

ART. XXI.—*Contributions of the Massachusetts Institute of Technology. I.—On Nitric Acid and Chlorate of Potassium as an Oxydizing Mixture applicable to Sulphur, Sulphids, Chromium, Arsenic, Organic Matters, etc.*; by FRANK H. STORER, Professor of General and Industrial Chemistry in the Massachusetts Institute of Technology.

SOME years since while studying the action of various oxydizing agents upon oxyd of chromium, I was struck by the superior oxydizing power of a mixture of ordinary nitric acid and chlorate of potassium over that of the mixtures of chlorate of potassium and chlorhydric or sulphuric acid, commonly used in analysis. Inasmuch as the fact of the great oxydizing power of a mixture of nitric acid and the chlorate had already been noticed and explained by several observers,* I at that time contented myself with a simple statement of my own observations of the action of the mixture upon chromic oxyd† without referring in any way to the general value of the mixture as an oxydizing agent. Since that time, however, I have had frequent occasion to employ the mixture for effecting the oxydation of many substances, besides oxyd of chromium, such as present themselves in the ordinary experience of an analytical laboratory, and have satisfied myself that the merit of the process has not hitherto been duly appreciated.

Experience has convinced me, not only that a mixture of nitric acid and chlorate of potassium oxydizes more rapidly than the common mixture of chlorhydric acid and chlorate of potassium, but that it is really to be preferred in the great majority of cases to any of the agents ordinarily employed to effect oxydation in the wet way. Instead of occupying as now a secondary or alternative place in the treatises on analysis it ought to take precedence of the other processes of oxydation. It may be used with advantage in many instances where dry methods of oxydation are now recommended. With the exception perhaps of the sulphids, or other compounds, of antimony and tin, there are probably but few cases where its use will be found inadmissible.

The following notes include the results of several researches made by students of the Massachusetts Institute of Technology with the view of testing the capabilities of the process :—

* Compare Gmelin's Handbook of Chemistry, iii, 61.

† Proceedings of American Academy, 1859, iv, 342; Journal für practische Chemie, lxxx, 44.

Estimation of Sulphur in Organic Compounds ; by A. H. PEARSON.

It is easy to determine sulphur in non-volatile organic compounds by oxydizing the substance with chlorate of potassium and nitric acid, precipitating the sulphuric acid as sulphate of barium and washing the latter with a solution of acetate of ammonium, to remove any nitrate of barium which may have adhered to it.

To oxydize the sulphur compound, place a weighed quantity of it in a porcelain dish, pour upon it three or four table spoonfulls of strong nitric acid (39° B.), free from sulphuric acid, and add to the acid half a teaspoonful of chlorate of potassium. Cover the mixture with an inverted glass funnel, the stem of which has been bent to a right angle. Place the dish on a wire gauze support and heat its contents. From time to time lift the funnel slightly and throw a small fragment of chlorate of potassium into the hot acid.

The funnel must be of such size that its rim may fall within the rim of the dish and rest securely upon the sides of the dish, above the liquid; it serves to retain the particles of liquid which are thrown up from the dish by the gas evolved during the decomposition of the chlorate.

The oxydation will be completed more or less rapidly according to the character of the substance operated upon. Only five or ten minutes are required to completely oxydize a third of a gram of sulphocyanid of potassium, while from half to three quarters of an hour are needed to destroy the same weight of ordinary free sulphur. It may be observed in passing, that sulphur which has just been distilled dissolves twice as rapidly in a mixture of nitric acid and chlorate of potassium as sulphur which has long been exposed to the air.

Several samples of sulphocyanid of potassium, oxydized in this way, gave the following results :—

- A. 0.2015 grm. of the sulphocyanid gave 0.5114 grm. of sulphate of barium. (I).
- A. 0.265 grm. of the sulphocyanid gave 0.6547 grm. of sulphate of barium. (II).
- B. 0.149 grm. of the sulphocyanid gave 0.3796 grm. of sulphate of barium, (I).
- B. 0.012 grm. of the sulphocyanid gave 0.03 grm. of sulphate of barium. (II).
- C. 0.101 grm. of the sulphocyanid gave 0.2387 grm. of sulphate of barium.
- D. 0.028 grm. of the sulphocyanid gave 0.067 grm. of sulphate of barium. (I).
- D. 0.084 grm. of sulphocyanid gave 0.204 grm. of sulphate of barium. (II).

