for the test could be weighed out and dissolved in a definite quantity of water; (2) a larger quantity of sugar could be dissolved and the solution boiled down to a syrup, which could then be tested as a syrup.

Under the direction of the senior author, Mr. J. M. Scott in 1913 determined the conductivity values of some twenty pure sugars by both of these methods of procedure. For the first, 15 g. of sugar were dissolved in hot water and made up to 50 cc. at 250° C. For the second method a solution of the sugar was boiled until the temperature reached 219° F. The values obtained were seldom identical; in some instances the former method, in other instances the latter method, gave the higher result. This indicated variation in sampling, and as material suitable for a study of the question of sampling was not immediately available the investigation was laid aside. It has now been resumed with reference to the volumetric lead test as well as to the conductivity test.

Ten of the syrups of the season of 1915 used in the work reported in Papers VI and VII were used in these new experiments. About 200 cc. of each were boiled to 243–245° F., poured into moulds, and allowed to stand for a day or two. The sugars thus obtained were redissolved, boiled to 219° F. and filtered through cotton wool. The conductivity values and the volumetric lead numbers were then redetermined on the regained syrups and compared with those found in the original syrups. The results are given in Table I. They show no material difference between the original syrup and that obtained by redissolving the sugar. This method of applying the tests to maple sugar is, therefore, satisfactory.

TABLE I.—COMPARISON OF VALUES IN ORIGINAL AND REGAINED SYRUPS

No.	10	13	14	16	18	19	22	27	29	43	Av.
CONDUCTIVITY VALUE:											
Original Syrup.....	107	119	99	106	97	108	112	109	117	125	109.9
Syrup from Sugar.....	106	119	99	106	98	106	112	110	113	125	109.4
VOLUMETRIC LEAD NO.											
Original Syrup.....	5.3	5.3	5.1	5.3	5.8	6.0	5.7	5.1	5.6	5.2	5.44
Syrup from Sugar....	5.4	5.6	5.3	5.4	5.4	6.2	5.6	5.0	5.5	5.8	5.52

The tests have been applied in the same manner to 16 sugars of the season of 1913, which were collected from the makers with the syrups reported in Paper III.¹ 75–100 g. of sugar were dissolved, the solution boiled to 219° F. and filtered through cotton wool.

The conductivity values found vary from 97 to 148 and the volumetric lead numbers from 5.1 to 6.5. These results are all within the limits found in pure maple syrups.² The conductivity values obtained by Mr. Scott by this same method (22 pure sugars) are also within the limits found in pure maple syrups.

Three sugars collected from grocers in the western provinces of Canada in 1912, tested in like manner, gave the following results:

No.	Conductivity Value	Volumetric Lead No.
1.....	16	0
2.....	146	5.6
3.....	79	0

Nos. 1 and 3 are condemned by the tests, while No. 2 appears to be a genuine maple sugar.

METHOD—Dissolve a fairly large representative sample (say 100 g.) of the sugar in hot water. Boil

to 219° F. (103.9° C.). Filter through cotton wool. Test the resulting syrup as directed in Papers VI and VII.

SUMMARY

Pure maple sugars converted into syrups give conductivity values and volumetric lead numbers within the limits found in genuine maple syrups.

MACDONALD COLLEGE, PROVINCE OF QUEBEC

DETERMINATION OF TARTARIC ACID

By B. G. HARTMANN, J. R. EOFF AND M. J. INGLE

Received December 30, 1915

The determination of tartaric acid in numerous soda fountain beverages, grape juices, wines and other food products, has necessitated a modification of the Halenke and Möslinger method, the provisional method of the Association of Official Agricultural Chemists.¹ Since modifications of this method presented as reports of the Associate Referee on Wine of the above Association have not thus far been available to many chemists who may be doing work of this nature, it is considered desirable to review briefly the recent methods for the determination of tartaric acid² and to give the results of a successful search for the cause of the discrepancies noted in the determination of this acid. These variations in results, even of the same analyst, were noted especially on wines containing free acid and alcohol.³

Most of the earlier methods depended on the precipitation of potassium acid tartrate, the original method being that of Berthelot and Fleurieu⁴ published in 1889. This method was modified by Halenke and Möslinger⁵ in 1895. Of the numerous methods which have been described for the quantitative determination of total tartaric acid in wines, this method may be considered as deserving first mention as to simplicity of manipulation, accuracy and adaptability to varying conditions. This is the method which the authors have still further modified.

