sults agree with them as closely as is to be expected, most of the probable errors in earlier work tending to make the results too high.

The more important results of this research may be briefly summed up as follows:

1. Pure silver chromate was prepared.
2. It is shown that silver chromate cannot be completely dried without decomposition.
3. The proportion of residual water was determined in salt dried at definite temperatures.
4. The specific gravity of unfused silver chromate is found to be 5.625 at 25° referred to water at 4°.
5. The per cent. of silver in silver chromate is found to be 65.0333 by two closely agreeing methods.
6. With several assumed values for the atomic weight of silver referred to oxygen, the atomic weight of chromium is found to have the following values:

If Ag = 107.93 Cr = 52.06
If Ag = 107.88 Cr = 52.01
If Ag = 107.85 Cr = 51.98

In the following paper the analysis of silver dichromate is described.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

CAMBRIDGE, MASS., December 10, 1908.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

SECOND PAPER.—THE ANALYSIS OF SILVER DICHROMATE.

BY GREGORY PAUL BAXTER AND RICHARD HENRY JESSE, JR.

Received March 13, 1909.

In the preceding paper is described a successful attempt to prepare pure silver chromate and to determine its silver content, with the object of throwing light upon the atomic weight of chromium, the value found in this way, 52.01, being about one-tenth of a unit lower than the one in common use. The preparation and analysis of silver dichromate was next investigated. Since the proportion of chromium in the dichromate is fifty per cent. larger than in the chromate, the effect of experimental uncertainty upon the final result is correspondingly reduced.

Silver dichromate possesses another great advantage over silver chromate for exact work in that it may be readily crystallized from nitric acid solutions, and thus be freed from impurities included or occluded during precipitation, with the exception of nitric acid and moisture. For, the silver and chromium being present in equivalent proportions during the crystallization, the inclusion of mother liquor could do no harm. If the concentration of the nitric acid is sufficiently high, there is no possibility of the separation of silver chromate as such during this crystallization, since Sherrill[1] has shown that silver chromate changes rapidly into silver dichromate under nitric acid solutions more concentrated than 0.075 normal. This is primarily due to the low value of the dissociation constant of the second hydrogen of chromic acid, which has been found by Sherrill to be 6×10^{-7}, the solubility product of silver chromate being 9×10^{-12}, and that of silver dichromate being 2×10^{-7}. Sherrill has also investigated the part which the hydrochromate ion plays in the equilibrium relations of chromates and dichromates in solution and has found the following equation to hold:

$$(Cr_2O_7^{--})/(HCrO_4^{-})^2 = 75.$$

Although obviously the concentration of the hydrochromate ion in dichromate solutions (in a 0.1 molal solution of potassium dichromate 15 per cent. of the salt existing as hydrochromate) is always considerable, the precipitation of the solid phase $AgHCrO_4$ seems not to be possible. Sherrill was not able to find any indication of the presence of this salt in the precipitate formed by adding silver nitrate to chromic acid in nitric acid solution. Furthermore, since the water content of our material was carefully investigated, the presence of hydrochromate in traces could do no harm, for the latter substance upon sufficient heating would yield dichromate and water according to the following equation:

$$2AgHCrO_4 = Ag_2Cr_2O_7 + H_2O.$$

Although the presence of polychromates other than the dichromate seemed improbable, their absence from our material was shown by crystallizing silver dichromate from nitric acid of different concentrations. Since this variation was without effect, it may be reasonably supposed that more highly acid salts than the dichromates were neither precipitated as solid phases nor occluded.

Purification of Materials.

Only slight changes were made in the methods of purifying the materials used in the various preparations of silver dichromate and in the analyses from those described in the preceding paper.

Nitric Acid.—Nitric acid was freed from chlorine by several distillations through a platinum condenser.

Hydrochloric Acid.—This acid also after dilution was purified by distillation with a quartz condenser.