The sulphocyanid used for the experiments mentioned in the paragraphs marked "A" was prepared by fusing together ferrocyanid of potassium, carbonate of potassium, and sulphur in the usual way, treating the fused mass with hot alcohol and allowing the alcoholic solution to crystallize. That used for the experiments in paragraphs B was prepared in precisely the same way as the foregoing, but at another time. The salt prepared in this way is evidently contaminated with free sulphur, or some sulphur compound other than the sulphocyanid, which has been taken up by the alcohol.

The experiment recorded in paragraph C was made with crystals which separated from the alcoholic mother-liquid of B.

The experiments marked D, were made with purified crystals obtained as follows:—A quantity of the crude alcoholic crystals, similar to those used in experiments B, were dissolved in water, the solution was filtered to separate sulphur and placed under a bell glass, over strong sulphuric acid, to crystallize. The crystals thus obtained were redissolved in alcohol, the solution filtered to separate carbonate of potassium, then concentrated by evaporation and made to crystallize. The crystals were quickly pressed between folds of filter paper and portions of them were weighed out for the analyses.

The crystals obtained directly from the aqueous solution of the sulphocyanid were contaminated to a considerable extent, with carbonate of potassium, but after they had been recrystallized from alcohol only traces of the carbonate were found upon them.

Stated in terms of per cents, the results may be tabulated as follows:—

		I.	Found.	II.	Theory.
A.	} Impure {	34.85		33.91	
B.		34.98		34.33	
C.	-----	32.45		---	} 32.90
D.	-----	32.85		32.86	

I have applied the foregoing method not only to sulphocyanid of potassium and to free sulphur as above described, but also for estimating sulphur in vulcanized caoutchouc and in several samples of anthracite and bituminous coal. It is easy to completely oxydize either of these substances by means of the mixed chlorate of potassium and nitric acid. Anthracite dissolves even more readily than bituminous coal, since, unlike the latter, it does not fuse to a single mass in the hot acid.

It is not improbable that by a slight variation of the foregoing process it may be found practicable to determine the carbon of an organic compound at the same time as the sul-

phur. Thus, the oxydation might perhaps be effected in a flask provided with a wide funnel tube for the addition of the chlorate and a delivery tube through which the carbonic acid formed could be led into baryta-water or some other substance fit to absorb that gas. Upon this point, however, I have as yet made no experiments.

May, 1869.

Assay of Sulphur in Iron Pyrites ; by A. H. PEARSON.

The proportion of sulphur in iron pyrites ("Sulphur-ore") may be readily and accurately estimated as follows:—Weigh out a gram or less of the powdered ore, place the powder in a porcelain dish, together with a small quantity of chlorate of potassium, pour upon it some 50 c. c. of pure nitric acid of 39° B., and cover the mixture with an inverted glass funnel, with bent stem. Set the dish upon a water bath and heat the water to boiling. From time to time throw crystals of chlorate of potassium into the hot acid. By adding rather large crystals of the chlorate at frequent intervals it is easy to oxydize the whole of the sulphid in half an hour. But since the solution obtained in that case is highly charged with saline matter it will usually be found more advantageous to use less of the chlorate of potassium and to allow a somewhat longer time for the process of oxydation.

When all the sulphur has been oxydized, rinse the funnel with water and remove it from the dish. Evaporate the liquid to a small bulk, then add to it a little concentrated chlorhydric acid and again evaporate to absolute dryness in order to render silicic acid insoluble. Moisten the residue with concentrated chlorhydric acid, mix it with water and filter, to separate silicic acid and gangue.

To the filtrate from the silicic acid add a quantity of solid tartaric acid about as large as that of the pyrites originally taken, heat the liquid almost to boiling and add to it an excess of chlorid of barium to precipitate the sulphuric acid. After the sulphate of barium has been allowed to subside, wash it thoroughly by decantation first with hot water and afterward with a dilute solution of acetate of ammonium. The latter may be prepared at the moment of use, by mixing ammonia-water and acetic acid. The purpose of the acetate of ammonium is to dissolve any nitrate of barium which may adhere to the sulphate ; that of the tartaric acid is to prevent the precipitation of iron compounds together with the sulphate of barium. In an experiment where 0·7 grm. of pyrites was oxydized with chlorate of potassium and nitric acid, and the

filtrate from silica was acidulated with chlorhydric acid without the addition of tartaric acid, there was thrown down on the addition of chlorid of barium a bright yellow precipitate which became darker colored when the solution was boiled. It was not only found to be impossible to wash out the iron with which this precipitate was contaminated but the consistency of the precipitate was such that it was a difficult matter even to wash away the saline liquor in which the precipitate was formed.

