(1) Small amounts of potassium chloroplatinate in solution can be estimated colorimetrically with considerable accuracy. This will be true of any salt which gives the $PtCl_6$ anion, provided the color of the cathion is not such as to interfere.

(2) The chloroplatinate is less soluble in solutions of ethyl alcohol and water than in water solutions of either methyl or isobutyl alcohol. Only 0.0007 gram of the salt dissolves in 100 cc. of ethyl alcohol at 20°.

(3) The solubility of the chloroplatinate in potassium chloride solutions decreases with the increase in concentration of the potassium chloride, until a concentration of one gram molecule per liter is reached. Beyond this point, increasing the concentration of the potassium chloride has practically no effect.

(4) The solubility of the chloroplatinate in solutions of sodium chloride, increases rapidly until a concentration of 0.05 gram molecules per liter is reached. For more concentrated solutions the increase in solubility is small and almost proportional to the increase in concentration of the sodium chloride.

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ON A VOLUMETRIC METHOD FOR COPPER.

BY G. S. JAMIESON, L. H. LEVY AND H. L. WELLS.

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The process to be described is based upon the titration of cuprous thiocyanate with potassium iodate solution in the presence of a large excess of hydrochloric acid. This method of titrating a number of reducing substances, such as free iodine, iodides, arsenites and antimonites, in a very satisfactory manner, is due to L. W. Andrews.[1] The reaction depends upon the formation of iodine monochloride and the disappearance of the iodine color imparted to an immiscible solvent, such as chloroform or carbon tetrachloride.

We find that cuprous thiocyanate is oxidized by iodine chloride sharply and quantitatively with the formation of cupric salts, sulphuric and hydrocyanic acids, according to the equation

$$4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O.$$

This oxidation is similar to that obtained in Parr's method[2] for the titration of CuSCN by means of potassium permanganate solution, but we consider the iodate titration far preferable to the latter in simplicity and accuracy.

To show the applicability of the Andrews method to the titration of

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[1] THIS JOURNAL, 25, 756 (1903).

[2] *Ibid.*, 22, 685 (1900).

thiocyanates, the following experiments (by L. H. L.) were carried out, using the pure dry compounds and a solution containing 10.706 grams of potassium iodate per liter (1/20 of formula-weight), and titrating in glass-stoppered bottles in the presence of about 5 cc. of chloroform and about one-half of the final volume of concentrated hydrochloric acid.

	Substance taken. Gram.	KIO_3 used. cc.	Substance found. Gram.	Error. Gram.
NH_4SCN	0.1000	39.4	0.1000	0.0000
NH_4SCN	0.1000	39.5	0.1003	+0.0003
AgSCN	0.2000	36.05	0.1995	—0.0005
AgSCN	0.1000	18.1	0.1002	+0.0002
CuSCN	0.2000	57.5	0.1999	—0.0001
CuSCN	0.1000	28.8	0.1001	+0.0001

In some of the above experiments the substance was dissolved before titrating, in a hydrochloric acid solution of iodine monochloride which had been carefully adjusted over chloroform to the colorless point of the latter, but the use of this reagent was found to be unnecessary.

We find that filter paper has no effect upon this titration. This fact permits the use of paper for filtering cuprous thiocyanate in this process. It appears that organic substances are generally inactive towards iodine monochloride, for Andrews titrated tartar emetic directly with accurate results, and we have found by direct experiments that ethyl alcohol, acetic acid, formic acid, and formaldehyde do not interfere with the iodate titration.

The following results were obtained (by G. S. J.) by precipitating cuprous thiocyanate with sulphurous acid and ammonium thiocyanate from a measured solution of copper sulphate of known strength, filtering, sometimes on asbestos, sometimes on paper, and titrating in the manner previously mentioned. Another 1/20 formula-weight potassium iodate solution was used here: 1 cc. = 0.001817 g. Cu.

Copper taken. Gram.	KIO_3 used. cc.	Copper found. Gram.	Error. Gram.
0.0486	26.7	0.0485	—0.0001
0.0486	26.8	0.0486	0.0000
0.0388	21.3	0.0387	—0.0001
0.0351	19.45	0.0353	+0.0002
0.0486	26.7	0.0485	—0.0001
0.0486	26.9	0.0488	+0.0002

In applying the method to ores, we find that lead and antimony, if not removed, will produce high results, but both these metals are removed (to such an extent at least that they do not interfere in the slightest degree) by the evaporation with sulphuric acid in the process which will be described. Silver also must be removed.

For the sake of convenience, we have employed the normal potassium iodate in the place of the acid iodate used by Andrews. The normal iodate can be purchased in a pure condition (it should be perfectly neutral to test-paper), or it may be easily prepared by the method of Gröger[1] from potassium iodide and potassium permanganate. The salt should be dried at 100° before weighing. We have used, besides the previously mentioned 1/20 formula-weight solutions, one about twice as strong, but for convenience in calculation in determining copper we recommend the use of some multiple of 5.892 grams per liter which gives exact milligrams of copper per cubic centimeter, according to the multiple taken. For instance, with 11.784 grams KIO_3 per liter, 1 cc. = 0.002000 gram copper.