Magnier de la Source⁶ was perhaps one of the first to note the fact that when free tartaric acid was present the cream of tartar precipitate did not represent the total tartaric acid content. He, however, suggested the neutralization of one-fifth of the total acidity by adding standard alkali. This procedure did not give satisfactory results on wines containing much free tartaric acid, such as Catawba and Scuppernong. The Goldenberg method⁷ for the estimation of the tartaric acid content of argols or crude tartar, consisted in dissolving the argols in hydrochloric acid and, after completely neutralizing with potassium carbonate, adding acetic acid to transform the neutral salt to the insoluble acid tartrate. This procedure, however, was open to criticism, since (as noted by Lampert and by Ordonneau⁸) iron

¹ U. S. Bureau of Chemistry, *Bull.* **107** (1912), 86.

² R. P. Häussler, *Schweiz. Apoth. Zeit.*, **52** (1914), 525–7, 537–40, 553–6, 569–72.

³ B. G. Hartmann, *Proc. A. O. A. C.*, **1914**.

⁴ M. Berthelot, *Chimie Végétale et Agricole*, **4** (1889), 423, in collaboration with M. de Fleurieu.

⁵ A. Halenke and W. Möslinger, *Z. anal. Chem.*, **34** (1895), 263.

⁶ M. L. Magnier de la Source, *Ann. chim. anal.*, **1** (1896), 205–6.

⁷ *Zeit. anal. Chem.*, **47** (1908), 57–59 (from *Chemischen Fabrik*).

⁸ M. C. Ordonneau, *Bull. soc. chim.*, **7** (1910), 1034–41.

¹ THIS JOURNAL, **6** (1914), 216.

² See Papers VI and VII.

and aluminum, commonly present in argols, tend to lower the result. Heczko¹ calls attention to the fact that the freshly precipitated calcium carbonate tends to react with the neutral potassium tartrate. The Marseille method² was used as an approximate method for the determination of tartaric acid in argols and depended on the precipitation of neutral calcium tartrate from an ammoniacal solution.

The most recent precipitation method is that developed by A. Kling.³ This is an extremely satisfactory procedure and, as tried out at the Enological Laboratory of the Bureau of Chemistry, gave the best yield of any method tried. The principle of the method is the formation of the very insoluble calcium racemate under conditions which give a theoretical yield from synthetic solutions. When applied to two authentic wines representing the extremes in ratio between cream of tartar and free tartaric acid, it gave results which were all that could be desired.⁴ As the tartaric acid present in the grape and the commercial article derived from it is always the dextro form, the addition of an excess of laevo salt would form the racemate, so that by forming the calcium salt under the favorable conditions prescribed, a most efficient method is developed. This is accomplished by adding calcium acetate and alkaline laevo-tartrate of ammonia in excess, and titrating the calcium racemate precipitate with a standardized potassium permanganate solution.

Iron and aluminum introduce a source of error in this determination which has been corrected by a modification, using an ammonium citrate solution.⁵ The presence of esters of tartaric acid is also allowed for by saponification as detailed by Kling and Gelin.⁶ The present prohibitive price of laevo-tartrate of ammonia, the instability of a tartrate solution, which requires a preservative, and the need of a microscope, are all factors tending to inhibit a general use of this method in commercial laboratories.

Other investigators have made use of the reducing action of the tartaric acid radical; thus Chapman and Whitteridge⁷ oxidize a bismuth tartrate precipitate; Mestrezat⁸ and Kling also finally titrate with potassium permanganate. Pozzi-Escot⁹ oxidizes barium tartrate, while Ferentzy¹⁰ ignites magnesium tartrate and weighs the resultant MgO, but Gowing-Scopes¹¹ modifies this method and titrates the magnesium tartrate with permanganate.

Evaporation, with a subsequent addition of alcohol, or alcohol and ether, has been advanced by Pasteur, Reboul, Magnier de la Source, and Malvezin. The addition of potassium bromide brings the free

tartaric acid into the reaction, so that on the addition of the alcohol-ether mixture all the tartaric acid is precipitated as tartar. These methods are not considered satisfactory as the evaporation is productive of losses through volatilization of esters and possible decomposition, and acid malates are titrated as tartrates¹ as are also other acid-reacting substances. This method as given by Malvezin was also tried out in the Enological Laboratory, and gave concordant but uniformly high results.