In another experiment, the attempt was made to remove the iron from the filtrate from silica before adding the barium salt to throw down the sulphuric acid. But in that case a considerable portion of the sulphuric acid was dragged down, as sulphate of potassium, by the iron precipitate and so lost. The precipitation of the iron was effected in this experiment by adding an excess of ammonia-water to the acidulated filtrate from silica and washing the precipitate for a long time, by decantation, with boiling water. To prove that the iron precipitate really retained sulphuric acid a quantity of the precipitate was dried, ignited and powdered and the powder boiled with water. The clear liquid thus obtained was acidulated with chlorhydric acid and tested with chlorid of barium. An abundant precipitate of sulphate of barium was at once thrown down.

After the sulphur of the pyrites has been determined by precipitating it from a tartaric acid solution, as above described, the iron might perhaps be estimated in the filtrate by one of the new methods of titration with hyposulphite of sodium. I have made no experiments with the hyposulphite, but have failed completely in several attempts to determine the iron as a sulphid, by precipitating with sulphid of sodium, as directed by Fresenius. I found it impossible to wash the sticky, slimy mass of sulphid of iron. It is not easy, on the other hand, to destroy the tartaric acid by igniting the dried filtrate, from sulphate of barium, in a muffle, for on evaporating this solution the saline matters with which it is charged continually creep over the edges of the dish.

November, 1868.

Assay of Copper pyrites ; by F. P. PEARSON.

The following method of treating copper pyrites has been found more advantageous than the ordinary process of oxidizing the mineral with aqua regia and subsequently evaporating the solution repeatedly with chlorhydric acid, or with sulphuric acid, to expel the last traces of nitric acid :—

Place a weighed quantity of the powdered mineral together with some chlorate of potassium in a porcelain dish.—Five grams of a variety of pyrites containing about 18 per cent of copper was found to be enough for one analysis, and a quantity of chlorate of potassium equal to a small teaspoonful, was added to the ore.—Invert a glass funnel with bent stem in the dish above the pyrites and pour upon the latter rather more ordinary strong nitric acid than would be sufficient to completely cover the powder. Place the dish upon a water-bath, and, from time to time, throw into it small quantities of chlorate of potassium. The doses of the chlorate must be repeated at frequent intervals until free sulphur can no longer be seen in the dish. If need be, add nitric acid also from time to time, to replace that lost by evaporation.

As a general rule it is safer and more convenient to heat the mixture on a water-bath than upon sand, though I find that the oxydation of sulphur can be effected more easily and quickly when the mixture of nitric acid and chlorate is heated to actual boiling than at the temperature obtainable by means of a water-bath. When the last particles of sulphur have been destroyed remove the inverted funnel from the dish, rinse it with water and collect the rinsings in a beaker by themselves. Allow the liquid in the evaporating dish to become cold, pour upon it a quantity of ordinary strong chlorhydric acid rather larger than the quantity of nitric acid taken at first, evaporate the mixed solution to dryness and heat the dry residue, to render silica insoluble in case any silica be present.

Pour water upon the cold residue, and, without filtering the liquor, wash the contents of the dish into the beaker which contains the rinsings of the funnel. Heat the liquid in the beaker nearly to boiling, add to it about 25 c. c. of a strong aqueous solution of ferrous sulphate slightly acidulated with sulphuric acid, and keep the mixture at a temperature near boiling during four or five minutes, in order to destroy the small quantity of nitric acid which has escaped decomposition in spite of the evaporation with chlorhydric acid.

The ferrous salt seldom or never acts instantaneously, but the reducing action proceeds rapidly and perfectly satisfactorily when once begun. If need be, add more of the ferrous solution, little by little, until the entire contents of the beaker became dark colored, or almost black, and no more gas is disengaged.

In order to be sure that all the nitric acid has been reduced, it is well enough, after the mixture of liquid and solution of ferrous sulphate has been duly heated, to place a drop of the mixture upon porcelain and test it with ferrieyanid of potas-

sium. In general, however, the coloration of the liquor in the beaker due to the formation of nitrous or hyponitric acid will be a sufficient indication that the copperas has done its work. The nitrous fumes quickly disappear from the liquid at a subsequent stage of operations when metallic iron is immersed in the solution.

