ART. XXVII.—*The Gravimetric Determination of Free Bromine and Chlorine, Combined Iodine, and Oxidizing Reagents by means of Metallic Silver;* by CLAUDE C. PERKINS.

[Contributions from the Kent Chemical Laboratory, Yale Univ.—ccix.]

In a former paper* a method for the gravimetric determination of free iodine by means of metallic silver was described in detail. This paper has to do with the application of the same process to the determination of free bromine and chlorine, other members of the halogen group, to the estimation of combined iodine, and, indirectly, to the determination of the oxidizing power of certain oxidizing reagents.

The silver best adapted for this process is obtained electrolytically in a very finely divided state, being deposited as a black mass (probably silver hydride†) upon a small moving cathode. As long as the mass adheres to the electrode it remains perfectly intact but as soon as it is shaken off into the solution it immediately turns to a dull gray color, the hydrogen escapes, and the silver settles to the bottom in a fine flour-like powder. The mass of silver hydride should not be allowed to adhere to the electrode after it begins to change color, as the silver then collects in a crystalline form which does not absorb iodine readily.

Determination of Free Bromine and Chlorine.

In applying the process to the determination of bromine and chlorine a definite amount of the aqueous solution of these haloids was introduced into a flask containing an excess of potassium iodide made acid with hydrochloric acid and the whole shaken in an atmosphere of hydrogen with a weighed amount of silver. The residue of silver and silver iodide was collected in a Gooch crucible, washed, dried, and weighed. The increase in weight of the silver should represent the weight of iodine liberated from the iodide and from this the amount of halogen may be easily calculated. Table I shows the results of three determinations with bromine and five determinations with chlorine in which the average error falls within 0.0002 grm.

Determination of Potassium Iodide.

In applying the process to the determination of combined iodine a definite amount of a solution of potassium iodide, previously standardized by the distillation method with sul-

* This Journal, xxviii, 33, 1909.

† Bartlet and Rice, Am. Chem. Jour., xix, 49.

TABLE I.

Silver taken gram.	Halogen taken gram.	Iodine found gram.	Calculated amt. of halogen gram.	Error gram.
(a) Determination of bromine.				
3.0000	0.0213	0.0336	0.0211	−0.0002
3.0000	0.0426	0.0678	0.0427	+0.0001
3.0000	0.1065	0.1694	0.1067	+0.0002
(b) Determination of chlorine.				
3.0000	0.0161	0.0574	0.0160	−0.0001
3.0000	0.0322	0.1146	0.0320	−0.0002
3.0000	0.0322	0.1145	0.0320	−0.0002
3.0000	0.0322	0.1141	0.0318	−0.0004
3.0000	0.0483	0.1716	0.0479	−0.0004

phuric acid and potassium hydrogen arseniate,* was introduced into a flask with an excess of the calculated amount of an oxidizing reagent (usually potassium nitrite or hydrogen peroxide), the whole made acid with hydrochloric acid, and shaken with a weighed amount of silver. The increase in the weight of the silver indicates the amount of iodine liberated from the potassium iodide and from this the amount of potassium iodide may be easily calculated. Table II shows the results of five determinations with potassium iodide in which the average error is −0.0002 gram. between limits of −0.0005 and +0.0002 gram.

TABLE II.

Determination of potassium iodide.

Silver taken gram.	KI taken gram.	Iodine found gram.	Calculated amt. of KI gram.	Error gram.
2.7803	0.1144	0.0872	0.1141	−0.0003
3.0028	0.1346	0.1026	0.1342	−0.0004
2.7800	0.1279	0.0978	0.1281	+0.0002
2.0008	0.1279	0.0974	0.1274	−0.0005
3.0001	0.1346	0.1029	0.1346	±0.0000

Determination of Oxidizing Reagents.

The process has also been applied to the indirect determination of several of the common oxidizing reagents with a view to showing that it may be used for the estimation of oxidizers that will liberate iodine quantitatively. In these experiments definite amounts of the oxidizer, standardized in the usual way, were added to an excess of a solution of potassium iodide acidified with hydrochloric acid, and the whole shaken with a

* Gooch and Browning, this Journal, xxxix, 188, 1890.

weighed amount of silver in an atmosphere of hydrogen. The value of the oxidizer is then calculated from the increase in weight of silver which represents the amount of liberated iodine. Table III shows the results obtained in the determination of potassium permanganate, hydrogen peroxide, potassium dichromate, and ferric chloride, in all of which the error is well within experimental variation.

TABLE III.

Silver taken gram.	Oxygen represented by oxidizer gram.	I found gram.	Calculated amt. of oxygen gram.	Error gram.
(a) Determination of potassium permanganate.				
3.0000	0.0123	0.1956	0.0123	± 0.0000
3.0000	0.0123	0.1936	0.0122	-0.0001
3.0100	0.0123	0.1964	0.0124	$+0.0001$
3.0100	0.0123	0.1968	0.0124	$+0.0001$
4.0101	0.0185	0.2926	0.0184	-0.0001
4.0101	0.0247	0.3886	0.0245	-0.0002
(b) Determination of hydrogen peroxide.				
3.0000	0.0202	0.3200	0.0202	± 0.0000
3.0000	0.0202	0.3214	0.0203	$+0.0001$
3.0100	0.0404	0.6427	0.0405	$+0.0001$
3.0000	0.0311	0.4937	0.0311	± 0.0000
3.0000	0.0322	0.5128	0.0323	$+0.0001$
3.0000	0.0606	0.9590	0.0604	-0.0002
(c) Determination of potassium dichromate.				
3.0000	0.0080	0.1272	0.0080	± 0.0000
3.0000	0.0160	0.2552	0.0161	$+0.0001$
3.0000	0.0201	0.3141	0.0198	-0.0003
3.0000	0.0402	0.6390	0.0403	$+0.0001$
3.0000	0.0160	0.2552	0.0161	$+0.0001$
3.0000	0.0160	0.2571	0.0162	$+0.0002$
(d) Determination of ferric chloride.				
3.0000	0.0218	0.3470	0.0219	$+0.0001$
3.0000	0.0218	0.3476	0.0219	$+0.0001$
3.0000	0.0437	0.6922	0.0436	-0.0001
3.0000	0.0218	0.3489	0.0220	$+0.0002$
3.0000	0.0262	0.4183	0.0264	$+0.0002$
3.0000	0.0218	0.3516	0.0222	$+0.0004$

The results obtained fully justify the statement that metallic silver may be used for the determination of free bromine and chlorine, and combined iodine, and for the estimation of the oxidizing power of those reagents whose reaction with potassium iodide is definitely known to set free iodine quantitatively.