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H. W. WILEY, Chief of Bureau.

THE ESTIMATION OF IODIN IN ORGANIC COMPOUNDS AND ITS SEPARATION FROM OTHER HALOGENS.

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In the examination of a number of samples of commercial erythrosin the determination of iodine was considered to be one of the most important factors in establishing the identity and purity of the dye. As many of the colors contained varying amounts of common salt, and contamination with chlorine and bromine substitution products of fluorescein was also to be sought and detected, the problem of estimating iodine under these conditions by a method that would not require a prohibitive amount of manipulation and time presented itself. At first an attempt was made to estimate the total halogens by the Carius method, from which the halogen due to common salt (estimated in another portion after separation of the color acid) was deducted. A qualitative test for chlorine and bromine in the residue left after ignition of the color acid with alkali was relied upon to detect these halogens in organic combination.

The Carius method was found to yield erratic and unreliable results with erythrosin, confirming the experience of other analysts with iodine compounds. Linnemann^a ascribed the difficulty to the solubility of silver iodide in nitric acid containing an excess of silver nitrate. The authors have observed crystals of free iodine in the bomb tubes after removal from the furnace, and on heating they were seen to volatilize with the formation of the characteristic violet vapors. An ample excess of silver nitrate over that required for the iodine present had been added in every case. As the results of the determinations by the Carius method were almost invariably too low, it is the opinion of the authors that some of this free iodine is lost in transferring the oxidizing mixture from the bomb tubes.

^a Ann. Chem. Pharm. 1871, 160: 205.

A number of methods have been suggested for the estimation of iodine in the presence of other halogens in inorganic soluble compounds. Those involving the conversion of iodide into iodate by potassium permanganate ^a have been described by Reiniger ^b and by Baubigny and Rivals. ^c The application of these and of most other methods requires a preliminary destruction of the organic matter, and this, if accomplished in the usual way by fusion with potassium carbonate or a similar alkaline substance, requires much care, and in the case of mixtures containing sulphonated dyes, yields a melt which contains reducing sulphur compounds. These compounds must be removed before the application of Reiniger's method, which is also subject to the limitations of volumetric processes in general. With Baubigny's method the distillation requires close attention and much difficulty was experienced in driving off all chlorine without loss of iodine.

Experiments proved that if a solution containing erythrosin is treated with potassium permanganate and nitric acid the organic matter is completely decomposed and chlorine and bromine are converted into volatile products, while all of the iodine remains as iodic acid. The permanganate is converted into a voluminous hydrated oxide of manganese. The chlorine apparently is partly liberated as such and partly converted into an oxygenated compound which is boiled off with difficulty, but may be volatilized in a current of steam or driven off by evaporating the mixture to dryness on a steam bath. When much chlorine is present the last of it can be removed only by treating the residue twice with nitric acid and again evaporating to dryness. That no iodine is lost in this process is shown in Table 1. Iodine may be determined in the residue left after oxidation by the permanganate by taking up in a little water, adding nitric acid, and then dissolving the oxide of manganese in an excess of sulphur dioxide solution, the iodic acid being at the same time reduced. Silver nitrate is added to the clear solution, which is then boiled until the excess of sulphur dioxide is driven off and the silver iodide has coagulated. This is filtered, washed, dried, and weighed in the usual manner.

The experimental results given in Table 1 were obtained on mixtures containing measured amounts of a solution of pure iodine. To prepare this, resublimed iodine was dissolved in a concentrated solution of potassium iodide and a large part of it then precipitated by the addition of water. The precipitated portion was collected on a perforated plate, thoroughly washed with water, and sublimed. The sublimate was dried over calcium chloride. Portions of this

^a Hempel, *Ann. Chem. Pharm.* 1858, 107: 100.

^b *Zts. anal. chem.* 1870, 9: 39.

^c *Compt. rend.* 1903, 137: 927.

iodin were dissolved in a little alkali and diluted to definite volume with water, the solutions so prepared being carefully kept in tightly stoppered flasks and used for the experiments in Table 1. The pipettes and flasks used had been standardized at the United States Bureau of Standards.

TABLE 1.—*Estimation of iodin in the presence of chlorin and bromin.*

SERIES A. (20 cc of solution=0.2640 gram of iodin used.)

Chlorin or bromin added.	Method.	Iodin found.	Per cent of iodin recovered.
<i>Gram.</i>		<i>Gram.</i>	
None.....	Direct precipitation.....	0.2643	100.1
Do.....	do.....	.2644	100.2
Do.....	Permanganate oxidation.....	.2646	100.2
Do.....	do.....	.2645	100.2
0.3 sodium chlorid.....	do.....	.2637	99.83
.3 potassium bromid.....	do.....	.2642	100.1
.05 sodium chlorid.....	} do.....	.2636	99.84
.10 potassium bromid.....			
.10 sodium chlorid.....		.2635	99.82
.05 potassium bromid.....	do.....		

SERIES B. (20 cc of solution=0.4885 gram of iodin used.)

