solutions, thus eliminating errors and rendering the calculations easy; and (3) the methods are not only rapid but accurate.

In the following table, 1 g. of bleaching powder (calculated) or 10 cc. of solutions were used in each analysis; the results are given in terms of *N*/10 $AgNO_3$:

Method.	"Hypo-bromite" solution.	"Bro-mate" solution.	"Hypo-chlorite" solution.	Bleaching powder.	"Hypo-iodite" solution.
I	76.74	62.04	12.77	78.43	100.30
I	76.72	62.12	12.68	78.49	100.42
II	138.44	62.15	23.79	92.57	101.45
II	138.30	62.04	23.65	92.51	101.43
III	142.34	73.28	24.02	96.90	121.36
III	142.27	73.20	24.01	96.96	121.25
N/10 Na_3AsO_3	123.01	.....	22.04	28.20	......
Calculated per cent. of total halogen					
HX	53.91	84.76	52.96	80.91	82.73
HOX	43.32	0.02	45.62	14.61	0.91
HXO_3	2.77	15.22	1.42	4.48	16.36

It will be observed that the arsenite method of direct titration of hypohalous acids gives results in close agreement with the above methods. Though the three halogen ions of the above homologous mixtures may be estimated by combination of Method III above, the arsenite method, and the iodometric method, three additional volumetric solutions are required, *viz.*, *N*/10 sodium arsenite, *N*/10 sodium thiosulphate, and *N*/10 iodine and potassium iodide. For the reason that these solutions are unstable, the superiority of the above-described methods is evident.

SEATTLE, WASH., February 22, 1909.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

FIRST PAPER.—THE ANALYSIS OF SILVER CHROMATE.

BY GREGORY PAUL BAXTER, EDWARD MUELLER AND MURRAY ARNOLD HINES.

Received March 13, 1909.

Introduction.

The following table[1] gives the results of investigations upon the atomic weight of chromium from the time of Berzelius, recalculated with the use of recent atomic weight ratios upon the basis of silver (107.88) and oxygen (16.000).[2]

[1] Clarke, A Recalculation of the Atomic Weights, Smith Misc. Coll., 1897.

[2] The following atomic weights are used in the recalculation of the older values: Ag = 107.88; Cl = 35.457; Pb = 207.09; N = 14.01; Ba = 137.37; S = 32.07; H = 1.008; K = 39.095; As = 74.96; I = 126.92. The values of Rawson and Meineke are reduced to the vacuum standard; the others are not so corrected.

Date.	Investigator.	Ratio determined.	Atomic weight.
1818	Berzelius[1]	$Pb(NO_3)_2 : PbCrO_4$	55.95
1844	Peligot[2]	$CrCl_2 : 2AgCl$	52.33
		$2CrCl_2 : Cr_2O_3$	51.58
		$4AgCl : Cr_2O_3$	51.61
1846	Berzelius[3]	$BaCrO_4 : BaSO_4$	54.5
1846	Berlin[4]	$Ag_2CrO_4 : 2AgCl$	52.65
		$2Ag_2CrO_4 : Cr_2O_3$	52.41
		$Cr_2O_3 : 4AgCl$	52.46
		$Ag_2Cr_2O_7 : 2AgCl$	52.11
		$Ag_2Cr_2O_7 : Cr_2O_3$	52.34
1848	Moberg[5]	$Cr_2(SO_4)_3 : Cr_2O_3$	53.42
		$(NH_4)_2Cr_2(SO_4)_4,24H_2O : Cr_2O_3$	53.46
1850	Lefort[6]	$BaCrO_4 : BaSO_4$	53.04
1853	Wildenstein[7]	$BaCl_2 : BaCrO_4$	53.56
1855	Kessler[8]	$K_2Cr_2O_7 : KClO_3$	52.23
1861	Kessler[9]	$K_2Cr_2O_7 : KClO_3$	52.32
		$2K_2Cr_2O_7 : 3As_2O_3$	51.92
1861	Siewert[10]	$CrCl_3 : 3AgCl$	52.05
		$Ag_2Cr_2O_7 : 2AgCl$	52.14
		$Cr_2O_3 : 2AgCl$	52.04
		$Cr_2O_3 : Ag_2Cr_2O_7$	52.05
1884	Baubigny[11]	$Cr_2(SO_4)_3 : Cr_2O_3$	52.13
1889	Rawson[12]	$(NH_4)_2Cr_2O_7 : Cr_2O_3$	52.09
1890	Meineke[13]	$(NH_4)_2Cr_2O_7 : Cr_2O_3$	52.11
		$2Ag_2CrO_4 : Cr_2O_3$	52.10
		$Ag_2CrO_4 : 2AgCl$	52.03
		$4AgCl : Cr_2O_3$	52.14
		$2Ag_2CrO_44NH_3 : Cr_2O_3$	52.27
		$Ag_2CrO_44NH_3 : 2AgCl$	51.62
		$4AgCl : Cr_2O_3$	52.14
		$Ag_2CrO_4 : 3I$	52.41
		$Ag_2CrO_44NH_3 : 3I$	52.05
		$K_2Cr_2O_7 : KHIO_3$	52.14
		$(NH_4)_2Cr_2O_7 : KHIO_3$	52.13