When enough of the ferrous sulphate has been added, filter the mixed solution into a wide beaker, precipitate the copper, in the metallic state, upon a sheet of iron in the usual way and ignite the copper in a porcelain crucible, in a current of hydrogen, before weighing it.

By means of the ferrous salt, the last traces of nitric acid may be got rid of far more quickly, conveniently and certainly than by the old system of evaporating the pyrites solution with several successive portions of chlorhydric acid. By treating the pyrites with chlorate of potassium and nitric acid it is easy to oxydize and dissolve every particle of the sulphur in the mineral so that no portion of the latter can escape decomposition by becoming enveloped in free sulphur. When aqua regia is used on the other hand, or a mixture of chlorate of potassium and chlorhydric acid, a certain proportion of sulphur almost invariably remains undissolved and might easily enclose portions of the mineral so as to protect them from the solvent action of the acids.

The method of oxydation above described can manifestly be employed with advantage for dissolving many other sulphuretted ores besides copper pyrites.

January, 1869.

Estimation of Sulphur in Sulphid of Mercury ; by E. W. BOWDITCH.

In order to contrast the action of the mixed nitric acid and chlorate of potassium with that of the mixture of chlorhydric acid and chlorate of potassium ordinarily employed by chemists, as an oxydizing agent, a series of comparative experiments were made upon commercial vermilion.

Eight portions of the vermilion were operated upon in succession, as follows :—In each instance about 0.5 or 0.6 gm. of the vermilion was placed in a small glass flask set in an inclined position upon a wire gauze support above a lamp. A quantity of nitric acid, of 39° B., or of concentrated chlorhydric acid as the case might be, was poured into the flask, a small quantity of chlorate of potassium was added and the mixture heated. From time to time small bits of chlorate of potassium were thrown into the flask, the contents of which were maintained near the boiling point until all the sulphur, or as much of it as possible, had dissolved.

In every instance where nitric acid was employed, the vermilion was in a short time oxydized and dissolved so completely that no trace of free sulphur could be seen in the liquor. But when chlorhydric acid was used to decompose the chlorate, there remained, invariably, floating upon the liquid, one or more yellow globules of undissolved sulphur, varying in size from that of a pin's head to a flax seed. These floating globules could not be destroyed by any practicable amounts of the chlorate and acid. In fact, it may be said to be impossible to destroy such globules with these reagents.

Whenever chlorhydric acid was used, therefore, to decompose the vermilion, the solution obtained had to be filtered, to separate the free sulphur, before the sulphuric acid in the solution could be precipitated as sulphate of barium. The presence of free sulphur is objectionable not only because time is lost in collecting, washing, drying and weighing it, but also on account of its liability to enclose and conceal particles of the substance to be analyzed, which would be dissolved by the acid if the latter were able to act upon them. The determination of sulphur may thus be rendered incorrect by weighing the undissolved substances with the sulphur.

When nitric acid was used with the chlorate, it happened sometimes, when the proportion of nitric acid was small, that a considerable quantity of saline matter crystallized in the flask. It was found, however, that enough water to redissolve this precipitate might be added to the mixture without impairing to any material extent the oxydizing power of the chlorate subsequently added. The acid liquor resulting from the action of nitric acid and chlorate of potassium upon the vermilion was evaporated to dryness on a water bath and the residue treated with strong chlorhydric acid in order to destroy most of the nitric acid before proceeding to precipitate the sulphuric acid with chlorid of barium. Before adding the chlorhydric acid to the residue the latter must be allowed to become perfectly cold lest the mixture froth violently and portions of it be thrown out of the flask. After the acid has once been added, however, the mixture may be heated gently without risk of loss.

No matter whether chlorhydric or nitric acid is employed with the chlorate, the solution must at last be largely diluted with water before adding the chlorid of barium.

In my experiments, nothing but hot water was employed to wash the sulphate of barium. Naturally enough it was more difficult to wash in this way the precipitates obtained from solutions contaminated with nitric acid, than those from the solutions which contained only chlorhydric acid. But in spite

of this disadvantage and of the long time required to wash out the last traces of nitrate of barium I have always found that a sulphur determination made by the nitric acid process requires much less time for its completion than one made by the old way with chlorhydric acid.