Hydrobromic Acid.—Hydrobromic acid was prepared from bromine which had been twice distilled from solution in potassium bromide, the bromide in the second

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[1] THIS JOURNAL, **29**, 1641 (1907).

distillation being essentially free from chlorine. The hydrobromic acid was synthesized by passing carefully cleansed hydrogen (made from the lead-sodium alloy "hydrone" and water) through the bromine at about 40° and then over hot platinized asbestos, the acid being collected in pure water. Iodine was eliminated from the acid by boiling with free bromine several times. Finally it was redistilled through a quartz condenser three times with rejection of the extreme fractions. The acid, diluted to normal concentration, was kept in a well-protected glass bottle.

Silver Nitrate.—Silver nitrate was prepared from silver which had been precipitated once as chloride, and then reduced with invert sugar. The nitric acid solution of the fused mass was evaporated to crystallization, and the salt was then three times more crystallized from nitric acid solutions, the crystals being drained centrifugally in a centrifugal machine, employing platinum Gooch crucibles as baskets.[1] Heating was carried out over electric stoves in order to avoid contamination by the combustion products of illuminating gas, both in this and in all other preparations in this research.

Potassium Dichromate.—The best commercial material was crystallized four times, once from aqueous solution in Jena glass, and three times in platinum vessels.

Chromic Acid.—This substance was three times recrystallized in platinum vessels as described in the preceding paper.

Silver Dichromate.—Silver dichromate was prepared by combining either potassium dichromate or chromic acid with silver nitrate in nitric acid solution in platinum vessels. Precipitation was carried out in fairly concentrated solution, since in the subsequent crystallization of the silver salt from nitric acid solution any included substance was sure to be eliminated. Although the inclusion of nitric acid during the crystallization was to be feared, and was actually found to have taken place, a method was devised for the determination of this nitric acid, together with the moisture retained by the solid.

Sample I.—Silver nitrate and potassium dichromate were dissolved in equivalent proportions in 3 normal nitric acid, the concentration of each salt being 0.7 normal. The cold silver nitrate solution was added very slowly, with constant vigorous stirring, to the dichromate solution. After the precipitate had been allowed to settle, the mother liquor was decanted, and the precipitate was centrifugally drained, and rinsed in the centrifugal machine with 3 normal nitric acid.

The salt was then five times recrystallized from solution in 3 normal nitric acid with centrifugal drainage after each crystallization. Owing to the small solubility of silver dichromate in nitric acid solutions the following scheme of crystallization was adopted. The dichromate was heated with the nitric acid solution upon the electric stove until the acid was saturated with silver dichromate. Then the hot solution was decanted into a dish through a platinum Gooch crucible without a mat of any sort but with small holes, in order to remove particles of silver dichromate either suspended in the solution or floating on the surface. These particles were always of considerable size, so that the resulting solution was clear. After the saturated solution had cooled and had deposited the greater part of its charge of salt, the mother liquor was continuously used to dissolve fresh portions of the salt. About one liter of acid was used for the crystallization of about fifty grams of dichromate. Although by this method the impurities in the original salt accumulate in the mother liquor, on account of the relatively large volume of the mother liquor, there was little danger of these impurities being carried into the second crop of crystals. It was shown for instance, that the mother liquor from the third crystallizations was free from potassium. This mother liquor was evaporated to small bulk, neutralized with ammonia, and reduced and

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[1] THIS JOURNAL, **30**, 286 (1908).

precipitated with hydrogen sulphide. The filtrate after evaporation and expulsion of the ammonium salts gave no spectroscopic flame test for potassium.

The silver dichromate was not allowed to come in contact with water or any solution except the 3 normal nitric acid solution.

All of the above operations were carried out in platinum vessels.

Sample II.—This sample was made exactly as in the case of Sample I, except that chromic acid was employed instead of potassium dichromate, and that both precipitation and crystallization took place from 0.8 normal nitric acid. The silver dichromate was crystallized five times.