The value chosen by the International Atomic Weight Committee, 52.1, which is based chiefly upon the more recent determinations, seems to be fairly close to the truth, with an uncertainty of one tenth of a unit.

[1] *Pogg. Ann.* 8, 22 (1826).

[2] *Ann. chim. phys.* [3], **12**, 530 (1844).

[3] *Berzelius' Jahresbericht*, **25**, 46 (1846).

[4] *J. prakt. Chem.*, **37**, 509; **38**, 149 (1846).

[5] *Ibid.*, **43**, 114 (1848).

[6] *Ibid.*, **51**, 261 (1850).

[7] *Ibid.*, **59**, 27 (1853).

[8] *Pogg. Ann.*, **95**, 208 (1855).

[9] *Ibid.*, **113**, 137 (1861).

[10] *Zeit. gesammte Naturwissenschaften*, 17, 530 (1861).

[11] *Compt. rend.*, **98**, 146 (1884).

[12] *J. Chem. Soc.*, **55**, 213 (1889).

[13] *Liebig's Ann.*, **261**, 339 (1890).

It has been repeatedly shown, especially in this laboratory, that most of the earlier work upon atomic weights has been vitiated by neglect of certain fundamental precautions. The incomplete drying of solids has been responsible for many of the discrepancies and errors which exist. Neglect of the solubility of precipitates, together with the use of too concentrated solutions during precipitation, so that perceptible inclusion and occlusion took place, undoubtedly have influenced many gravimetric processes. Volumetric processes have been affected by inaccurately prepared standard solutions, as well as the difficulty inherent in measuring exactly large volumes of solution.

In discussing in detail the applications of the above causes of constant error to the individual investigations, at the best it is only possible merely to indicate the nature of the difficulties; as a rule it is impossible to estimate the magnitude of the error without repetition of the experimental work. Hence in this paper attention is called only to points in the earlier work which have been experimentally investigated. The uncertainty in most of the previous determinations is emphasized by the lack of agreement in the individual analyses in each series, as well as in the different series.

The choice of method for this investigation was influenced by several considerations. In the first place, the substance to be analyzed must be definite in composition and capable of being either fused or heated to a high temperature in order to insure the elimination of moisture. In the second place, in view of the fact that chromium is hard to handle satisfactorily in a quantitative fashion, the analytical operation should involve the determination of some other element. The halogen compounds, which have been employed very successfully many times, especially in this laboratory, for the determination of the atomic weights of metallic elements, are less suited for use in the case of chromium on account of the difficulty in the complete precipitation of the halogens by means of silver nitrate. All things considered, the chromates of silver seemed to offer the most promising possibilities on account of the ease with which their silver content may be determined. It is true, in order to determine the ratio of the atomic weight of chromium to that of either silver or oxygen, this method necessitates a knowledge of the exact ratio of the atomic weights of silver and oxygen, knowledge which is at present lacking. The per cent. of silver in the compound being known, however, the analytical data may be used at any subsequent time for the calculation of the atomic weight of chromium. Furthermore, since the value for the atomic weight of chromium at present accepted depends very largely upon the analysis of silver chromate, a study of this salt with the application of the most modern methods seemed to promise interesting results, and therefore was first taken up. In a following paper is given a description of the analysis of silver dichromate.

Purification of Materials.