In a final trial made expressly for the purpose of testing this point, the precise times consumed in making each experiment were carefully noted. Two portions of the vermilion were weighed out into flasks and treated, one with chlorhydric acid and chlorate of potassium and the other with nitric acid and the chlorate. The portion treated with chlorhydric acid weighed 0.5695 grm. and the other 0.519 grm. The flask containing the sample treated with chlorhydric acid was taken from the fire a few minutes before the last traces of sulphur in the nitric acid flask had been destroyed and the separation of the undissolved sulphur was proceeded with as rapidly as possible, but in the end it was found that eleven hours and three quarters were required to complete the determination of sulphur in the portion of vermilion treated with chlorhydric acid while the estimation of sulphur in the other portion, treated with nitric acid was finished in nine hours and a half. 14.32 per cent of sulphur was found in the portion treated with nitric acid and 14.25 per cent in the portion treated with chlorhydric acid, instead of the 13.79 per cent required by theory.

February, 1868.

Estimation of Chromium as Chromate of Barium; by A. H. PEARSON.

As Prof. Storer has shown,* chromic oxyd is quickly changed to chromic acid, when boiled with a mixture of concentrated nitric acid and chlorate of potassium. All the chromium in half a gram of hydrate of chromium or of any of the ordinary chrome salts can in this way be converted into chromic acid in a few moments, and even compounds as refractory as chrome-iron-ore, or oxyd of chromium which has been strongly ignited, can be oxydized in less time than would be required to complete their oxydation by the process of fusion ordinarily employed.

As will appear from the experiments which follow, the chromic acid thus formed in the wet way, can be readily and accurately estimated in the form of chromate of barium, if care be taken to wash the precipitated chromate with acetate of ammonium or some other saline solution in which chromate of barium is insoluble.

I. A quantity of anhydrous chromic oxyd was prepared by heating bichromate of potassium with an excess of strong chlor-

* Proceedings of American Academy, 1859, iv, 342.

hydric acid, until chlorine ceased to be evolved, saturating the acid liquor with ammonia water, washing and drying the precipitated hydrate and finally igniting it intensely in a platinum crucible over a blast-lamp.

0.102 grm. of this anhydrous oxyd was placed in an evaporating dish, together with a quantity of nitric acid and some chlorate of potassium, and covered with an inverted funnel with a bent stem. The acid was heated and fragments of chlorate of potassium were added to it from time to time, until the chromic oxyd had completely disappeared. This result was attained in the course of half an hour.

The acid solution was diluted with water, then neutralized with ammonia and the ammoniacal solution in its turn treated with enough acetic acid to make it slightly acid. After the acidulated solution has become cold, a solution of chlorid of barium was added to it, in slight excess, and the mixture was left at rest for ten or twelve hours. The precipitated chromate of barium was washed, by decantation, with a cold solution of acetate of ammonium, then collected on a filter, rinsed with water, dried, heated in a crucible to expel the last traces of water and of the ammonium salt, and weighed.

The amount of chromate of barium obtained in this experiment was equal to 0.336 grm., which is equivalent to 68.31 per cent of chromium instead of 68.62 per cent as required by theory.

The precipitate of chromate of barium must be allowed to stand for some time before filtering lest it pass through the pores of the filter and render the filtrate cloudy.

The acetate of ammonium employed for washing serves to dissolve any nitrate of barium or chlorid of barium which may have been precipitated with the chromate. It has the further advantage of dissolving less of the chromate of barium than pure water would.

II. A quantity of hydrate of chromium precipitated from a solution of reduced bichromate of potassium, as in the previous experiment, was dried at 115° and the proportion of water retained by the dried hydrate was determined once for all by ignition.

0.11 grm. of this dried hydrate, equal to 0.0688 of the anhydrous oxyd, was then treated with nitric acid and chlorate of potassium as in experiment I. It was found that the oxydation was completed as soon as the acid became hot enough to decompose the chlorate. Less than five minutes were sufficient in this instance for the complete conversion of the chromium to chromic acid.

The chromate of barium obtained weighed 0.2286 grm., equiv-

alent to 68.65 per cent of chromium in the oxyd taken instead of the theoretical 68.62 per cent.

III. 0.113 grm. of the dried hydrate containing 0.0707 grm. of the anhydrous oxyd of chromium was mixed with a quantity of nitrate of magnesium,—prepared by dissolving carbonate of magnesium in nitric acid—before the treatment with nitric acid and chlorate of potassium. 0.2346 grm. of chromate of barium was obtained. In other words, 68.60 per cent of chromium instead of the 68.62 per cent required by theory.