Sample III.—The most dilute nitric acid which was used in the preparation of the silver dichromate was about 0.16 normal, solutions of this concentration being employed in the precipitation and crystallization of Sample III. This sample was made from chromic acid and silver nitrate, and was six times crystallized from 0.16 normal nitric acid.

The chief difference in the purification of the three specimens, aside from the concentrations of acid used in their preparation, lies in the fact that Sample I was prepared from recrystallized potassium dichromate, and Samples II and III from chromic acid. All three samples were crystallized many times as silver dichromate.

After the final drainage in the centrifugal apparatus, the crystals were dried in an electric oven at 150° for several hours. Then they were powdered gently in an agate mortar and kept in platinum vessels.

The Determination of Silver in Silver Dichromate.—In preparing the silver dichromate for analysis, the complete elimination of moisture by fusion of the salt was impossible, owing to the ease with which silver dichromate decomposes. Even at the comparatively low temperature of the melting point of the dichromate, about 400°, oxygen is given off rapidly, while at temperatures considerably below this point, 300°, and to a very slight extent at 250°, there seemed to be evidence of decomposition, since salt heated to these temperatures did not give an absolutely clear solution in dilute nitric acid. In order to be on the safe side, the drying of the salt took place at 200°.

The heating of the dichromate was affected much as described in the preceding paper in the case of silver chromate. The salt, contained in a weighed platinum boat, was heated in a current of pure dry air in a hard glass tube for four hours at 200°, the air being purified and dried by passing over hot copper oxide, solid potassium hydroxide, concentrated sulphuric acid containing dichromate, and resublimed phosphorus pentoxide successively. An oven composed of solid aluminum blocks[1] was used, by means of which the temperature could be maintained constant within two degrees.

After the boat had been allowed to cool in the tube, it was transferred to the weighing bottle by means of a "bottling apparatus,"[2] and was reweighed. Then the dichromate was transferred to a flask and was dissolved in hot 0.8 normal nitric acid. The solution, which was always perfectly clear, was quantitatively transferred to a 3-liter glass-stoppered precipitating flask, and at a dilution of about one liter was reduced by the addition of a very slight excess of sulphur dioxide. When the solution was cold, a slight excess of hydrobromic acid was diluted to about 800 cc. and then was slowly added to the silver solution with continual agitation. The flask was stoppered and vigorously shaken. After twenty-four hours' standing, the flask was again shaken, and then was allowed to stand two days or more, until the supernatant solution was clear.

Next the silver bromide was collected upon a weighed Gooch crucible, dried, and weighed. The asbestos mechanically detached from the Gooch crucible was collected

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[1] Baxter and Tilley, THIS JOURNAL, 31, 206 (1909).

[2] Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896).

upon a small filter paper. In order to avoid any danger from adsorption of chromic salts by the filter paper, at the end of the filtration the paper was rinsed with hot dilute hydrobromic acid. The correction for asbestos could have been avoided if it had been possible to employ a Gooch-Munroe-Neubauer crucible with a mat of platinum sponge. It has already been shown, however, in the preceding paper,[1] that such crucibles lose appreciably in weight when exposed to the action even of dilute *aqua regia* of the mother liquors of these analyses. The moisture retained by the silver bromide was found by fusing the dried salt in a porcelain crucible, the loss in weight on fusion being determined. The fused silver bromide was always light yellow and gave every indication of purity.

As in the preceding research, a small quantity of silver bromide dissolved in the filtrate and wash waters was found by evaporating the combined filtrate and wash waters until nearly all the excess of acid had been expelled, and then, after slight dilution, precipitating the silver as sulphide. The sulphide was collected on a small paper, the ash of which, after ignition, was treated with nitric acid. The amount of silver thus obtained was found by comparison in a nephelometer of precipitates of silver bromide produced in this solution and in very dilute standard solutions of silver.

In Analysis 9, the silver was precipitated as silver chloride, the only other difference in the procedure being that the precipitate was washed with dilute hydrochloric acid instead of pure water.

