little polysulfide may be formed because of separation of sulfur or action of ferric ion.

The process is carried out as follows: To a given quantity of the solution (say 45 cc.) add one-ninth of its volume (5 cc.) of concentrated hydrochloric acid and a few drops (0.5 cc.) of nitric acid. The laboratory hydrochloric acid is usually about 10 *N* and the solution is thus made about normal. If much acid is already present allowance must be made for it. Transfer the mixture to an Erlenmeyer flask and boil it half away under the hood. The residual liquid is about 2 *N* in HCl since but little acid is lost on boiling at this concentration. The nitric acid has oxidized stannous to stannic ion, has prevented separation of metals by reduction, and has probably raised the valence of a portion of the arsenic. Pass a rapid stream of hydrogen sulfide through the hot liquid, heating again to boiling once or twice and shaking vigorously. The precipitation of arsenic begins quite promptly and proceeds rapidly. When no more precipitate forms (5 to 10 minutes), add enough water (80 cc.) to make the volume a little more than twice the original (100 cc.). This reduces the HCl concentration below 0.5 *N*. Continue to pass the gas until the liquid is cold and until no more precipitate falls (10 to 15 minutes), filter and wash. For a somewhat similar process, except as to the boiling, see Noyes and Bray.[1]

Transfer the precipitate to a beaker, cover it with concentrated ammonium hydroxide, pass a rapid stream of hydrogen sulfide for one or two minutes, warm gently, shake well, filter and wash. The sulfides of arsenic, antimony and tin dissolve very promptly, carrying with them generally only a trace of copper. Filtrate and residue are treated in the usual way.

The advantages of this method are as follows: (1) A definit acid concentration is secured; (2) the precipitation of arsenic is certain, prompt and complete in a few minutes; (3) after dilution the other metals are thrown down with similar ease and certainty; (4) the use of yellow ammonium sulfide is avoided; (5) the time is much shortened, 30 to 45 minutes being sufficient for the whole process.

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THE QUANTITATIVE DETERMINATION OF PERCHLORATES.[2]

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In the course of a study of certain cobaltammines it became necessary

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[1] THIS JOURNAL, **29**, 167, Proc. 21.

[2] Read before the Section of Inorganic and Physical Chemistry of the American Chemical Society at the Washington Meeting, December 28, 1911.

to make accurate analyses of perchlorates. A study of the literature indicated that no really satisfactory method of analysis had been worked out, and a number of trials by several methods confirmed this conclusion. We finally located the disturbing factor in the simplest of these methods, and by a proper mode of procedure eliminated it altogether, so that now we can determin perchlorates with ease, speed and accuracy.

A fusion method for the analysis of perchlorates, followed by the determination of the chloride formed, would seem to present no special difficulties. As a matter of fact, in spite of many attempts, it appears that no accurate results have heretofore been obtained in this way. Many different fusion mixtures and different methods of procedure have been suggested. The method of Bangley,[1] according to which the perchlorate is ignited with ammonium chloride, has been recommended, but it is admitted that an accuracy greater than 1% cannot be expected. A method described by Carnot[2] has also been recommended.[3] In this method the perchlorate is mixed with sand in a platinum crucible and this is heated to a dull red color. Carnot claimed an accuracy of 0.1%, but in spite of repeated trials we have been unable to approach this accuracy. The results of our last two trials, made with a pure sample of potassium perchlorate, were the best, and are given in Table I:

TABLE I.—ANALYSIS OF POTASSIUM PERCHLORATE BY CARNOT'S METHOD.

No. of. expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.
1	0.4562	0.4720	0.0000	0.4593	—0.0127	—2.69
2	0.4677	0.4805	0.0000	0.4771	—0.0034	—0.70

It will be seen that the errors are very considerable. It appeared in earlier trials as though these errors might be due to a loss by volatilization, and the temperature was therefore kept as low as possible; but this could not be carried too far as there was, on the other hand, the danger of incomplete decomposition due to too low a temperature. There is no sure way by this method of avoiding these alternative difficulties.

Dupré[4] apparently appreciated these difficulties, for in determining the perchlorates in saltpeter by ignition, he used a platinum crucible surrounded by a specially constructed oven which maintained a constant temperature of 545°. His results appear to be somewhat better than those we have obtained by the Carnot method. The results of the only analyses he publishes, where adequate amounts of perchlorate were used, are given in the following table (Table II):

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[1] Treadwell and Hall, "Analytical Chem.", Vol. II.

[2] *Compt. rend.*, **122**, 452 (1896).

[3] Sutton, "Volumetric Analysis," p. 175 (1904).

[4] *J. Soc. Chem. Ind.*, **21**, 825 (1902).