IV. 0.114 grm. of the dried hydrate of chromium, containing 0.0713 grm. of the anhydrous oxyd, was mixed with nitrate of aluminum,—prepared by dissolving hydrate of aluminum in nitric acid—before the treatment with chlorate of potassium. 0.2356 grm. of chromate of barium, was obtained. That is to say, 68.31 per cent of chromium instead of 68.62 per cent.

V. A small quantity of chrome-iron-ore was ground to very fine powder and treated in a dish with nitric acid and chlorate of potassium as above described. At the end of half an hour, that portion of the ore which still remained undissolved was washed with water, dried, fused with a mixture of carbonate of sodium and nitrate of potassium, and the fused mass boiled with water; but the solution thus obtained gave no reaction for chromium when tested for that substance.

It appears from the foregoing experiments that chromium can be readily estimated, in this way, in presence of aluminum and magnesium. The process can doubtless be employed also for separating chromium from iron, cobalt, nickel and zinc. As a matter of course, special care must always be taken to employ reagents which are absolutely free from any contamination of sulphuric acid.

April, 1869.

On the use of Chromate of Barium in Quantitative Analysis;
by R. H. RICHARDS.

A sample of pure bichromate of potassium examined simultaneously by three of the students in the Institute's laboratory for the purpose of determining the percentage of chromium by precipitating that element in the form of chromate of barium, gave the following discordant results. The method of analysis was similar to that described below.

Name of experimenter.	Grms. of $K_2O, 2CrO_3$ taken.	Grms. of BaO, CrO_3 found.	Percentage of Chromium.	
			Found.	Theory.
N. F. Merrill,	0.516	0.8640	34.67	35.56
F. P. Pearson,	0.500	0.8788	36.38	“ “
C. E. Avery,	----	----	36.31	“ “
“ “ “	----	----	36.24	“ “

At the suggestion of Prof. Storer, I have examined other portions of the same sample of bichromate of potassium, with the view of discovering, if possible, the sources of error which vitiated the foregoing analyses.

A quantity of the bichromate was heated until it fused, the cold mass powdered and several portions of it, weighing from one to two grams each, were taken for analysis. Each of the weighed quantities of bichromate was dissolved in distilled water, the solution was heated nearly to boiling and a lump of acetate of sodium twice the volume of the bichromate of potassium taken was thrown into the hot liquor. Acetic acid was then added to strongly acid reaction, and afterward a solution of chlorid of barium, with occasional stirring, until no more precipitate was formed on the further addition of chlorid of barium and until the supernatant fluid became absolutely colorless. It is easy to hit this point in a hot solution but not so easy when the liquid is cold.

After the precipitate had been allowed to stand for some time, the clear liquid above it was decanted into a filter. The precipitate was then washed with cold water, first by decantation in the beaker and afterward upon the filter. The filtrate proper, that is to say, the clear liquor decanted from the precipitate, was in every instance colorless. It gave a white residue when evaporated on platinum foil and no precipitate when tested with acetate of lead. But all the subsequent liquors obtained by decantation and washing came through the filter distinctly yellow-colored. They gave yellow residues when evaporated upon foil and bright yellow precipitates when tested with acetate of lead. It was, consequently, no easy matter to determine when to stop washing. The precipitates were in fact put aside to dry as soon as there was any reason to suppose that the saline mother-liquor had all been washed out from them.

In the 2nd of the following experiments the chromate of barium was weighed upon a tared filter, as was the case also in the experiments cited above, but in Nos. 1, 3 and 4 the dry precipitate was ignited gently in a porcelain crucible before weighing.

No. of the Experiment.	Grms. of $K_2O, 2CrO_3$ taken.	Grms. of BaO, CrO_3 found.	Percentage of Chromium found.	Theory.
1.	1.0095	1.7301	35.47	35.56
2.	1.0175	1.8444	37.53	
3.	1.5456	2.7541	37.74	
4.	1.5020	2.5696	35.49	

Experiments 3 and 4 were carried out side by side, and every effort made to treat them exactly alike.

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From the appearance and behavior of the wash-water, as above described, it appears that chromate of barium is somewhat soluble in pure water, but is insoluble in tolerably strong saline solutions, even in the presence of acetic acid. This observation agrees in the main with a statement* in Prof. Storer's Dictionary of Solubilities to the effect that "chromate of baryta is very slightly soluble in water, and even insoluble when other salts are present in solution."

