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ESTIMATION OF IODIDES IN COMPLEX MIXTURES.*

BY J. B. FULLERTON, W. J. WATKINS AND C. L. GRAHAM.

The estimation of inorganic iodine in complex mixtures has frequently been a source of difficulty. There have been numerous methods in the literature for the determination of iodine in ferrous iodide pills; but there will be no attempt made to list the papers describing the various methods. None of the methods recommended were successful in this laboratory, and it is assumed they were not generally satisfactory, else we would not find references to so many attempts on the problem.

Scott (1) gives a method for the decomposition of an iodide with nitrous acid and the subsequent extraction of the free iodine by means of carbon disulfide. The solution of iodine is then titrated with standard thiosulfate. In the same connection there is also given a method for liberation of iodine by the addition of hydrogen peroxide to a solution acidified with phosphoric acid. The liberated iodine is then distilled into a solution of potassium iodide and titrated with thiosulfate.

Working on a modification of Scott's method we have arrived at the following procedure:

Weigh enough of the finely powdered material to represent approximately 5 grains of potassium iodide (or an equivalent amount of iodine), and transfer to a separatory funnel. Add 50 cc. of water and, if alkaline, neutralize with phosphoric acid, finally adding 5 cc. in excess. Add 25 cc. of hydrogen peroxide and agitate thoroughly. Allow to stand a few minutes to be sure the reaction is complete and extract the liberated iodine with several portions of chloroform until the iodine has been removed, as can be told from the color. Collect the chloroform extractions in an iodine flask containing about 4 Gm. of potassium iodide in 25 cc. of water. Titrate with $N/10$ thiosulfate solution using starch as indicator.

The reaction between hydrogen peroxide and iodide in an acid solution is expressed by the following equation:

$$H_2O_2 + 2I^- + 2H \rightleftharpoons 2H_2O + I_2$$

We have found this method to be rapid, accurate and capable of a wide variety of uses. As previously stated, it was originally devised for the determination of iodine in ferrous iodide pills and has since been used for the estimation of iodine in various complex pill and tablet mixtures. It is satisfactory for mixtures of iodides with drug extracts, ferrous salts, reduced iron or arsenic. Obviously the same method could be used for the separation of iodine from the other halogens; but for simple mixtures of such, it is not as convenient as the well-known method of titration with KIO_3.

* From the Control Laboratory of the Upjohn Co., Kalamazoo.

An idea of the results to be expected by using this method on various mixtures may be obtained from the following tables.

Table I shows comparative results using the U. S. P. titration and the proposed method, with potassium iodide alone.

TABLE I.—POTASSIUM IODIDE ALONE.

		U. S. P. Titration.		Proposed Method.	
KI	0.35 Gm.	0.3490 Gm.	99.71%	0.3496 Gm.	99.99%
		0.3486 Gm.	99.60%	0.3498 Gm.	99.99%

Table II gives the results obtained in mixtures of potassium iodide with sodium chloride and sodium bromide: (*a*) the three salts are in equal proportions, (*b*) sodium chloride and sodium bromide are each present in twice the quantity of the potassium iodide and (*c*) the sodium chloride and sodium bromide are present in one-half the quantity of the potassium iodide.

TABLE II.—POTASSIUM IODIDE WITH OTHER HALIDES.

(*a*) Mixture Contains:		Potassium Iodide Recovered.	
KI	0.35 Gm	0.3510 Gm.	100.28%
NaCl	0.35 Gm.	0.3505 Gm.	100.10%
NaBr	0.35 Gm.	0.3517 Gm.	100.50%
(*b*) Mixture Contains:		Potassium Iodide Recovered.	
KI	0.35 Gm.	0.3470 Gm.	99.14%
NaCl	0.70 Gm.	0.3465 Gm.	99.00%
NaBr	0.70 Gm.	0.3475 Gm.	99.28%
(*c*) Mixture Contains:		Potassium Iodide Recovered.	
KI	0.35 Gm.	0.3510 Gm.	100.28%
NaCl	0.17 Gm.	0.3505 Gm.	100.10%
NaBr	0.17 Gm.	0.3508 Gm.	100.20%

Table III gives comparative results on syrup of hydriodic acid, using the U. S. P. method and the proposed method.