Water.—The laboratory redistilled water was twice distilled, once from alkaline permanganate and once from very dilute sulphuric acid. In both distillations, block-tin condensers were employed, no cork or rubber connections being necessary.

Silver Nitrate.—The preparation of pure neutral silver nitrate for the precipitation of silver chromate followed the lines laid down in previous researches in this laboratory. A large quantity of heterogeneous silver residues were reduced to metallic silver by means of sticks of pure zinc in slightly acid solution. After the silver had been washed with water until free from halogens, it was dissolved in nitric acid, and the solution was filtered. Silver chloride was precipitated from the diluted nitrate by means of hydrochloric acid, and the precipitate of silver chloride was thoroughly washed. From this silver chloride, metallic silver was again obtained by reduction with cane sugar in strongly alkaline solution. After being washed until free from chloride, the metal was again dissolved in nitric acid in a Jena glass flask. By reduction with ammonic formate (prepared from redistilled formic acid and redistilled ammonia), the silver was once more obtained in metallic state. The beautiful mass of crystals was then dissolved in the purest nitric acid, and the nitrate after concentration of the solution was four times recrystallized from the purest water in platinum until free from acid. In this crystallization, and in all others, centrifugal drainage in a machine employing platinum funnels as baskets[1] was always used, in order to free the crystals entirely from any adhering mother liquor, the mother liquors always being rejected.

Hydrochloric Acid.—Hydrochloric acid was prepared by distilling the commercial chemically pure acid, after dilution with an equal volume of water.

Hydrobromic Acid.—The methods for obtaining pure bromine have been recently tested by one of us.[2] The processes found suitable for the purpose were employed here. A considerable quantity of hydrobromic acid was prepared by passing a current of pure, washed hydrogen sulphide through a layer of bromine covered with water. After the precipitated mixture of sulphur bromide and sulphur had been removed by decantation and filtration, the acid was boiled, with the occasional addition of small portions of recrystallized potassium permanganate. This was done to eliminate any iodine which might have been present. The hydrobromic acid was then heated with the calculated quantity of recrystallized potassium permanganate, the bromine being condensed in a Jena flask cooled with running water. The greater part of the chlorine was undoubtedly eliminated by this operation, since the original bromine was fairly pure. In order to be on the safe side, however, the bromine was again reduced to hydrobromic acid, and this in turn was changed to bromine as above. From the product, the final hydrobromic acid was prepared with hydrogen sulphide. After filtration and distillation, it was preserved in Jena glass.

Chromic Acid.—This was prepared from Merck's "Highest Purity Chromic Acid." The material was dissolved in pure water, and the solution was filtered through a Gooch crucible with a mat of platinum sponge, a quantity of sandy material being thus separated. The solution was then evaporated to saturation and three times systematically recrystallized in platinum dishes with centrifugal draining, each mother liquor being used for the crystallization of three crops of crystals on account of the small temperature coefficient of solubility of chromic acid. The mother liquors from

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[1] Richards, THIS JOURNAL, 27, 110 (1905).

[2] Baxter, *Ibid.*, 28, 1322 (1906).

the first crystallization, on testing in the nephelometer, indicated only traces of sulphates and halogens.

Potassium Chromate.—Some of the purest commercial salt, after solution in water, was filtered through a Gooch-Munroe-Neubauer crucible. It was then four times crystallized in platinum, each crop of crystals being centrifugally drained.

Silver Chromate.—The point in the investigation requiring the most attention was the preparation of normal silver chromate free from both basic and acid salts. Since the salt cannot be crystallized, owing to its slight solubility in water, it is necessary so to regulate the conditions during the precipitation that neither acid nor basic salts can separate as a distinct solid phase. Even then the *occlusion* of traces of either basic or acid salts is still possible, and it is necessary to form the salt under a fairly wide range of conditions in order to show constancy of composition.

Fortunately data are available which indicate the conditions under which silver dichromate or hydrochromate can exist. Sherrill[1] has recently shown that silver chromate changes into silver dichromate rapidly under a saturated solution in nitric acid more concentrated than 0.075 normal, while silver dichromate changes into silver chromate under a saturated solution in nitric acid less concentrated than 0.06 normal. Some time before, Krüss[2] had shown that silver dichromate is converted into silver chromate by contact with water.