On the other hand, the excess of precipitate found in experiments 2 and 3, would go to show that chlorid of barium is liable to be dragged down by chromate of barium in the same way that it is apt to go down with sulphate of barium. It would appear therefore that some saline solution, competent to dissolve chlorid and nitrate of barium, should be used instead of water for washing chromate of barium. [P. S.—In accordance with this view Mr. A. H. Pearson has recently employed a solution of acetate of ammonium, with the best results, for washing both the chromate and the sulphate of barium.]

April, 1868.

Approximate Determinations of the Solubilities of Nitrate of Barium, Chlorid of Barium, Perchlorate of Potassium and Chlorate of Potassium in several saline solutions; by A. H. PEARSON.

The following experiments were undertaken in order to discover a saline solution proper to wash out from precipitated chromate of barium the difficultly soluble substances which might be thrown down with it in the operations described above, on page 199.

Quantities of dry nitrate of barium, chlorid of barium, perchlorate of potassium (tolerably, but not absolutely, pure), and chlorate of potassium were finely powdered and a number of small equal portions of each of the powders were measured out into test-tubes. The contents of each of the tubes were then treated with successive drops of the solvent until the last particles of the powders had dissolved. A special dropping tube was provided for each of the solvents and the drops were of such size that 50 of them were very nearly equal to 1 c. c. The test-tubes were thoroughly shaken immediately after the addition of each drop of the solvent, then allowed to stand for some time and again shaken before adding another drop of the liquid. Due allowance was made for the excess of liquid in case the last drop of the solvent was manifestly more than sufficient to dissolve the last traces of the salt.

The powdered salts were measured in a small glass tube, such as is provided in Plattner's blowpipe apparatus, for measuring

* Cited from Dumas's *Traité de Chimie appliquée aux Arts*.

powdered lead. As the mean of several weighings, it was found that the charge of nitrate of barium weighed 0.15 grm., that of chlorid of barium 0.12 grm., that of perchlorate of potassium 0.1 grm. and that of chlorate of potassium 0.08 grm.

For the experiments made "at the temperature of boiling water," long, narrow open tubes, to condense aqueous vapor, were fitted to the mouths of the test-tubes by means of perforated corks and the test-tubes were kept immersed in a bath of boiling water. By means of pasteboard screens the tops of the tubes were protected from the steam and heat of the bath.

The results of the experiments may be tabulated as follows:--

Nitrate of Barium.

I. Experiments made at the ordinary temperature of the air.

Name of solvent.	No. of drops of the solvent required to dissolve the charge (= 0.15 grm.) BaO, N ₂ O ₅ .	No. of c. c. of the solvent required to dissolve one grm. of BaO, N ₂ O ₅ .
Water, -----	100	13.33
Chlorid of ammonium, -----	104	13.67
Ammonia water (strong), -----	110	14.67
Acetate of sodium, -----	110	14.67
Ammonia water (weak), -----	124	16.50
Acetate of ammonium, -----	130	17.33
Acetate of copper, -----	130	17.33
Grape-sugar, -----	140	18.67
Nitrate of ammonium, -----	180	24.00
Chlorhydric acid (dil.), -----	210	28.00
Acetic acid, -----	220	29.00
Nitric acid (dil.), -----	Insoluble.	

II. Experiments made at the temperature of boiling water.

Acetate of ammonium, -----	33	4.33
Water, -----	35	4.67
Chlorid of ammonium, -----	35	4.67
Acetate of sodium, -----	40	5.33
Ammonia water (strong), -----	43	5.67
Acetate of copper, -----	45	6.00

Chlorid of Barium.

I. Experiments made at the ordinary temperature of the air.

Name of solvent.	No. of drops of the solvent required to dissolve the charge (= 0.12 grm.) of BaCl ₂ .	No. of c. c. of the solvent required to dissolve one grm. of BaCl ₂ .
Water, -----	24	4.00
Ammonia water (strong), -----	30	5.00
“ “ (weak), -----	32	5.33
Chlorhydric acid (dil.), -----	32	5.33
Grape sugar, -----	34	5.67
Acetate of ammonium, -----	36	6.00
Chlorid of ammonium, -----	36	6.00
Acetate of copper, -----	38	6.33
Acetate of sodium, -----	40	6.67
Acetic acid, -----	48	8.00

Perchlorate of Potassium.