The Determination of Moisture and Nitric Acid in Silver Dichromate.—Silver dichromate which has been crystallized from nitric acid, after being dried at 200°, contains traces of both nitric acid and water. Both of these substances can be expelled from the salt by fusion, although slight decomposition of the salt takes place simultaneously. Since the only readily volatile substance which can be formed by the decomposition of the salt is oxygen gas, the problem of the determination of the moisture and nitric acid consisted in that of absorbing in a quantitative fashion the water, nitric acid, and nitric peroxide formed by decomposition of the nitric acid. This was effected by passing the current of air containing the moisture and nitrogen compounds through two weighed U-tubes, one containing a concentrated solution of potassium hydroxide and solid potassium hydroxide and the other resublimed phosphorus pentoxide. The air current passed first through the potassium hydroxide tube in order that moisture vaporized from the hydroxide might be retained by the pentoxide tube. That the absorption of oxides of nitrogen was complete was shown by the fact that no test for nitric acid could be obtained beyond the phosphorus pentoxide tube either with moist litmus paper or with diphenylamine.

Since the three samples of silver dichromate were crystallized from nitric acid of different concentrations, it was necessary to make separate determinations of the moisture and nitric acid content with each sample. Extreme purity of material was unnecessary, and, as rather large quantities of salt were desired, three samples were prepared from ordinary silver nitrate and potassium dichromate and then were crystallized from nitric acid of the concentrations 3 normal, 0.8 normal and 0.16 normal, respectively, glass vessels being employed throughout.

Weighed portions of the silver dichromate were heated for four hours at 200° in a current of pure dry air exactly as in preparing the salt for the silver analyses. Then the weighed potassium hydroxide and phosphorus pentoxide tubes were attached to the hard glass tube, with a protection tube containing phosphorus pentoxide at the end. The silver dichromate was gradually heated to complete fusion, and the air current was allowed to pass through the system for one-half hour in order to make

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[1] Page 536.

certain that all the vapors expelled from the dichromate were carried into the absorbing tubes. The absorption tubes were then reweighed.

Before the tubes were weighed, they were carefully wiped with a clean damp cloth and were allowed to stand near the balance case for one hour. The tubes were provided with ground glass stopcocks lubricated with Ramsay desiccator grease. During the weighing, one stopcock in each tube was open to equalize the air pressure within and without the tubes. In order to lessen the error in weighing, as well as to save time and labor, the tubes were not weighed separately, but together as one system. Counterpoise tubes of the same shape and size were always employed. Blank determinations showed that the air current and manipulation of the tubes caused an increase in weight of 0.00010 gram in one-half hour. This quantity is applied as a correction in every case.

In place of a platinum boat a superficially oxidized copper boat was used in these experiments. At the low temperature of fusion of silver dichromate there is little danger of decomposition of nitric acid or oxides of nitrogen by the oxidized copper. It is to be noted that if the nitric acid is decomposed during the experiment according to the following equation:

$$2HNO_3 = H_2O + 2NO_2 + O,$$

and is absorbed by the potassium hydroxide as NO_2, there is a slight loss of oxygen. The proportion of nitric acid present being very small, however, this error could have no appreciable effect on the results.

Sample.	Weight of $Ag_2Cr_2O_7$.	Gain in weight of absorption tubes.	Gain. Weight of $Ag_2Cr_2O_7$.
I	22.52	0.00448	0.000194
I	20.74	0.00378	0.000177
I	12.25	0.00235	0.000184
	Average		0.000186
II	13.13	0.00309	0.000235
II	15.91	0.00317	0.000193
II	21.35	0.00391	0.000178
II	19.60	0.00373	0.000185
	Average, rejecting the first determination,		0.000186
III	20.89	0.00353	0.000164
III	19.94	0.00348	0.000169
	Average		0.000167

It is somewhat surprising that Samples I and II contain the same proportion of volatile matter. This agrees with the result of the silver determinations, however, the samples proving to be otherwise very similar. As is to be expected, Sample III contains less impurity than either of the other two.