It has been demonstrated in routine work by the authors that the Halenke and Möslinger method is unreliable when employed on wines and fruit juices containing a considerable amount of free tartaric acid, such as Catawba, Iona, or Scuppernong grape juices or wines. This is due to the failure of the method to precipitate the free tartaric acid quantitatively as potassium acid tartrate and is attributable to the reversibility of the main reaction ($H_2T + KCl \rightleftharpoons HKT + HCl$). It has been noted by the authors that the addition of potassium acetate for the purpose of offsetting the disturbing influence of the hydrochloric acid formed ($KAc + HCl \rightleftharpoons KCl + HAc$) does not altogether correct this fault, one-fifth to one-third of the free tartaric acid being lost.² Furthermore, the addition of the potassium acetate to wines not containing free tartaric acid has a tendency to decrease the yield by dissolving the potassium acid tartrate.³

Having thus recognized that the value of the Halenke-Möslinger method was in the main dependent upon the elimination of the disturbing influence of the hydrochloric acid liberated, the authors decided that the best preventive for the formation of hydrochloric acid was to completely neutralize the acidity of the wine and to add the molecular equivalent of tartaric acid for the alkali added in order to convert the neutral tartrates into acid tartrates, and from this point on to proceed as prescribed in the Halenke-Möslinger method, omitting the potassium acetate addition altogether. By this procedure no intermediate products which might possibly interfere with or redissolve the potassium acid tartrate were to be expected, thus forming favorable conditions for a quantitative separation of the total tartaric acid as potassium acid tartrate. Trials of the procedure upon various synthetic solutions of tartaric acid and its salts proved its superiority to the older method.

Unfortunately, these experiments are not final since they were for the greater part undertaken on aqueous solutions, but it is quite possible that the behavior of a wine containing various other ingredients, such as phosphates and sulfates, may augment the usefulness of the method.

This modification has the decided advantage over the Halenke-Möslinger method in that, where there is a small amount of tartaric acid present in a wine (as in ports, sherries, and other fortified wines), the

¹ Arnold Heczko, *Z. anal. Chem.*, **60** (1911), 73-82.

² M. d'Hector de Rochefontaine, *Ann. chim. anal.*, **1** (1896), 25.

³ Andre Kling and L. Gobert, *Ann. fals.*, **4** (1911), 185.

⁴ *J. Assoc. of Offic. Agr. Chem.*, **1** (1915), 136.

⁵ M. Andre Kling and D. Florentin, *Proc. 8th Intern. Cong. Appl. Chem.*, **1** (1912), 237-9.

⁶ M. Andre Kling and E. Gelin, *Ibid.*, **1** (1912), 251-6.

⁷ Alfred C. Chapman and Percy Whitteridge, *Analyst*, **32** (1907), 163-6.

⁸ Note of M. W. Mestrezat presented by M. Müntz, *Compt. rend.*, **143** (1906), 185.

⁹ Em Pozzi-Escot, *Ann. chim. anal.*, **13** (1908), 266-9.

¹⁰ Josef V. Ferentzy, *Chem. Zeit.*, **31** (1907), 1118.

¹¹ L. Gowing-Scopes, *Analyst*, **33** (1908), 315-19.

¹ M. L. Magnier de la Source, *Ann. chim. anal.*, **2** (1897), 281-3.

² B. G. Hartman, Bureau of Chemistry, *Bull.* **162** (1913), 71.

³ *Ann. chim. anal.*, **1** (1896), 205-6.

addition of the tartaric acid insures a precipitation that otherwise might not occur.

HARTMANN AND EOFF METHOD

FOR WINES—Neutralize 100 cc. of wine with normal sodium hydroxide. The amount of alkali necessary for neutralizing may be calculated from the acidity of the wine previously determined. To the neutralized wine add the molecular equivalent in grams, of powdered tartaric acid,¹ corresponding to the amount of alkali required for neutralization. After the tartaric acid has dissolved add 2 cc. glacial acetic acid and 15 g. potassium chloride and after solution add 15 cc. alcohol (95 per cent). Stir until precipitation has started, then allow to stand over night at a temperature not above 15° C. After this interval filter the solution through either a Gooch crucible prepared with filter paper pulp or a Buchner funnel of 7 cm. diameter, into which is fitted exactly

TABLE I—DETERMINATIONS OF TARTARIC ACID BY HARTMANN-EOFF METHOD

SUBSTANCE	Results in Grams Tartaric Acid per 100 cc. Liquid			
	Actual Content	Hand Stirred	MECHANICALLY STIRRED 30 min.	15 min.
Tartaric Acid Solution...	0.481	...	0.482	...
	0.481	...	0.483	...
	0.241	...	...	0.238
	0.241	...	...	0.236
	0.241	...	...	0.238
	0.120	...	...	0.110
	0.048	0.042	0.025	...
California Hock Wine ..	0.254(b)	0.240	0.012(a)	...
California Sauterne Wine.	0.221(b)	0.215	0.255	...
California Zinfandel Wine	0.233(b)	0.211	0.217	...
California Sherry Wine...	...	0.088	0.243	...
California Port Wine...	...	0.113	0.099	...
California Sherry No. 2...	...	0.101	0.120	...
California Port No. 2...	...	0.120	0.100	...