TABLE II.—ANALYSES OF POTASSIUM PERCHLORATE BY DUPRÉ'S METHOD.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.
1	0.0035	0.995	0.0000	0.986	—0.009	— 1.0
2	0.0035	0.498	0.0000	0.492	—0.006	— 1.2
3	0.0035	0.249	0.0000	0.250	+0.001	+ 0.4
4	0.0035	0.099	0.0000	0.099	±0.000	+ 0.0
5	0.0035	0.050	0.0000	0.054	+0.004	+ 8.0
6	0.0035	0.025	0.0000	0.028	+0.003	+12.0

These results are still very unsatisfactory.

A method proposed by Dietrich and Ballenbach[1] appears to be the most successful modification, so far, of the fusion method. These authors fused the perchlorate with a mixture of potassium nitrate and nitrite. The only results they have published are reproduced in Table III:

TABLE III.—ANALYSES OF POTASSIUM PERCHLORATE BY DIETRICH AND BALLENBACH.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Error. Gram.	Error. Per cent.	Flux added.
1	0.3924	0.4062	0.0000	0.4070	+0.0008	+0.19	KNO_3 and KNO_2
2	0.4436	0.4589	0.0000	0.4574	—0.0015	—0.32	KNO_3 and KNO_2

While better than any of the previously cited results their errors are still considerable.

Influenced by the ill success of these various modifications of the fusion method a number of investigators[2] have worked out methods of reduction and analysis in solution. One by Rothmund,[3] using titanium sulfate, appears to be the most successful of them, but while apparently accurate enough, it is long and time consuming when compared with the direct fusion method. It seemed to us worth while, therefore, to locate the source of error in the fusion method and to remove it if possible.

The sign of the errors in all the modifications of this method so far tried has been almost always negative; that is, too little silver chloride has been obtained. Such a result would be caused by either of the two alternatives above mentioned, that is, either by incomplete reduction or by volatilization.

To obtain evidence bearing upon these alternatives we fused samples of pure potassium perchlorate with many different fluxes; with potassium bisulfate and zinc, with sodium carbonate alone, and with sodium carbonate mixed with sodium sulfite or powdered charcoal, or with powdered charcoal and titanium sulfate. It is not necessary to give the results of these fusions in detail. Low results were again obtained in every case, but the error was fairly constant and never amounted to

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[1] *Ber.*, **38**, 751 (1905).

[2] Rothmund, *Chem. Ztg.*, **33**, 1245 (1909). Sjollema, *Z. anorg. Chem.*, **42**, 127 (1904). Kreiden, *Z. anorg. Chem.*, **10**, 277 (1895).

[3] *Loc. cit.*

more than 1.0%, even where no reducing agent was present. The fusions with the flux containing sodium carbonate, carbon and titanium sulfate gave the best results, but even they were always from 0.2–0.4% low. The use of a double crucible with a double cover seemed to be only a slight improvement. These experiments indicated that the reducing agent was of little importance and that the small discrepancies were probably due not to incomplete reduction but to a slight loss by volatilization.

To test this conclusion a number of fusions were carried on in a glass combustion tube through which a slow current of air was drawn. Plugs of asbestos wool were inserted near the outlet end of the tube, and to this two U-tubes containing beads wet with water were attached in series. The perchlorate with flux was placed in a platinum boat and heated for about twenty minutes. The plugs of asbestos and the moistened beads prevented the escape of any chloride vapor or fumes, for, although the water in the first U tube usually gave a slight test for chlorides after a fusion, no chloride was ever detected in the second U tube. After cooling, the contents of the combustion tube and the U tube were washed upon a platinum gooch filter with hot water, the chloride precipitated, and the silver chloride dried in an electric oven at 170°–180°. Different fusion mixtures were employed; first sodium carbonate mixed with powdered charcoal and titanium sulfate; later the titanium sulfate and then the charcoal too were omitted. Since the charcoal, titanium sulfate and asbestos were all found to contain traces of chlorides, blank determinations were made upon each of them and appropriate corrections, always very small, were applied. The use of warm water in washing resulted in a rapid removal of the silver and potassium nitrate from the precipitate, but according to the measurements of Böttger[1] and Kohlrausch[2] must have entailed a slight loss of silver chloride. The temperature of the wash water was about 60° and its total volume, since it was applied in small quantities at a time, amounted only to between 50–75 cc. A saturated solution of silver chloride in pure water of this volume and temperature would have contained about 0.4 mg. of silver chloride, but since the washing was soon discontinued after the wash waters showed no test for silver ions, the first two-thirds of the wash water could have contained only a negligible quantity of silver chloride. The loss of silver chloride then must have been only about 0.1 mg. We have added this almost negligible correction to the observed weights of silver chloride. The results of these experiments are given in Table IV.

These results, with an average deviation from theory of only 0.2 mg. of silver chloride or 0.1%, demonstrate that accurate results can be obtained by the fusion method; that reducing agents are unnecessary and

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[1] *Z. physik. Chem.*, 46, 603 (1903).