Method of Analysis.—To 0.5 gram of the ore in a 6 oz. flask, add 6 to 10 cc. of strong nitric acid, and boil gently, best over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 cc. of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 cc. Now add gradually and carefully, best after cooling somewhat, 6 cc. of strong sulphuric acid, and continue the boiling until sulphuric acid fumes are evolved copiously. Allow to cool, add 25 cc. of cold water, heat to boiling, and keep hot until the soluble sulphates have dissolved.[2] Filter into a beaker, and wash the flask and filter thoroughly with cold water.[3] Nearly neutralize the filtrate with ammonia and add 10 to 15 cc. of strong sulphur dioxide water. Heat just to boiling and add 5 to 10 cc. of a 10 per cent. solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 or 10 minutes, filter on paper, and wash with hot water until the ammonium thiocyanate is completely removed.

Place the filter with its contents in a glass-stoppered bottle of about 250 cc. capacity, and by means of a piece of moist filter paper transfer into the bottle also any precipitate adhering to the stirring rod and beaker. Add to the bottle about 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (the two latter liquids may be previously mixed). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then dimin-

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[1] *Z. angew. Chem.*, 1894, 13.

[2] The decomposition and conversion into sulphates here described closely follows the directions of Low, "Technical Methods of Ore Analysis," p. 79, in connection with the iodide method.

[3] With substances containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulphate or antimonic oxide that may be present.

ishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

In order to make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 cc. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference with the results of the titration.

In the following experiments (by G. S. J.) weighed quantities of pure copper were put through the above course of analysis in the presence of antimony, and in some cases lead also:

(1 cc. KIO_3 = 0.003610 gram Cu.)

Copper taken. Gram.	Antimony. Gram.	Lead.	Iodate used. cc.	Copper found. Gram.	Error. Gram.
0.1136	0.06	.....	31.35	0.1131	—0.0005
0.0691	0.06	.....	19.05	0.0688	—0.0003
0.0733	0.06	present	20.30	0.0733	0.0000
0.0673	0.06	present	18.75	0.0677	+0.0004
0.0650	0.06	.....	18.08	0.0651	+0.0001
0.0486	0.03	.....	13.50	0.0487	+0.0001
0.0486	0.03	.....	13.48	0.0486	0.0000

Several ores, sulphides, some of which contained lead or antimony, were analyzed by the process (by G. S. J.) in order to compare the results with other methods: (KIO_3 10.706 g. in 1000 cc; 1 cc = 0.001817 g. Cu.)

	Ore taken. Gram.	Iodate used. cc.	Copper found. Per cent.	Copper by other method.
I	0.5000	32.2	11.70	11.71 Electrolytic
II	0.5000	39.8	14.46	14.50 "
III*a*	0.3584	41.2	20.88	20.70 Iodide
III*b*	0.2000	22.9	20.80	20.70 "
III*c*	0.5000	28.9	20.86	20.70 "
IV*a*	0.2000	21.08	19.15	19.02 Electrolytic
IV*b*	0.2000	21.10	19.16	19.02 "
V	0.2000	20.8	18.89	18.80 Iodide

So far as ease and rapidity are concerned, one of us (G. S. J.) has made in just one hour an analysis of a copper ore, including weighing and calculation, by the method given above. Following Low's[1] modification of the much-used iodide method, the time was one hour and twenty minutes. There is no doubt that the iodate method is the easier and quicker of the two.

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[1] *Loc. cit.*

In view of the large excess of potassium iodide employed in the iodide method, it is probable that the iodate method is cheaper.

The potassium iodate solution is perfectly stable and can be preserved without change for years, if protected from evaporation. Ordinarily it is unnecessary to standardize the solution, except by weighing out a known amount of the salt and dissolving it in a known volume. However, should there be any uncertainty in regard to the purity of the salt, or in connection with the relations of the volumetric apparatus, it would be advisable to standardize with pure copper, putting it through all the operations of the process, and thus eliminating also any slight constant errors.

With the precaution just mentioned, the process is capable of reaching a very high degree of refinement, for the method of titration is one of the sharpest and most uniform in its results. Since most of the iodine goes into the small volume of chloroform, the accuracy of the end-reaction is extraordinary.

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SODIUM PEROXIDE IN CERTAIN QUANTITATIVE PROCESSES.

BY S. W. PARR.

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Sodium peroxide as a reagent in qualitative analysis, described by the writer,[1] has been found, after a number of years of actual service, to have advantages which entitle it to a far wider recognition and a more detailed study for that particular purpose. The same article states "that other properties have developed, mainly of interest in quantitative methods, which it is hoped will be of sufficient value to warrant further notice." It is in connection with this latter phase of the subject that the following processes are offered.

The adaptations of sodium peroxide here referred to are largely the outgrowth of the writer's experience in the use of that substance as a combustion medium for calorimetric determinations. This material has been recognized for some time as a good fusion reagent where both solution and oxidation are to be effected, but the usual methods of fusion in an open vessel are characterized by too great violence and danger of loss as well as by serious decomposition of the containing vessel. By carrying on the fusion in a closed vessel, it is possible to so adjust reagents as to bring about a quiet fusion without spurting. Owing to the concentration of the very great heat within the mass, the walls of the containing vessel must be kept relatively cool by submerging the same in water, thus preventing the corrosion of the container while at the same time there is no interference with the chemical reaction. An idea of

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[1] THIS JOURNAL, 19, 341.