In the light of these facts it is obvious that the solutions of the soluble chromates can safely be employed for the precipitation of silver chromate without the least danger of the precipitation of silver dichromate, and even that the presence of a slight amount of free acid could do no harm.

Owing to the weak nature of the second hydrogen of chromic acid, the first hydrogen dissociating to the same extent as that of hydrochloric acid,[3] but the second hydrogen having the constant 6.0×10^{-7} at 18°,[4] appreciable hydrolysis of solutions of its salts takes place, to a greater extent the weaker the base with which the chromic acid is combined. Sherrill has found, for instance, that ammonium chromate in 0.05 molal solution is 2.7 per cent. hydrolyzed. The basicity of the solutions, on the other hand, will be greater the stronger the base. In order to determine whether this hydrolysis is sufficient to produce precipitation or occlusion of basic chromates, precipitates of silver chromate were formed by means of solutions of both ammonium and potassium chromates. The comparison of precipitates formed in this way will show whether the presence of basic salts is to be feared.

Sample I.—Ammonium chromate was prepared by adding to a solution of the pure chromic acid a slight deficiency of the purest freshly distilled ammonia. The solution was diluted until about tenth normal, and was slowly poured with constant shaking into a solution of an equivalent quantity of silver nitrate of about the same concentration. The dark red precipitate of silver chromate was washed six times by decantation with large portions of water, centrifugally drained to remove as much water as possible and dried at gradually increasing temperatures in an electric oven, finally at 160° for a long time. The dried lumps were then gently ground to a fine powder in an agate mortar in order to facilitate further drying as well as to insure homogeneity.

During the addition of the chromate to the silver solution, since the chromate solution was slightly deficient in ammonia, acid accumulated in the silver nitrate solution. Hence each succeeding portion of precipitate was formed under conditions of greater

[1] THIS JOURNAL, **29**, 1673 (1907).

[2] *Ber.*, **22**, 2050 (1889).

[3] Walden, *Z. physik. Chem.*, **2**, 49 (1888).

[4] Sherrill, *loc. cit.*

acidity, although the concentration of acid in the solution could never have approached that found by Sherrill to be necessary for the existence of the silver dichromate.

Sample II.—This preparation was practically identical with Sample I, since part of the precipitate obtained as above was washed by decantation with water eight times more, each wash water being allowed to stand in contact with the precipitate for many hours, and the precipitate being shaken with the wash water very thoroughly at intervals, in order to leach out any accidentally enclosed or adsorbed soluble salts. The prolonged extra washing evidently was unnecessary, since the results with this sample are practically the same as those obtained with Sample I.

Sample III.—This sample was prepared from the four times recrystallized potassium chromate. A quantity of this material in about tenth normal solution was precipitated with an equivalent amount of silver nitrate, equally dilute. The precipitation took place in Jena glass, the silver solution being slowly poured into the chromate, in order to accentuate the effect of the hydrolysis if possible. It will be recalled that in the case of Samples I and II prepared with the ammonium salt, the chromate was added to the silver solution. The precipitate was then transferred to the platinum and washed seven times with the purest water, the chromate being thoroughly agitated with each washing. After the removal of the greater part of the adhering water by centrifugal settling, this sample was dried in a preliminary fashion at 150° and was pulverized in an agate mortar, as in the case of Samples I and II. The salt was soft and crystalline, and greenish black in color.

Sample IV.—A fourth sample also was prepared from recrystallized potassium chromate, which in turn was made from recrystallized chromic acid. In the first place, potassium hydroxide was prepared by the electrolysis of three times recrystallized potassium oxalate, with the use of a mercury cathode and decomposition of the amalgam with pure water in a platinum dish, as in the preparation of potassium hydroxide in an investigation upon the atomic weight of potassium.[1] The solution of the pure hydroxide was added to a solution of three times recrystallized chromic acid, contained in a platinum dish, until the normal chromate had been formed as indicated by the yellow color. From this solution, by three systematic crystallizations, potassium chromate was separated.

