

The results obtained with these three sets of solutions were as follows:

COMPARISON OF COLORIMETRIC AND GRAVIMETRIC RESULTS ON PLANT SOLUTIONS.

No. of solution.	Sample.	Parts PO ₄ per million of solution.	
		Colorimetric.	Gravimetric.
24.	Corn plant.....	60.5	60.4
25.	Potato plant.....	43.9	45.2
26.	Corn plant.....	44.5	{ 46.0 43.5

The results presented above show that, in general, there is a good agreement between those obtained by the colorimetric and the gravimetric methods. The satisfactory degree of accuracy shown by the colorimetric method, together with its great speed and ease of manipulation, and the comparatively small amount of solution required, makes it one of great value where small concentrations are involved.

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THE RAPID ANALYSIS OF CREAM OF TARTAR AND TARTARIC ACID BAKING-POWDERS.

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THE simple method of analysis given below, utilizing principally carbon dioxide determinations before and after fusion and Kenrick's¹ polariscopic method for tartaric acid, was worked out by the writer in connection with his study of the official methods of analysis for baking-powders and baking-powder chemicals, for which he was appointed associate referee by the Association of Official Agricultural Chemists, at the annual convention in November, 1903.

The analysis of a baking-powder containing cream of tartar (potassium bitartrate) and free tartaric acid, as outlined in the provisional official methods of the Association of Official Agri-

¹ This Journal, 24, 936.

cultural Chemists, and commonly used in food control work, involves three rather tedious determinations in addition to the usual available and total carbon dioxide estimations and the various tests necessary to ascertain the qualitative character of the sample.

These three determinations are: First, a total tartaric acid determination by the Goldenberg-Geromont-Heidenhain method of converting the free acid into tartrate, treating with acetic acid, precipitating with alcohol, filtering, washing, redissolving in hot water and titrating with specially standardized alkali; secondly, a potash determination (as chlorplatinat) with an equally tedious preceding estimation of mixed chlorides; and thirdly, a starch determination by the combined Sachsse and Allihn methods of converting into "dextrose," determining the copper-reducing power and calculating into starch.

As the Goldenberg-Geromont-Heidenhain method for total tartaric acid is not adapted for baking-powders and chemicals containing the usual adulterants (alum, phosphates, lime salts, etc.) the writer was first impelled to give the polariscopic method of Messrs. Edgar and Frank Kenrick a thorough trial, with most satisfactory results. In every conceivable mixture of cream of tartar and its usual adulterants and of cream of tartar and tartaric acid, singly and together in baking-powders, the amounts of tartaric acid found by means of the polariscope, and those taken, agreed very closely, the possibility of getting practically theoretical results being dependent upon the ability of the analyst to make a correct polariscopic reading.

The details of this method, the performance of which requires less than fifteen minutes of actual working time, are as follows: Weigh out accurately 0.4 gram of the sample into a dry 200 cc. flask, add 5 cc. of 10 per cent. citric acid solution and 10 cc. of ammonium molybdate solution¹ and let stand ten minutes with an occasional shaking. Then add 5 cc. of magnesium sulphate solution² and 15 cc. of 5 per cent. ammonia water and allow to stand a few minutes (not more than an hour). Now filter on a dry filter, take 20 cc. of filtrate and neutralize with 5 per cent. hydrochloric acid, using methyl orange as indicator. Finally, add 10 cc. more of ammonium molybdate solution, make

¹ Eighty-eight grams in 500 cc. water.

² Sixty grams of crystallized salt in 500 cc. water.

up to 50 cc. and polarize in a 200 mm. tube. The rotation in minutes (if over forty), multiplied by 0.001168 and added to 0.0075, gives the tartaric acid in grams. If less than forty minutes (which would rarely be the case) the square root of the rotation value times 0.001601 plus the rotation value multiplied by 0.001086 gives the result in grams.

The reason for the excess of ammonium molybdate solution used is that this substance has the property of greatly increasing the rotation of tartaric acid, so that the small rotation, due to traces of inverted starch (from a baking-powder for instance), is rendered entirely insignificant.

This process, of course, gives no clue as to the proportion of combined tartaric acid when both cream of tartar and free tartaric acid are present, as is often the case in many so-called "Cream of Tartar" powders. In the absence of any other potassium salt the potash determination gives us means for calculating the potassium bitartrate. On account, however, of the great expenditure of time and labor required for this determination (which must be preceded by a determination of mixed chlorides), the method was tried of calculating the combined tartaric acid (as potassium bitartrate) from the results of: (a) The determination of total alkalinity in the completely fused powder by titration with standard acid, and (b) the determination of carbon dioxide, in the original powder, by use of Knorr's or a similar apparatus, when estimating the proportion of bicarbonate present. The amount of carbon dioxide corresponding to the total alkalinity of the fused powder minus that found in the bicarbonate estimation equals that corresponding to the potassium bitartrate present. From the amount of the bitartrate thus estimated and the total tartaric acid (determined with polariscope preferably) the quantity of free tartaric acid present can readily be calculated.

This method was tried with several baking-powder mixtures with very satisfactory results.

A. Straight cream of tartar powder: 0.5 gram sodium bicarbonate, 1 gram potassium bitartrate and 0.5 gram starch.

(a) One gram of the above was fused in a platinum dish by charring over an ordinary burner and then heating in a blast-burner until a white melt was obtained, which required

about five minutes. The residue was dissolved in water and titrated with decinormal sulphuric acid, using methyl orange as indicator. This required 56.25 cc., which, multiplied by 0.0044, gives the carbon dioxide corresponding to alkalinity of the fused mixture, or 0.2475 gram.