TABLE III.—SYRUP OF HYDRIODIC ACID.

		U. S. P. Method.	Proposed Method.
Hydriodic acid per 100 cc.	(*a*)	1.397 Gm.	1.389 Gm.
	(*b*)	1.393 Gm.	1.387 Gm.
	(*c*)	1.384 Gm.	1.388 Gm.

Tables IV, V, VI and VII give the results obtained for the analysis of known amounts of iodides in mixtures frequently encountered in pill and tablet assays.

TABLE IV.

		KI Recovered.	
KI	0.25 Gm.	0.2502 Gm.	100.1%
Ferrous sulfate	0.65 Gm.	0.2510 Gm.	100.4%
Sugar	0.15 Gm.	....	....

TABLE V.

		Iodine Theory.	Iodine Recovered.	
Potassium iodide	0.30 Gm.	0.2405 Gm.	0.2381 Gm.	99.00%
Mercuric iodide	0.02 Gm.	....	0.2400 Gm.	99.79%
Ext. echinacea	0.60 Gm.	....	0.2360 Gm.	98.12%
Ferrous carbonate	5.00 Gm.	....	0.2420 Gm.	100.60%

TABLE VI.

		Iodine Theory.	Iodine Recovered.	
Potassium iodide	0.30 Gm.	0.2330 Gm.	0.2280 Gm.	97.8%
Mercuric chloride	0.002 Gm.	....	0.2306 Gm.	99.0%
Mercuric iodide	0.0026 Gm.	....	0.2295 Gm.	98.5%
Arsenic iodide	0.0026 Gm.	....	0.2350 Gm.	100.8%
Ferrous carbonate	0.090 Gm.	....	....	....
Ext. nux vomica	0.002 Gm.	....	....	....

TABLE VII.

		Iodine Theory.	Iodine Recovered.	
Potassium iodide	0.30 Gm.	0.2310 Gm.	0.2331 Gm.	100.90%
Mercuric iodide	0.003 Gm.	....	0.2300 Gm.	99.56%
Hyoscyamus			0.2320 Gm.	100.40%
	0.02 Gm.	....	0.2280 Gm.	98.70%

We have also used a modification of this method for the determination of total iodine in Iodine Ointment as follows:

Place in a separatory funnel about 4 or 5 Gm. of the ointment accurately weighed, and dissolve in about 50 cc. of ether with vigorous shaking. Add an excess of $N/10$ sodium thiosulfate solution, about 30 cc., and mix well. Transfer the aqueous portion to a 250-cc. separatory funnel and extract the ether solution with three more 25-cc. portions of water. Combine all the aqueous washings in the 250-cc. separatory funnel, adding 5 cc. of phosphoric acid and 25 cc. of hydrogen peroxide. Extract the liberated iodine with chloroform and complete the determination as outlined previously.

Table VIII gives comparative results for total iodine in Iodine Ointment as determined by the U. S. P. XI method and by the proposed method.

TABLE VIII.

Ointment.		U. S. P. XI Method.	Proposed Method.
No. 1	Total iodine	6.85%	6.83%
		6.81%	6.89%
No. 2	.....	6.80%	6.85%
		6.90%	
No. 3	.....	6.70%	6.81%
		6.77%	6.65%

SUMMARY AND CONCLUSIONS.

The method outlined has been developed for the determination of iodides in complex mixtures often encountered in control work on tablets and pills. It has also been found satisfactory for total iodine in Iodine Ointment U. S. P.

As yet we have not found any mixture containing an inorganic iodide in which the iodine could not be determined according to this method.

REFERENCE.

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