The silver chromate was prepared from this material and the purest silver nitrate by slowly adding a six hundredths normal solution of the chromate to a silver nitrate solution of equivalent concentration, this procedure being the reverse of that used in the preparation of Sample III. The dark brownish-red precipitate was allowed to settle in the flask in which precipitation took place. Then, the supernatant solution having been decanted, the silver chromate was transferred to a platinum dish and washed very thoroughly with water. After being freed from water by centrifugal settling, the silver chromate was dried at about 160° in an electric oven, and powdered in an agate mortar.

Since in the case of Sample III the silver nitrate was added to the chromate, while in preparing Sample IV precipitation took place in the reverse fashion, a comparison of the two samples would not only throw light upon the effect of hydrolysis, but also show whether the occlusion of potassium chromate or silver nitrate was to be feared.

The Analysis of Silver Chromate.—The fact that salts dried by prolonged heating at 100°, or at even higher temperatures, usually contain appreciable amounts of moisture, owing to included mother liquor, is a point which has been overlooked by most earlier investigators,[2] and the oversight throws doubt on much otherwise very careful work. In exact work, the residual water must either be corrected for or entirely avoided.

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[1] Richards and Mueller, THIS JOURNAL, **29**, 645 (1907).

[2] Richards, *Proc. Am. Phil. Soc.*, **42**, 28 (1903).

The simplest fashion of drying a substance perfectly is to fuse it in a current of dry gas. In the case of the silver chromate, however, this is not practicable, for even at 300° incipient decomposition sets in. Upon attempting to dissolve in nitric acid samples dried in air at that temperature, a slight insoluble residue was always obtained, while heating in a current of oxygen gave no better results. Since the moisture cannot be entirely expelled from silver chromate by heating at a moderate temperature it must be determined by the analysis of separate portions of the substance which have been treated in some definite fashion.

Experiments showed that at temperatures below 225° the salt was not appreciably changed, hence this temperature was chosen as a suitable one at which to heat the salt preparatory to analysis. The silver chromate was therefore always heated in a current of pure dry air for two hours at 225°, in order to obtain the separate portions in as nearly as possible the same condition.

The drying apparatus was constructed entirely of glass, rubber connections being especially avoided. A current of air was passed first over red-hot copper oxide to destroy organic matter, then through successive Emmerling washing towers. In the first were beads drenched with silver nitrate solution, in the second with a strong solution of potassium hydroxide containing much potassium manganate, and in the last three with concentrated sulphuric acid. The already very dry air was then passed through a long tube containing resublimed phosphoric anhydride spread over a large surface of glass beads and ignited asbestos. From the drying apparatus the air passed into the tube in which the boat containing the silver chromate was placed.

The Determination of Silver in Silver Chromate.—During the drying of the silver chromate it was contained in a platinum boat which had been weighed, in a weighing bottle, by substitution for a similar bottle which with its contents displaced the same amount of air as the bottle with the boat. The boat was placed in a hard glass tube connected by a carefully ground joint with a bottling apparatus by means of which the boat could be transferred to the weighing bottle, after being heated, without the slightest exposure to moist air.[1] The tube was heated by means of two solid aluminum blocks which were grooved to contain the tube, by means of which the temperature could be maintained constant within a very few degrees.[2] After two hours' heating at 225° the boat was transferred to the weighing bottle and was allowed to stand in a desiccator near the balance for several hours before being weighed.

Next, the weighed quantity of silver chromate was transferred to a three-liter glass-stoppered Jena glass flask with a carefully ground stopper and, after the boat and bottle had been cleaned with hot dilute nitric acid and water, the rinsings were poured into the flask and the silver chromate dissolved by the application of gentle heat. If the salt had not been heated above 225°, the solution was absolutely clear. Specimens heated above this temperature always showed more or less turbidity.

The chromate was next reduced to the chromic state by the addition of a very slight excess of sulphur dioxide which had been freshly distilled into pure water. The slight excess of sulphurous acid was soon oxidized under the combined influence of heat and nitric acid. In Analyses 1, 2, 3, 12, 13 and 14, the reduction was effected by means of recrystallized hydrazine sulphate, in order to avoid to a large extent the presence of sulphuric acid, for Richards and Jones[3] found that silver chloride occludes silver sulphate very tenaciously. This method of reduction, however, was without effect on the results.

Since in the reduction of the chromate by hydrazine nitrogen gas is evolved, the flask

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[1] Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896).

