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VOLUMETRIC DETERMINATION OF SODIUM SALICYLATE.

BY M. W. EVANS.

There has been considerable work done on this subject. Messinger and Vortmann originated the method,¹ and different variations have been used up to that used by J. M. Wilkie, given in *J. Soc. Chem. Ind.*, 1911, page 398. He claims many advantages for this modification. The following results, Table 1, were obtained, carrying out his method with the exception that 50 cc water were used instead of 150 cc. Good results were obtained in several cases, while impossible ones in others, with no apparent reason for the divergence of results, except the uncertainty of the end-point.

TABLE 1.

DETERMINATION OF SODIUM SALICYLATE BY METHOD GIVEN BY WILKIE IN *J. Soc. Chem. Ind.*, 1911, p. 398.

Wt. sample.	No. cc. iodine.	N/10 factor.	Cc sodium thiosulphate.	N/10 factor.	Cc N/10 I ₂ used up.	Factor for sodium salicylate.	Wt. sod. salicylate calculated.	Per cent. sod. salicylate.
0.04004	30	1.0402	14.88	1.0929	14.95	0.0026674	0.039878	99.59
0.04004	30	1.0402	14.77	1.0929	15.07	0.0026674	0.040198	100.39
0.04004	30.17	1.0402	14.80	1.0929	15.21	0.0026674	0.040571	101.33
0.04004	30	1.0385	14.75	1.0929	15.04	0.0026674	0.040118	100.19
0.04008	30	1.0325	14.57	1.0929	15.06	0.0026674	0.040171	100.23
0.04008	30	1.0325	14.43	1.0929	15.21	0.0026674	0.040571	101.23
0.04008	30	0.9567	12.35	1.0929	15.20	0.0026674	0.040544	101.16
0.04008	32	0.9567	14.10	1.0929	15.20	0.0026674	0.040544	101.16

¹ *J. Soc. Chem. Ind.*, 1900, p. 568.

Mr. Wilkie states that at the end of five minutes' standing, the reaction product is wholly tri-iodophenol. In every experiment above there was a precipitation, and the conversion went, at least partially, to the red quinone before the end of five minutes, in some cases to a greater extent than others, judging by the color. The further the conversion and the darker the color of the precipitate, the harder it becomes to distinguish the starch end-point. This is very likely the cause of the divergence in the results given above.

It occurred to me that the addition of carbon disulphide might aid in detecting the true end-point, by dissolving the precipitate. The apparent end-point was taken in two cases, then CS₂ was added and the end-point redetermined. The results are given in Table 3. Even then, the end-point is not very distinct and the method still tends to give high results.

TABLE 2.

0.04001	31.50	0.9583	**13.70	1.0929	15.22	0.0026674	0.040598	101.47
			*13.85	1.0929	15.05	0.0026674	0.040144	100.33
0.04001	31.50	0.9583	13.65	1.0929	15.27	0.0026674	0.040731	101.80
			13.90	1.0929	15.00	0.0026674	0.040011	100.00
0.04001	31.60	0.9583	*13.95	1.0929	15.03	0.0026674	0.040091	100.20

** without CS₂.

* with CS₂.

Three analyses were run on the sample No. 4885, just as Mr. Wilkie directs, adding 150 cc water. In this case no precipitation occurred before acidification and the conversion went only slightly to the red quinone, but the results were still high. Three results obtained are: 100.89, 101.09, 100.83.

The following method, a modification of Messinger and Vortmann's, has been found quantitative in every case for the assay of sodium salicylate. The determination is based on the fact that iodine, in alkaline solution, will react with sodium salicylate to form tetra-iododiphenylene quinone (C₆H₂I₂O)₂. The tri-iodophenol which is formed first, decomposes into the above.¹

Seidell² has shown that this reaction does not take place quantitatively under all conditions, but under the following conditions it is quantitative.

METHOD.

Weigh up 0.8 gram sodium salicylate accurately, dissolve, and make up to exactly 250 cc in a volumetric flask. Pipette into a glass-stoppered iodine flask 25 cc of the above solution. Add 30 cc of an approximately *N*/10 Na₂CO₃ solution. Add the equivalent of 33 cc of standardized *N*/10 iodine solution slowly from a burette. No precipitation should occur. Gradually heat the iodine flask, loosening the stopper every few minutes to relieve the pressure, until a precipitate forms and turns purple. Let the mixture stand for fifteen minutes. Cool and acidify with diluted sulphuric acid. Shake. The reddish purple precipitate coagulates nicely.

Filter quickly into a 500-cc Erlenmeyer flask, washing the flask and filter with water. Titrate with standardized *N*/50 sodium thiosulphate. Table 3 gives the consecutive results obtained by this method.

¹ *J. Soc. Chem. Ind.*, 1911, page 398.

² *J. Am. Chem. Soc.*, 1909, page 1168.

TABLE 3.
DETERMINATION OF SODIUM SALICYLATE BY METHOD DESCRIBED ABOVE.