The negative corrections as found above are applied to all the final weights of silver dichromate given in the table of analyses.

The Specific Gravity of Silver Dichromate.—The specific gravity of silver dichromate has been found by Schroeder[1] to be 4.669, but on account of the uncertainty of most of the older specific gravity determinations, this constant was very kindly redetermined for us by Mr. Victor Cobb. The silver dichromate was precipitated from dilute nitric acid solution and once recrystallized from normal nitric acid. Then it was dried at

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[1] *Liebig's Jahresb.*, 1879, 31.

200° for many hours. The determination was effected by displacement of toluene of specific gravity 0.86218. Care was taken to extract entangled air from the crystals by exhausting the air from the pycnometer in a vacuum desiccator.

Weight of $Ag_2Cr_2O_7$ in vacuum. Grams.	Weight of toluene displaced in vacuum. Grams.	Specific gravity of $Ag_2Cr_2O_7$. 25°/4°.
29.308	5.299	4.769
25.330	4.578	4.770

The following corrections were applied:

	Specific gravity.	Vacuum correction.
Weights	8.3	......
Toluene	0.862	+0.00126
Silver dichromate	4.770	+0.000107
Silver bromide	6.473	+0.000041
Silver chloride	5.56	+0.000071

A No. 10 Troemner balance easily sensitive to one-fiftieth of a milligram was used in all the weighings. The gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.[1]

Weighing was always carried out by substitution, with the use of a counterpoise as nearly as possible like the object weighed, both in material, shape, and volume.

SERIES III.

$2AgBr : Ag_2Cr_2O_7$

$Ag/AgBr = 0.574453$[2]

Number of analysis.	Sample of $Ag_2Cr_2O_7$.	Corrected weight of $Ag_2Cr_2O_7$ in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgBr from filtrate. Gram.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio 2AgBr : $Ag_2Cr_2O_7$.
1	II	5.71554	4.97107	0.00024	0.00025	0.00007	4.97149	0.869820
2	II	4.87301	4.23870	0.00019	0.00003	0.00004	4.23888	0.869869
3	II	7.45476	6.48380	0.00034	0.00019	0.00008	6.48425	0.869813
4	III	4.75269	4.13409	0.00020	0.00003	0.00012	4.13420	0.869865
5	III	8.15615	7.09477	0.00022	0.00005	0.00009	7.09495	0.869890
6	III	6.15412	5.35306	0.00007	0.00007	0.00011	5.35309	0.869839
7	I	6.83662	5.94656	0.00030	0.00009	0.00017	5.94678	0.869842
8	I	5.39883	4.69610	0.00027	0.00007	0.00013	4.69631	0.869876
9	III	6.26657	4.16034[3]	0.00018	0.00040	0.00016	4.16076	0.869903[4]
		Average						0.869857
Total ..		55.60829					48.37126	0.869854
		Average from Sample I						0.869859
		Average from Sample II						0.869834
		Average from Sample III						0.869874
		Average						0.869856

Per cent. of Ag in $Ag_2Cr_2O_7$, if $2AgBr : Ag_2Cr_2O_7 = 0.869857 : 1.000000$ .. 49.9692

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[1] THIS JOURNAL, **22,** 144 (1900).

[2] Baxter, THIS JOURNAL, 31, 1322 (1906).

[3] AgCl.

[4] Calculated from the ratio AgBr : AgCl = 131.0171 : 100.0000. Baxter, *loc. cit.* 4.16076 grams AgCl =⊂= 5.45131 grams AgBr.

The preceding table gives the results of all the final experiments in the order in which they were carried out. The preliminary analyses, which were defective in various ways, are not recorded.