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

[3] *Ibid.*, **29**, 831 (1907).

in which the reduction took place was protected from loss by spattering by means of a long column of bulbs fitting loosely into the neck of the flask. The solution of hydrazine sulphate was added through a funnel with a long fine stem which extended through the column of bulbs nearly to the bottom of the flask. After the addition of the hydrazine, the reaction was allowed to continue slowly, with occasional shaking, and was completed by heating the solution upon a steam bath for a short time. In the presence of acid a dilute solution of hydrazine is without effect upon silver salts.

After the solution had been allowed to cool, it was diluted to a volume of one and one-half liters, and the silver was precipitated as chloride or bromide by the addition of a very dilute solution of an excess of either hydrochloric or hydrobromic acid. The flask with its contents was shaken thoroughly for a few moments and was then allowed to stand several days, until, the silver bromide having settled, the supernatant solution was perfectly clear.

Since the mother liquor of the silver halide contained both nitric and hydrobromic acids in excess, the use of a Gooch-Munroe-Neubauer crucible seemed to be attended with danger on account of solution of platinum. Such a possibility has already been pointed out,[1] and an actual loss was found to take place in blank experiments carried out at the beginning of this research. Accordingly, the ordinary platinum Gooch crucible with an asbestos mat was used.

The precipitated silver chloride or silver bromide was next collected upon the weighed Gooch crucible, dried and weighed. The moisture retained by the precipitate was determined by fusion in a porcelain crucible, and the asbestos mechanically detached from the Gooch crucible was collected upon a small filter.[2]

Another correction was necessary. The filtrate contained dissolved silver salt, even though an excess of halogen acid was used in the precipitation. The larger part of the dissolved halide is due to the marked solubility in solutions of chromic salts, the amount dissolved increasing with increasing concentration of the chromic salts. Berlin overlooked the correction, which was afterwards pointed out by Siewert. Meineke later determined experimentally the quantity of dissolved material, and also proposed the method of separation which was adopted in this work. The entire filtrate of three to four liters was evaporated to small bulk, nearly neutralized with ammonia, and then the silver was precipitated from hot solution as sulphide. The precipitate was collected upon a filter paper, which was ignited. The residue was converted to the nitrate by digestion with dilute nitric acid, and the solution was then filtered into a graduated flask, in which it was diluted to known volume. By comparison in the nephelometer of this solution with standard solutions of silver, the quantity of silver in solution was determined. In using the nephelometer all necessary precautions, as pointed out by Richards,[3] were taken.

That all the dissolved silver was recovered in this way was shown by adding an excess of ammonia to the filtrate of the silver sulphide in one analysis, the hydrogen sulphide having been expelled, and after removal of the chromic hydroxide by filtration, testing the acidified filtrate for silver. None could be detected.

The Determination of Moisture in Silver Chromate.—The proportion of moisture in the silver chromate was found by fusing weighed quantities of the salt in a current of pure dry air and collecting the water vapor produced in a weighed phosphorus pentoxide tube. During the fusion of the salt, oxygen is evolved, but since the fusing

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[1] Morse, "Exercises in Quantitative Chemistry," p. 203 (1905).

[2] For details concerning these operations see Richards and Wells, THIS JOURNAL, 27, 515 (1905); Baxter, *Ibid.*, 28, 1329 (1906).

[3] *Am. Chem. J.*, 35, 510 (1906).

point is low, there is no danger of volatilization of either silver or chromium compounds.

In order to avoid the necessity of removing the fused silver chromate from a platinum boat, boats of copper foil which had been cleaned and ignited were employed.

It was desirable to determine not only whether the proportion of water could be made constant at any one temperature, but also how much the proportion of water is affected by variations in temperature. Experiments were therefore carried out with silver chromate which had been dried for two hours at 200°, 225° and 300°, in dry air which had been purified as previously described.

After the salt had been dried, a carefully weighed U-tube containing resublimed phosphorus pentoxide was attached to the end of the tube. This U-tube was provided with ground glass stopcocks lubricated with Ramsay desiccator grease. The silver chromate was gradually heated until fusion took place, and a slow current of air was allowed to pass through the system for one-half hour in order to make certain that all moisture was carried into the absorption tube. Finally the phosphorus pentoxide tube was reweighed.

