. The conditions already stated apply equally as well for both tenth-normal and thousandth-normal titrations, but the further procedure of either of these titrations is quite different.

I. For titrations with *thousandth-normal* potassium iodide, in order to obtain the end point so that the uncertainty is minimized to the utmost, it is proposed that the titrations be carried on in the presence of a gum arabic to prevent the precipitation of the silver iodide and palladious iodide. For these titrations it is necessary to select a definite and permanent hue of the indicator (reddish brown for dilute solutions) in the unknown, then to compare from above, by reflected light, the unknown with a blank, always attempting to make the blank as nearly equivalent to the unknown as possible. A correction is then applied to the unknown for the amount of thousandth-normal potassium iodide required to produce the definite coloration in the blank. The volume of indicator to be used may be from 0.25 to 0.5 cc. while 1 cc. of a 5% gum arabic solution is sufficient.

II. For *tenth-normal* solutions, when 5 cc. of a 5% gum arabic solution are used, no dilution of the liquid is necessary and the end point can easily be obtained with 0.5 to 1 cc. of indicator. However, in those cases where the solutions are colored, the gum arabic may be omitted with good advantage and the end point determined by observing by transmitted light the supernatant liquid for a permanent slight change in the color of the liquid. For these colored solutions a similar check precipitation without any indicator present is helpful but not necessary. When gum arabic is not used, the volume of the indicator should be at least 1 cc. for each 100 cc. of the liquid to be titrated. The correction to be applied for tenth-normal titrations is 0.03 cc. of tenth-normal potassium iodide, the volume required to produce the coloration. It may be noted here that palladious iodide can easily be distinguished in almost any colored solution because of its dark color—dark brown (almost black) in concentrated solutions and reddish brown in dilute solutions. If all these recommended conditions are observed the personal factor, it is believed, will play a very small part toward obtaining reliable and satisfactory results.

Summary.

1. The application of palladious nitrate as an indicator for silver titrations has been tested and found to be satisfactory.
2. The sensitiveness of the indicator is little affected by dilution.
3. The stability of palladious iodide is greater than that of ferric sulfocyanate.
4. Excellent reproducibility and a satisfactory accuracy can easily be obtained for both tenth- and thousandth-normal concentrations of silver nitrate.
5. The use of gum arabic to avoid occlusion of silver nitrate and potassium iodide has given very good results and is to be recommended.
6. The application of palladious nitrate as an indicator apparently overcomes difficulties which arise with the Volhard method in the presence of mercury, palladium and other interfering metallic salts.
7. The errors of the method have been discussed.
8. Finally, the ease and rapidity with which the indicator and also the silver nitrate and potassium iodide solutions can be prepared are advantages.

ROCHESTER, N. Y.

OBSERVATIONS ON THE RARE EARTHS. V. HOLMIUM AND DYSPROSIUM.[1]

BY H. C. KREMERS AND C. W. BALKE.

Received November 30, 1917.

1. Introduction.

This investigation has had in mind a twofold purpose. The preliminary part of the work has had in view the development of better and more rapid methods of separation of the rare earth elements, since this is the most difficult portion of all rare earth work. Many of the rare earths have never been obtained in a pure state and it is, therefore, highly desirable to obtain methods of separation more nearly quantitative in nature. Accordingly, the yttrium group has been studied with attention directed toward a contentration of dysprosium and holmium and the separation of holmium from yttrium.

---

[1] Part of a thesis submitted by H. C. Kremers to the graduate school of the University of Illinois as partial fulfilment of the requirements for the degree of Doctor of Philosophy.