The results of the foregoing experiments are as concordant as one can reasonably expect, since the insoluble silver salts are in general difficult to obtain definite in composition.[1] The extreme values differ by only one one-hundredth of a per cent., while the averages of the different samples show an extreme difference of less than five-thousandths of a per cent. The composition of the dichromate is evidently not affected by the concentration of the nitric acid from which it is crystallized, since the averages from the different samples do not vary regularly with the concentration of the nitric acid, the average result obtained from Sample II being lower than that of either Sample I or Sample III.

If the per cent. of silver in silver dichromate is 49.9692, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the molecular weight of the chromate the atomic weight of chromium by difference. Since the ratio of the atomic weights of silver and oxygen is somewhat uncertain at the present time, these calculations have been made with various possible assumed values for the atomic weight of silver, oxygen being assumed to have the value 16.000. It is to be noted that the percentage error in the determination of the molecular weight of silver chromate is multiplied four times in the atomic weight of chromium.

If Ag = 107.930	$Ag_2Cr_2O_7$ = 431.986	and Cr = 52.063
If Ag = 107.880	$Ag_2Cr_2O_7$ = 431.786	and Cr = 52.013
If Ag = 107.850	$Ag_2Cr_2O_7$ = 431.666	and Cr = 51.983

In the following table are given the results of the preceding research upon silver chromate by Baxter, Mueller, and Hines, together with the average of their values and those presented in this paper:

	Baxter, Mueller and Hines.	Average.
If Ag = 107.930	Cr = 52.062	52.063
If Ag = 107.880	Cr = 52.008	52.011
If Ag = 107.850	Cr = 51.976	51.980

The agreement of the two independently determined values is highly satisfactory, no matter which value for the atomic weight of silver is assumed, although the higher values for silver give slightly better agreement.

The atomic weights of both chromium and silver may be calculated independently of any assumption except the atomic weight of oxygen from the following equations,

$$2Ag/(2Ag + Cr + 64) = 0.650333$$
$$2Ag/(2Ag + 2Cr + 112) = 0.499692,$$

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[1] Baxter and Coffin, THIS JOURNAL, 31, 247 (1909); Baxter, Mueller, and Hines, preceding article.

to be 52.074 and 107.941 respectively. However interesting these results may be, they have little real significance, since an error of five-thousandths of a per cent. in either ratio causes an error of over one-tenth of a unit in the atomic weights of both silver and chromium.

The most important results of this research are as follows:

1. Pure silver dichromate was prepared.
2. It is shown that silver dichromate cannot be completely dried without decomposition.
3. It is shown that silver dichromate when crystallized from nitric acid retains traces of the nitric acid.
4. The proportion of moisture and nitric acid in silver dichromate treated in definite fashions was determined.
5. The specific gravity of silver dichromate is found to be 4.770 at 25° referred to water at 4°.
6. The per cent. of silver in silver dichromate is found to be 49.9692.
7. With several assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of chromium is found to have the following values:

If Ag = 107.93 Cr = 52.06
If Ag = 107.88 Cr = 52.01
If Ag = 107.85 Cr = 51.98

8. If these results are averaged with those previously found by Baxter, Mueller, and Hines, the atomic weight of chromium is found to be as follows:

If Ag = 107.93 Cr = 52.06
If Ag = 107.88 Cr = 52.01
If Ag = 107.85 Cr = 51.98

We are greatly indebted to the Carnegie Institution at Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

CAMBRIDGE, MASS., December 10, 1908.

THE CENTRIFUGE IN QUANTITATIVE ANALYSIS.

BY H. G. PARKER.

Received March 5, 1909.

The centrifuge has proved so successful an adjunct to qualitative analysis as to suggest the possibility of using this sort of separation for quantitative determinations, as ordinarily made in the usual gravimetric analysis. For this purpose various forms of apparatus were constructed and put to the test of the ordinary requirements of the quantitative laboratory. The method developed in a very unexpected manner. It was thought at the outset, that determinations in a few favorable cases might be af-