Temperature of heating.	Weight of silver chromate. Grams.	Weight of water. Gram	Per cent. of water.
200°	4.87	0.00097	0.0199
200°	4.74	0.00098	0.0207
200°	4.43	0.00093	0.0210
	Average		0.0205
225°	9.01	0.00136	0.0151
225°	10.85	0.00188	0.0173
225°	10.11	0.00125	0.0124
225°	7.95	0.00105	0.0132
225°	8.23	0.00114	0.0139
	Average		0.0144
300°	3.50	0.00034	0.0097

The pentoxide tube was weighed by substitution with the use of a counterpoise of the same size and weight. Before being weighed, both tubes were carefully wiped with a damp cloth and were allowed to stand near the balance case for thirty minutes. Care was taken to equalize the pressure inside and outside the tubes by opening one stopcock immediately before hanging on the balance.

In order to test the efficiency of the drying apparatus, blank experiments were carried out by allowing a slow current of air to pass through the apparatus into the weighed pentoxide tube. The variations in the weight of the tube were never much larger than the probable error in weighing the tubes.

As is to be expected, the water content gradually decreases with increasing temperature of heating. The extreme variations with specimens of silver chromate which have been heated at 225° amount to only five-thousandths of a per cent. Evidently the percentage of residual water is as constant as can be reasonably expected, and the mean can safely be assumed to represent with sufficient exactness the average proportion of water in the salt. Hence, from every apparent gram of silver chromate, 0.000144 gram is subtracted.

Density of Silver Chromate.

In order to correct the weight of silver chromate to a vacuum standard, a knowledge of its specific gravity is necessary. This has already been determined by Playfair and Joule[1] and Schroeder,[2] who obtained the values 5.77 and 5.53 respectively. On account of the marked difference between these values, new determinations of the density were made by the displacement of toluene with weighed amounts of salt. The toluene was first dried by stick soda and was then distilled. Its specific gravity at 25° referred to the water at 4° was found to be 0.86156. Great pains were taken to remove air from the chromate when covered with toluene by placing the pycnometer in an exhausted desiccator before setting.

Weight of silver chromate in vacuum. Grams.	Weight of toluene displaced in vacuum. Gram.	Density of silver chromate. 25°/4°.
5.1584	0.7898	5.628
3.6012	0.5520	5.621
	Average	5.625

The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction per gram.
Weights	8.3	
Toluene	0.862	+0.00126
Silver chromate	5.625	+0.000069
Silver chloride	5.56	+0.000071
Silver bromide	6.473	+0.000041

Balance and Weights.—All weighings were made by substitution upon a nearly new short-armed Troemner balance, easily sensitive to one-fiftieth of a milligram with a load of fifty grams.

The gold-plated Sartorius weights were carefully standardized by the method described by Richards,[3] and were used for no other work.

SERIES I.

$2AgCl : Ag_2CrO_4$

$Ag/AgCl = 0.752632$[4]

Number of analysis.	Sample of Ag_2CrO_4.	Corrected weight of Ag_2CrO_4 in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos. Gram.	Dissolved AgCl from filtrate. Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio $2AgCl : Ag_2CrO_4$.
1	II	10.30985	8.90835	0.00063	0.00117	0.00019	8.90908	0.864132
2	II	8.26920	7.14327	0.00063	0.00211	0.00017	7.14492	0.864040
3	IV	6.56679	5.67324	0.00039	0.00136	0.00023	5.67444	0.864111
							Average	0.864094

Per cent. of Ag in Ag_2CrO_4, 65.0345.

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[1] *Mem. Chem. Soc.*, **2**, 401 (1845).

[2] *Lieb. Ann.*, **173**, 72 (1874).

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

[4] Richards and Wells, *Pub. Car. Inst.*, No. 28 (1905).

Series II.