(b) The carbon dioxide was determined in the remaining gram of the mixture in Knorr's carbon dioxide apparatus. Found, 0.13 gram, which corresponds to 0.248 gram of sodium bicarbonate.

Subtracting 0.13 gram CO_2 from 0.2475 gram CO_2 leaves 0.1175 gram CO_2 , which is equivalent to 0.502 gram potassium bitartrate.

B. Cream of tartar-tartaric acid powder: One gram sodium bicarbonate, 1.5 grams potassium bitartrate, 0.5 gram tartaric acid and 1 gram starch.

The total tartaric acid was first determined in 0.4 gram by Kenrick's polariscopic method. Found, 0.17177 gram.

(a) Fused and titrated, as in the above experiment, 0.4 gram of the mixture. Carbon dioxide corresponding to alkalinity, equaled 0.088 gram.

(b) The sodium bicarbonate was estimated in 0.8 gram in Knorr's apparatus. Found, 0.2001 gram, the weight of the CO_2 being 0.1048 gram.

The CO_2 from 0.1 gram of bicarbonate (0.4 gram of mixture) would be 0.0524 gram. This subtracted from 0.088 gram CO_2 leaves 0.0356 gram CO_2 , which is equivalent to 0.1521 gram potassium bitartrate, or 0.1214 gram free tartaric acid. This last figure, subtracted from the total tartaric acid, gives 0.05037 gram as the amount of free tartaric acid found.

To recapitulate, we will give the amounts of bicarbonate, bitartrate and tartaric acid taken for analysis in experiments A and B and the amounts found.

	Taken.		Found.	
	A. Gram.	B. Gram.	A. Gram.	B. Gram.
Sodium bicarbonate....	0.25	0.10	0.248	0.1000
Potassium bitartrate....	0.50	0.15	0.502	0.1521
Tartaric acid.....	...	0.05	...	0.0504

It will be seen from the above results that the free tartaric acid, as well as the starch, is without effect on the above fusion

method of estimating bitartrate and bicarbonate in a "Cream of Tartar" powder, the decomposition of the free acid being complete and without decomposing action on the carbonates already present or formed in the fusion.

The potassium bitartrate result, it will be noticed, is a little too high. This was due to the dissolved fusion mixture being titrated to a full bright pink color, with methyl orange, which required a tenth of a cubic centimeter more of decinormal sulphuric acid than did the titration to the first change in color. The potassium bitartrate, calculated from a titration observing this precaution, gave theoretical results.

This method, which requires much less time than any method previously devised for cream of tartar or cream of tartar-tartaric acid baking-powders, has been suggested to the writer's collaborators in the Association of Official Agricultural Chemists official method work for further trial and criticism, and is now respectfully submitted to the analytical chemical public for the same purpose.

With reference to the estimation of starch in these baking-powders, which is frequently desirable for completeness of legal evidence, the writer has found the simple method suggested by McGill¹ to be fully as accurate and much easier of operation than the conversion into "dextrose" and estimation of copper-reducing power method. With powders containing alum or phosphates, singly or together, however, the results may be from 1 to 2 per cent. too high. The details are as follows: Digest 1 gram of the powder with 150 cc. of 3 per cent. hydrochloric acid for twenty-four hours, at ordinary temperature, with occasional shaking. Filter in a Gooch crucible, wash thoroughly with cold water, then with alcohol and finally once with ether. Dry at 110° C. for four hours, cool and weigh. Now burn off the starch and weigh again. The loss in weight is the weight of the starch present.

In connection with the above work, the writer had occasion to test extensively the several qualitative tests for free and combined tartaric acid, given in the provisional official methods of analysis. The test for free tartaric acid, depending upon the solubility of the free acid in absolute alcohol and the insolubility of the bitartrate, worked very satisfactorily, there being no extracted matter giving a silver mirror when warmed with ammonia and

¹ Bulletin 65, Bureau of Chemistry, p. 105.

a crystal of silver nitrate from a powder containing no free tartaric acid. From a powder containing less than 0.5 per cent. of free tartaric acid, however, an extract giving a pronounced test was obtained.

The so-called Wolff test¹ for tartaric acid, either free or combined, in which 5 grams of the sample are shaken with 250 cc. of water for some time, filtered, the filtrate evaporated to dryness, a few drops of 1 per cent. resorcinol solution and 3 cc. strong sulphuric acid added and the mixture heated slowly with the development of a supposedly characteristic rose-red color when tartaric acid is present, proved to be very unsatisfactory in the writer's hands. Practically every usual adulterant of cream of tartar or baking-powder containing such gave a similar color, or one easily confused with it, by the above test, when absolutely *no tartaric acid, either free or combined, was present.*

The writer has always found the simple method of shaking a little of the sample with 10 per cent. ammonia water, filtering, adding a crystal of silver nitrate and warming (with the appearance of a silver mirror if free or combined tartaric acid be present) very satisfactory. No cream of tartar adulterant or substitute or any other usual ingredient of baking-powders gave the least trace of a mirror by this test; and from the standpoint of time required it is, of course, much quicker than any test involving the evaporation of a large volume of water, as does the so-called Wolff test. The use of this simple test upon a portion of the sample for tartaric acid generally and the similar testing of the alcoholic extract from another portion for free tartaric acid leaves nothing to be desired along the line of qualitative tartaric acid tests in baking-powder analysis.

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THE DETERMINATION OF WATER IN SUBSTANCES THAT ARE TO BE AFTERWARDS EXTRACTED WITH VOLATILE SOLVENTS.

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DURING the course of an investigation it became necessary to determine accurately the water and fat in a large number of

¹ *Rev. chim. anal. appl.*, 4, 263 (1899).