Wt. of sample.	No. cc iodine.	N/10 factor.	Cc sodium thiosulphate.	N/10 factor.	Cc N/10 I ₂ used up.	Factor for sodium salicylate.	Wt. sodium salicylates calculated.	Per cent. sodium salicylate.	
0.08000	33.00	1.0691	4.46	1.1885	29.98	0.0026674	0.079969	99.96	
0.08007	31.00	1.0691	2.65	1.1885	29.99	0.0026674	0.079995	99.91	
0.08007	31.00	1.0691	2.70	1.1885	29.93	0.0026674	0.079835	99.71	
			Cc. N/50.	N/50 factor.					
0.08007	31.01	1.0691	15.75	0.9809	30.06	0.0026674	0.080182	100.14	
0.08007	31.01	1.0691	15.65	0.9809	30.08	0.0026674	0.080235	100.21	
0.08002	31.01	1.0691	16.30	0.9809	29.95	0.0026674	0.079889	99.84	
0.08002	31.00	1.0691	15.92	0.9809	30.02	0.0026674	0.080075	100.07	
			N/10.	N/10 factor.					
0.08008	32.00	1.0402	3.07	1.0929	29.93	0.0026674	0.079835	99.69	
0.08016	33.02	1.0325	3.78	1.0929	29.96	0.0026674	0.079915	99.69	
			Different sample.						
0.08004	34.50	0.9583	2.92	1.0929	29.87	0.0026674	0.079675	99.54	
0.08004	34.50	0.9583	2.90	1.0929	29.89	0.0026674	0.079729	99.61	

A comparison of results obtained by this method and that of Mr. Wilkie is given in Table 4.

TABLE 4.
COMPARISON OF RESULTS OBTAINED BY PROPOSED METHOD AND THAT OF WILKIE.

Sample No.	Wt. per 250 cc.	Per cent. by proposed method.	Per cent. by Wilkie's method.	Remarks.
4290	0.4004	99.69	99.59	
			100.39	
			101.33	
	0.4008	99.69	100.19	
			100.23	
			101.23	
4885	0.8004	99.54	101.16	
			101.16	
	0.4001	99.61	101.47	Without addition of CS ₂
			101.80	
			100.33	
			100.00	With addition of CS ₂
		99.73	100.20	
			100.89	
			100.83	
			101.09	Adding 150 cc H ₂ O

This method has now been adopted in the laboratories of Lehn & Fink in replacement of the U. S. P. IX method for the assay of sodium salicylate. It requires less time and does not require continual repetition to secure concordant results as the U. S. P. method does.

Three new commercial samples, supposedly U. S. P., have just been analyzed by two chemists unfamiliar with the method of analysis, with the following results: *a*, 99.72, *b*, 99.54, *c*, 99.59; *c* was checked as 99.59% exactly.

A commercial sample of phenol was assayed in this way for comparison with the result obtained by the U. S. P. IX method. The results were: U. S. P. method, 99.53%; above method, 99.46%.

TABLE 5.

Remarks.	No. acetyl salicylic.	Wt. per 250 cc.	Cc N/10 I ₂ .	Factor for I ₂ .	Cc N/10 Na ₂ S ₂ O ₃ .	Factor for Na ₂ S ₂ O ₃ .	Cc N/10 I ₂ equivalent to aliquot.	Factor for acetyl salicylic.	Per Sample cent.	Sample Nos.
A good commercial sample	23275	0.8800	31.81	1.0366	3.76	1.0062	29.19	0.003001	99.54	1
No odor	23275	0.8800	31.80	1.0355	3.67	1.0062	29.24	0.003001	99.71	2
Recrystallized sample, dried at 40° and then over sulphuric	23275	0.8800	31.80	1.0266	3.45	1.0062	29.18	0.003001	99.51	3
	H	0.8837	33.00	1.0033	3.79	1.0083	29.29	0.003001	99.48	4
		0.8837	33.00	1.0033	3.78	1.0083	29.30	0.003001	99.50	5*
		0.8837	33.00	1.0033	3.77	1.0083	29.31	0.003001	99.54	6*
		0.8801	33.00	0.9988	3.72	1.0083	29.21	0.003001	99.60	7
Two old samples. Odor of acetic acid	5871 (2B)	0.8804	31.80	1.0266	3.53	1.0062	29.10	0.003001	99.19	8
	5872 (4C)	0.8801	31.80	1.0266	3.47	1.0062	29.16	0.003001	99.43	9
Limit of error										
1 drop in final titration									0.17%	

* Hastings.

LABORATORY OF
LEHN AND FINK, INC.

ACETYSALICYLIC ACID.

SUBMITTED BY WM. H. GESELL.*

The method now employed for assaying samples of sodium salicylate may be extended to the analysis of acetylsalicylic acid. Weigh up about 0.88 gram of the acid, add 20.2 cc N/2 KOH to this (0.2 cc excess of KOH over enough to convert the acid to the potassium salt) and heat on a steam-bath a half-hour. Transfer to a 250-cc volumetric flask, make up to volume, shake, and proceed as directed in the method for sodium salicylate. In the samples of recrystallized acetylsalicylic acid the above exact amount of KOH was not added, but about 20 cc of a 2% sodium hydroxide solution was used.

Samples Nos. 5 and 6 were analyzed by Miss Hastings.

The following results were obtained: The results obtained were much more satisfactory and more closely checked than those reported in the *Journal of Association of Official Agricultural Chemists*, May 15, 1922, page 582.

The volumetric bromine method as given there has two faults: (1) It is difficult to carry out the method without the loss of any trace of bromine. (2) The limit of error (1 drop in titration) is 0.35%. It has not been found possible to check the method very closely in our laboratory.

The gravimetric iodine method given as a tentative method is inaccurate in one respect. As has been pointed out in the literature by Messinger and Vortmann originally and later by Wilkie, the iodine compound only forms quantitatively under certain conditions, exactly the right concentrations of sodium carbonate and iodine. These conditions are realized in the above volumetric method but not in those of the Report.

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* October 9, 1922.