None.....	Direct precipitation.....	0.4876	99.84
Do.....	do.....	.4877	99.86
0.2 sodium chlorid + 0.1 potassium bromid.....	Permanganate oxidation.....	.4871	99.75
Do.....	do.....	.4888	100.1

In order to test the applicability of the method to the estimation of iodin in erythrosin a sample of this color was synthesized, the fluorescein, prepared from Kahlbaum's resorcin and phthalic anhydrid, being completely freed from chlorids by repeated precipitation from alkaline solution by acetic acid. This was combined with some of the purified iodin just described, and finally separated as the color acid. This preparation contained no halogen other than iodin, of which the alkaline fusion method indicated 56.40 per cent, as shown in Table 2. After further experimental work on the proper proportion of reagents to be employed the following procedure was adopted:

Place from 0.3 to 0.4 gram of the erythrosin in a porcelain casserol, dissolve this in 5 cc of a 10 per cent sodium hydroxid solution, then add 35 cc of a 7 per cent solution of potassium permanganate. After mixing, cover the vessel with a watch crystal, and add 10 cc of nitric acid, keeping the dish covered. Agitate the mixture, place on a steam bath, and keep covered until spattering ceases, after which remove the watch glass and allow evaporation to proceed to dryness.^a Treat the residue with 5 cc of 7 per cent potassium per-

^a In the operation of drying particular care should be observed to prevent access of reducing gases to the mixture.

manganate and 5 cc of concentrated nitric acid and again evaporate to dryness. Then add about 50 cc of water and 5 cc of concentrated nitric acid to the residue, following this by 40 cc of a saturated solution of sulphur dioxide, and allow the whole to stand with occasional stirring (breaking up the lumps with a glass rod) until the hydrated oxide of manganese has dissolved. Add an excess of silver nitrate to the clear solution, and boil until sulphur dioxide has been expelled and the silver iodide has flocculated. Filter this and weigh in the usual manner. The results obtained are given in Table 2.

TABLE 2.—*Estimation of iodine in erythrosin color acid.*^a

(Theory 60.75 per cent.)

Amount of color acid used.	Other substance added.	Method.	Iodine found.
Gram.	Gram.		Per cent.
0.4929.....	None.....	Alkaline fusion.....	56.50
.3987.....	do.....	do.....	56.22
.5062.....	do.....	do.....	56.49
.4255.....	do.....	Permanganate oxidation.....	56.22
.3682.....	do.....	do.....	56.46
.3763.....	do.....	do.....	56.37
.3717.....	do.....	do.....	56.03
.3344.....	do.....	do.....	56.36
.1725.....	{ 0.2 eosin color acid + .1 sodium chlorid.....	{ do.....	{ 56.39 56.36
.1843.....	{ 0.1 eosin color acid + .1 potassium bromid.....	{ do.....	{ 56.53 56.45
.3309.....	0.4 sodium chlorid.....	do.....	

^a The erythrosin color acid used in these estimations was air dry.

This procedure was applied to a number of commercial samples containing erythrosin in admixture with ponceau 3R and with amaranth, and in all cases a complete destruction of the organic matter and closely agreeing results were obtained.

It is believed that this method, with suitable modifications, is applicable to a number of other iodine compounds beside erythrosin, though detailed data substantiating this point have not yet been obtained. Iodine was determined in recrystallized iodoform by first saponifying with alcoholic potash in a pressure flask, evaporating the alcohol, and oxidizing the residue with permanganate as already given. The results are given in Table 3. This procedure may be adopted with the class of compounds that are volatile and easily saponified, but obviously it need only be employed in cases where halogens other than iodine are also present.

Phenyl iodide, as a representative of another water insoluble class, was heated with the oxidizing mixture in an acetylation flask, the reaction mixture being in this case introduced through the tube of the reflux condenser and boiled until the oily drops of phenyl iodide ceased to appear in the condenser, and then for some time longer, rinsing the condenser from time to time with a few cubic centimeters of the

permanganate solution. The reaction mixture was removed from the flask and evaporated to dryness, proceeding from this point as in the case of erythrosin. These results also are given in Table 3.

TABLE 3.—*Estimation of iodine in iodoform and in phenyl iodide.*

Grams of substance used.	Method.	Per cent of iodine found.
Iodoform (theory 96.7 per cent):		
0.5922.....	Saponification.....	95.90
.4393.....	do.....	95.98
.3097.....	Permanganate oxidation.....	95.80
.4798.....	do.....	96.18
.2435+0.3 sodium chloride.....	do.....	95.60
Phenyl iodide (theory 62.22 per cent):		
0.3599.....	do.....	60.80
.4042.....	do.....	60.61

These determinations have not yet been checked against those obtained by other methods, but pending further work to establish the limits of usefulness of the procedure they are reported as found. The method seems to answer perfectly for the estimation of iodine in erythrosin, either when this color alone is present or in a mixture with other colors or with salts of the other halogens. Attention is called particularly to the results given in Table 1, which shows the application of the method in inorganic analysis to the estimation of iodine in the presence of chlorides and bromides. The method seems to possess the double advantage of simplicity and accuracy.

Approved:

JAMES WILSON,

Secretary of Agriculture.

WASHINGTON, D. C., November 5, 1910.

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