

[CONTRIBUTION FROM THE LABORATORY OF QUALITATIVE ANALYSIS, COLLEGE OF THE CITY OF NEW YORK AND THE HARRIMAN RESEARCH LABORATORY, N. Y.]

THE INADEQUACY OF THE FERRIC BASIC ACETATE TEST FOR ACETATES.

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Received May 4, 1917.

Introduction.

In a perusal of the literature on the detection of acetates, it appeared to the authors, that the test depending upon the precipitation of ferric basic acetate would be the most suitable, both from the point of view of trustworthiness and ability to roughly indicate the proportion of acetate present, whereas, other tests, notably the odor tests, would not readily afford such quantitative indications. It was also apparent that there was a need for a definite procedure for the ferric basic acetate test, since the text-books supplied merely the vaguest directions to add ferric chloride to the nearly neutral solution, to dilute largely, to boil and to take the formation of a brown precipitate as an indication of the presence of acetates. It was, then, with the aim of devising a clear and definite procedure for the detection of acetates as ferric basic acetate, that the work recorded below was undertaken.

Procedure.

A definite volume of a standard sodium acetate solution was measured into a small beaker and was diluted to about 20 cc. One drop of a 1% phenolphthalein solution was then added and 1% sodium hydroxide solution to the formation of a pink color. The solution was then treated with dilute hydrochloric acid (1 : 10) to the disappearance of the pink color. 1 cc. of a ferric chloride solution¹ was finally added, the solution diluted to 50 cc., heated to boiling, boiled vigorously two minutes and filtered. A reddish brown residue on the filter indicated the presence of acetates.

Another set of parallel experiments was conducted in which the acetate was treated precisely as above except that the final dilution was made to 200 cc. in order to secure data regarding the effect of a larger volume.

Blanks were carried out for all solutions and conditions and were all satisfactory, *i. e.*, the formation of a precipitate did not occur.

The results found are recorded in Table I. The first column shows the strengths of the iron solutions while the remaining columns present the minimum amounts of acetate that it was possible to detect with the respective ferric chloride solutions.

All experiments were repeated; confirmatory results were obtained.

¹ 241.5 g. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water, diluted to 500 cc., filtered and allowed to settle several days. Aliquot parts of this solution were then drawn off and diluted to give ferric chloride solutions of desired concentrations.

TABLE I.

Mg. Fe per cc. in solns. used.	Sensitiveness in Mg. $C_2H_3O_4$.	
	Volume 50 cc.	Volume 200 cc.
.5	15-20 ¹	25-50
10	30-40	40-60
25	50-75	75- ²

Comments.

Three conclusions may be drawn from the above table: (1) That the test, as above conducted, is not sufficiently sensitive; (2) that, in spite of recommendations to "dilute largely," an excessive volume is not desirable, and (3) that increasing amounts of iron have the effect of diminishing the sensitiveness of the test. As a direct corollary of the last inference it may be said that the test is not capable of furnishing quantitative indications.

In an attempt to account for the surprisingly low sensitiveness of the test, it occurred to the authors that owing to the absence of appreciable amounts of salts in the solution, the ferric chloride might have been so transformed by boiling as to be unavailable for a reaction with the acetate. Moreover, in a systematic procedure, soluble salts would most probably be present in the solution in which the precipitation would be made. It was, therefore, for the above reasons, that another series of experiments was conducted with the addition of sodium chloride.

A procedure similar to that described above was followed with the addition of 4 cc. of a 25% sodium chloride solution after the measuring of the acetate solution.

Attempts to obtain blanks, by the modified procedure, with the ferric chloride solutions used in former experiments proved unsuccessful; a precipitation invariably occurred. It became necessary therefore to make up a set of ferric chloride solutions with definite, increasing amounts of hydrochloric acid and to submit them to blank tests by the modified procedure. For each concentration of iron, a number of solutions, containing hydrochloric acid, were found to give satisfactory controls; of these, that solution which contained the minimum amount of acid was tested for its sensitiveness to acetates.

The results are tabulated as before except that an additional column is

¹ In all cases, the lower figure indicates an experiment which gave a negative result; the higher figure gave a brown precipitate. Because of the low sensitiveness of the reagents tested, it was not considered worth while to determine the limit sensitiveness within 1 or 2 mg.

Distilled water was used throughout this investigation. When tap water was substituted for distilled water, the sensitiveness of the ferric chloride solutions to acetates was slightly increased. Experiments showed that the tap water had a lower hydrogen ion concentration than distilled water and hence favored the hydrolysis of iron.

² 75 mg. still failed to give a precipitate.

provided, giving the amount of hydrochloric acid in 100 cc. of the ferric chloride solution used.

TABLE II.

Mg. Fe per cc. in solns. used.	No. of cc. HCl. (sp. gr. 1.2) per 100 cc. FeCl ₃ soln.	Sensitiveness in Mg. C ₂ H ₃ O ₂ .		
		Volume 5 cc. ¹	Volume 50 cc.	Volume 200 cc.
5	0.5	10-20
10	1.0	25-35
5	3.0	...	20-30	20-30
10	3.5	...	25-35	30-40

The data in Table II apparently corroborate the original conclusions.

Summary.

1. It has been demonstrated that the ferric basic acetate test is not sufficiently sensitive.

2. The test, moreover, does not furnish a means of roughly estimating the amount of acetate present.

NEW YORK, N. Y.

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GRANULAR CALCIUM CHLORIDE AS A DRYING AGENT.

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Received April 21, 1917.

In measuring the efficiency of calcium chloride as a drying agent, Baxter and Starkweather² employed the fused salt. However, granular calcium chloride is much more commonly used, and is more rapid and efficient because its desiccating action is due to adsorption rather than to hydration, as is the case with the fused salt. Since the vapor pressure of an adsorbing substance is a function of the surface moisture that it already contains, it would be expected that granular chloride of calcium, when absolutely dry, would remove every trace of moisture from a gas passed over a sufficiently long column of it. Our experiments show this to be the case.

The method employed was to aspirate air containing a known amount of water vapor over a long column of absolutely anhydrous, granular calcium chloride, and absorb and weigh the residual moisture in a glass stoppered phosphorus pentoxide tube. To obtain the anhydrous chloride a tube containing a column of the chemically pure salt 100 cm. long and 2 cm. in diameter which was used for subsequent experiments was heated to 260-275°³ in a current of air dried over phosphorus pentoxide. Dry

¹ The experiments in a volume of 5 cc. were conducted in test tubes. The procedure as outlined above was followed except that only 1 cc. of the sodium chloride solution was added.

² THIS JOURNAL, 38, 2038 (1916).

³ Cf. Abegg, "Handbuch der Anorganischen Chemie," 2, 98.