I. Experiments made at the ordinary temperature of the air.

Name of solvent.	No. of drops of the solvent required to dissolve the charge (= 0.1 grm.) of K_2O, Cl_2O_7 .	No. of c. c. of the solvent required to dissolve one grm. K_2O, Cl_2O_7 .
Nitrate of ammonium, -----	80	16
Water, -----	110	22
Nitric acid (dil.), -----	112	22.4
Acetate of ammonium, -----	122	24.4
Chlorid of ammonium, -----	128	25.6
Acetate of sodium, -----	128	25.6
Cane sugar, -----	136	27.2
Acetate of copper, -----	146	29.2
Ammonia water (conc.), -----	148	29.6
“ “ (dil.), -----	152	30.4
Chlorhydric acid (dil.), -----	152	30.4
Grape sugar, -----	184	36.8
Acetic acid, -----	226	45.2.

II. Experiments made at the temperature of boiling water.

Water, -----	20	4.00
Nitrate of ammonium, -----	20	4.00
Nitric acid (dil.), -----	25	5.00
Acetate of ammonium, -----	30	6.00
Chlorid of ammonium, -----	30	6.00
Acetate of copper, -----	35	7.00
Acetate of sodium, -----	35	7.00

Chlorate of Potassium.

I. Experiments made at the ordinary temperature of the air.

Name of solvent.	No. of drops of the solvent required to dissolve the charge (= 0.08 grm.) $KClO_3$.	No. of c. c. of the solvent required to dissolve one grm. of $KClO_3$.
Nitrate of ammonium, -----	72	18.00
Water, -----	118	29.50
Nitric acid (dil.), -----	122	30.50
Chlorid of ammonium, -----	126	31.50
Acetate of copper, -----	126	31.50
Acetate of sodium, -----	130	32.50
Chlorhydric acid (dil.), -----	132	33.00
Cane sugar, -----	134	33.50
Acetate of ammonium, -----	136	34.00
Ammonia water (strong), -----	142	35.50
Grape sugar, -----	146	36.50
Ammonia water (weak), -----	156	39.00
Acetic acid, -----	192	48.00

The strengths of the various solutions employed as solvents were as follows :—

Ammonia-water, strong = ordinary liquor ammoniæ.

Ammonia-water, weak = a mixture of 1 volume of the strong ammonia-water with 3 vols. of water.

Nitric acid, dilute = a mixture of 1 volume of the strong acid (of 39° B.), with 5 vols. water.

Chlorhydric acid, dilute = 1 vol. of the ordinary concentrated acid with 4 vols. water.

Acetic acid = 1 vol. of the commercial acid mixed with 1 vol. of water.

Chlorid of ammonium = 1 part of the crystallized salt in 10 parts of water.

Nitrate of ammonium = 1 part of the crystallized salt in 10 parts of water.

Acetate of ammonium = ammonia-water dilute, neutralized with the acetic acid of the given strength.

Acetate of sodium was made by saturating a quantity of commercial acetic acid with carbonate of sodium and diluting the liquid with 4 volumes of water.

Acetate of copper was prepared according to the directions of Stolba.*

Cane sugar = 1 part of sugar in 10 parts of water.

Glucose (starch sugar) = 1 part of sugar in 10 parts of water.

It will be observed that the solvent power of acetate of copper,—recommended by Stolba for washing sulphate of barium,—is inferior to that of several other salts.

It may here be said that contrary to what might be supposed, no perchlorate of potassium seems to be carried down with chromate or sulphate of barium when these salts are precipitated, in the estimation of chromium or of sulphur, as described on pp. 191 and 198. At all events none of the perchlorate could be detected on searching for it in several samples of sulphate of barium precipitated from liquors obtained by oxydizing sulphur and sulphur compounds with a mixture of nitric acid and chlorate of potassium.

The method employed in testing for the perchlorate was as follows :—A few drops of an aqueous solution of iodid of potassium were placed in a porcelain crucible together with a small quantity of thin starch paste ; the mixture was acidulated with chlorhydric acid, free from chlorine, and a quantity of the precipitate to be tested was stirred into the mixture. In no instance did the starch become blue on the addition of the precipitate, although nothing but water was used for washing the latter. But a blue coloration was immediately produced, whenever a

* Zeitschrift analyt. Chem., ii. 390.

small speck of perchlorate of potassium was added to the acidulated mixture of starch and iodid.

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Arsenic Compounds.—Of the experiments with arsenic compounds, it will be sufficient to say that both metallic arsenic and arsenious acid are easily changed to arsenic acid by the action of nitric acid and chlorate of potassium, and that the arsenic acid thus formed may be precipitated without inconvenience in the form of arseniate of magnesium and ammonium.

Boston, May 20, 1869.