$2AgBr : Ag_2CrO_4$

$Ag/AgBr = 0.574453$[1]

Number of analysis.	Sample of Ag_2CrO_4.	Corrected weight of Ag_2CrO_4 in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Loss on fusion, Gram.	Weight of asbestos. Gram.	Weight of AgBr from filtrate. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $2AgBr : Ag_2CrO_4$.
4	I	2.63788	2.98579	0.00028	0.00056	0.00014	2.98621	1.13205
5	II	2.82753	3.20018	0.00008	0.00060	0.00014	3.20084	1.13203
6	III	2.33454	2.64054	0.00032	0.00220	0.00026	2.64268	1.13199
7	I	1.77910	2.01304	0.00050	0.00144	0.00004	2.01402	1.13204
8	I	2.33198	2.63988	0.00030	0.00034	0.00002	2.63994	1.13206
9	II	3.10402	3.51311	0.00033	0.00094	0.00018	3.51390	1.13205
10	III	2.92751	3.31411	0.00027	0.00033	0.00010	3.31427	1.13211
11	III	4.21999	4.77677	0.00055	0.00126	0.00014	4.77762	1.13214
12	II	5.24815	5.93939	0.00025	0.00170	0.00020	5.94104	1.13203
13	IV	6.24014	7.06401	0.00039	0.00104	0.00018	7.06484	1.13216
14	IV	7.92313	8.96913	0.00083	0.00129	0.00022	8.96982	1.13211
							Average	1.13207

Per cent. of Ag in Ag_2CrO_4 .... 65.0321

Average per cent. of Ag in Ag_2CrO_4........ 65.0333

	$2AgBr : Ag_2CrO_4$.
Sample I	1.13205
Sample II	1.13204
Sample III	1.13208
Sample IV	1.13214

	$2AgCl : Ag_2CrO_4$.
Sample II	0.86409
Sample IV	0.86411

Discussion of Results.

In comparing the analytical results, it is to be noted first that the compositions of the different samples agree within less than one one-hundredth of one per cent., as the following averages show. If anything, Samples I and II show a somewhat lower percentage of silver than Samples III and IV. These samples were made from ammonium chromate which contained a slight excess of chromic acid. This excess of acid accumulated in the solution during the precipitation of the silver chromate, so that the precipitate formed under distinctly acid conditions, although the acidity was not sufficient to present any danger of the formation of dichromate. Samples III and IV, on the other hand, since they were made from potassium chromate, which is markedly hydrolyzed, were formed under distinctly basic conditions, and the precipitation or occlusion of basic salts is to be feared. Such occluded basic salts would tend to raise the percentage of silver in the chromate. However, Sample IV yielded slightly higher results than Sample III, while on account of the method of precipitation the reverse is to be ex-

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[1] Baxter, THIS JOURNAL, **28**, 1322 (1906).

pected, for Sample III was precipitated by adding the silver nitrate to the chromate, while Sample IV was precipitated by adding the chromate to the silver solution, the mother liquor remaining neutral in both cases. Too much emphasis should not be laid upon the slight apparent difference in the composition of the different samples of salt, since the variations in the experiments with the same samples are as large as the differences between the samples. Hence the average result from the different samples is employed in the final calculations, all the analyses being given equal weight in each series.

In addition to the specimens of silver chromate, the preparation and analysis of which have been described, two other interesting specimens were prepared. One was formed by adding a 0.04 normal silver nitrate solution to a solution of chromic acid of similar concentration. On account of the solubility of silver chromate in nitric acid solutions, precipitation was only partial. The precipitate was washed and dried, and upon analysis was found to contain so little silver that the presence of a small proportion of dichromate was certain, a result which was hardly to be expected in the light of Sherrill's experiments.

The second sample was prepared by heating ammoniacal solutions of silver chromate in platinum vessels, the chromate being gradually precipitated as the ammonia was expelled. This material yielded somewhat irregular results, which on the whole indicated too high percentages of silver, and hence the presence of basic salts, a result which could have been predicted from a consideration of the conditions of preparation.

It is to be noted that Series I and Series II indicate percentages of silver differing by less than four-thousandths of a per cent., a highly satisfactory agreement, which indicates purity of the halogen acids employed as well as experimental accuracy.

If the percentage of silver in silver chromate is 65.0333, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the latter value 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 are carried out 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 determinations of the molecular weight of silver chromate is multiplied six times in the atomic weight of chromium.

If Ag = 107.93 Ag_2CrO_4 = 331.922 and Cr = 52.062
If Ag = 107.88 Ag_2CrO_4 = 331.768 and Cr = 52.008
If Ag = 107.85 Ag_2CrO_4 = 331.676 and Cr = 51.976

Although slightly lower than the previous investigations, these results 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.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

SECOND PAPER.—THE ANALYSIS OF SILVER DICHROMATE.

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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 oc-