[2] Kohlrausch and Holborn, "Leitvermögen," p. 216.

that the low results of previous analyses by the fusion method must have been due to losses by volatilization.

TABLE IV.—FUSION ANALYSES OF POTASSIUM PERCHLORATE IN A TUBE.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.	Flux added.
3	0.2049	0.2119	0.0015	0.2134	±0.0000	±0.00	$Na_2CO_3Ti(SO_4)_2$ and C
4	0.2005	0.2074	0.0015	0.2086	—0.0003	—0.15	"
5	0.2506	0.2592	0.0015	0.2603	—0.0004	—0.15	"
6	0.2605	0.2695	0.0010	0.2699	—0.0006	—0.22	Na_2CO_3 and C
7	0.2017	0.2086	0.0002	0.2085	—0.0003	—0.15	Na_2CO_3

With these points established we resorted to a much simpler and yet equally efficient form of apparatus. It consisted merely of a thin glass (Jena) test tube of 25–30 cc. capacity fitted with two plugs of asbestos wool. The plugs were 15 mm. thick; the first was placed 50 mm., the second 95 mm. from the bottom of the test tube. The perchlorate was weighed directly into the test tube, the plugs inserted, the tube clamped in a nearly horizontal position and the lower end gently heated. White fumes were formed as the oxygen was expelled but these were completely retained by the first plug. When effervescence had ceased, a somewhat larger flame was applied until all the chloride was thoroughly fused. The time required for this heating varies between 10 and 15 minutes. It is a decided advantage to be able to watch the progress of the fusion. After cooling, the contents of the tube were washed upon a filter with warm water, the chloride was precipitated and the silver chloride dried as before. The weights were carefully calibrated and vacuum corrections applied, taking 2.52 and 5.57 as the specific gravities of the potassium perchlorate and the silver chloride, respectively. As before, a correction of 0.1 mg. was applied for the silver chloride dissolved by the warm wash water.

The same sample of potassium perchlorate which was used in the combustion tube fusions was first analyzed by this method. This sample had been found to be free from chlorides, chlorates or sulfates and from other metals than potassium. The results of these analyses are given in Table V:

TABLE V.—ANALYSES OF SAMPLE NO. 1 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl Wt. found.	Deviation. Gram.	Deviation. Per cent.
8	0.2290	0.2369	+0.0002	0.2371	±0.0000	±0.00
9	0.3455	0.3574	+0.0002	0.3577	+0.0001	+0.03
10	0.5904	0.6107	+0.0002	0.6107	—0.0002	—0.03

The average deviation from the calculated value in the analysis is but 0.02%.

A second sample of potassium perchlorate was prepared from the above sample by a double recrystallization from redistilled water in Jena glass flasks, using as low temperatures as possible. The resulting 50 gms. of salt was ground and then dried to constant weight at 130° in an electric oven. Analyses made upon it are given in Table VI:

TABLE VI.—ANALYSES OF SAMPLE NO. 2 POTASSIUM PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
11	0.4561	0.4718	+0.0002	0.4720	±0.0000	±0.00
12	0.4437	0.4590	+0.0002	0.4590	—0.0002	—0.04
13	0.4501	0.4656	+0.0002	0.4658	±0.0000	±0.00

These results are practically identical with those obtained with the previous sample and demonstrate the purity of both.

This method was now employed to analyze a newly prepared aquopentammine cobalt perchlorate. It was necessary to dilute the cobaltammine, else a rather explosive decomposition took place; pure sodium nitrate was used for this purpose. The results are given in Table VII:

TABLE VII.—ANALYSES OF AQUOPENTAMMINE COBALT PERCHLORATE BY TEST TUBE METHOD.

No. of expt.	$KClO_4$. Wt. taken.	AgCl. Wt. calc.	Blank.	AgCl. Wt. found.	Deviation. Gram.	Deviation. Per cent.
14	0.2900	0.2704	+0.0002	0.2706	±0.0000	±0.00
15	0.3342	0.3121	+0.0002	0.3124	+0.0001	+0.03

They agree nearly as well with the requirements of theory as do the analyses of potassium perchlorate.

The above analyses demonstrate beyond question the accuracy of this method. The average duration from the calculated weight of silver chloride was less than 0.02%, which is certainly equal to the attainable accuracy of the chloride determination itself under these conditions. Moreover, *every* analysis made by this new process has been here recorded. The apparatus is very simple; a hard glass test tube is preferable to an ordinary soft one, but the treatment is not severe. We used the same thin glass test tube for the first three analyses without any perceptible injury to it. The fusion can be easily controlled and the whole analysis requires scarcely more time than an ordinary chloride determination. If this latter determination is made volumetrically, the whole analysis becomes a very rapid one.

In conclusion, then, we can present the above as a very accurate, simple and rapid method for the determination of perchlorates.

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