(a) Stirred one hour.

(b) Content determined by method given on p. 86 of U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 107 (Rev.).

a strong filter paper; use gentle suction and wash three times with 7 cc. of a solution composed of 100 cc. of water, 15 g. potassium chloride and 20 cc. of 95 per cent alcohol. Transfer the precipitate and paper to the original beaker with 50 cc. hot water, bring to a boil and immediately titrate with *N*/10 sodium hydroxide, using phenolphthalein as indicator. Increase the burette reading by 1.5 cc. as a correction for solubility, multiply by 0.015 and subtract the tartaric acid added. This will give the total tartaric acid in the wine in terms of grams per 100 cc.

OTHER MODIFICATIONS

STIRRING—It was noted that stirring until a precipitate actually formed was essential to the accuracy of the method. By means of the mechanical stirring of solutions the time factor was lessened and it was found practicable by this expedient to determine correctly the tartaric acid content of a synthetic solution in 15 to 30 minutes.

HALF-NEUTRALIZATION METHOD.—An attempt to neutralize one-half of the acidity of wine proceeding according to the Halenke-Möslinger method, omitting

TABLE II—DETERMINATION OF TARTARIC ACID IN WINES IN WHICH THE ACIDITY WAS HALF NEUTRALIZED

Experiment No.	1	2	3	4	5	6	7
Hartmann-Eoff Method.....	0.74	0.54	0.99	0.76	0.72	0.78	0.80
Half-Neutralization Method..	0.68	0.50	0.96	0.71	0.63	0.71	0.77

the potassium acetate addition, gave less accurate results than complete neutralization, from 3 to 9 per cent less acid being found than was present.

¹ The acid used should be pure and well dried.

TEMPERATURE—The authors also find that the temperature at which the reaction mixture of the Halenke-Möslinger method is held for 15 hrs. influences the precipitation, there being a decided increase in yield of tartrate at low temperatures.

TABLE III—EFFECT OF CHILLING ON PRECIPITATION WHEN UNMODIFIED METHOD WAS USED

No.	Temperature °C.	GRAM TARTARIC ACID Actual	Found	Per cent Acid Recovered
1	5	0.994	0.774	77.9
2	5	0.994	0.792	79.7
3	5	0.497	0.401	80.7
4	5	0.497	0.405	81.5
5	17	0.994	0.698	70.2
6	17	0.994	0.698	70.2
7	17	0.497	0.354	71.3
8	17	0.497	0.357	71.8

Before entering upon the final description of the methods resulting from these experiments it should be remarked that although other investigators have attempted to avoid the disturbing influence of mineral acids by neutralizing a part of the acidity of the wine, the authors have been unable to find records showing that this has been done with any marked degree of success and that the addition of tartaric acid to the neutralized solution for the purpose of precipitating potassium acid tartrate has evidently not been previously tried.

ROCHELLE SALT METHOD

The tartaric acid required may be efficiently added as Rochelle salt. In that case the method is based on the following reactions:

As Rochelle salt contains exactly four molecules of water of crystallization, it may be used without drying. For every cc. of normal alkali required for neutralization, add 0.141 g. of the salt. As only 53.17 per cent of the salt is normally tartaric acid, weighing errors are minimized. If this salt is ground or unduly exposed to the air it may lose some of its water of crystallization. It is, therefore, necessary to obtain the actual acid content at the time used. This may be done by dissolving 1 g. of the salt in 100 cc. of water, adding 2 cc. acetic acid, 15 g. KCl, and 20 cc. of 95 per cent alcohol, stirring until precipitation starts, and allowing to stand in an ice box with a maximum temperature of 15° C. The addition of alkali may, therefore, be dispensed with.

The following results were obtained on five samples of grape juice, using the proposed method and the Rochelle salt method:

TABLE IV

No.	Grams Rochelle Salt Added	Grams Tartaric Acid in Salt	TARTARIC ACID IN JUICE USING Rochelle Salt	Tartaric Acid H.-E. Method
1	0.776	0.031	0.624	0.627
2	1.297	0.720	1.170	1.205
3	0.874	0.485	0.624	0.636
4	1.199	0.665	0.620	0.638
5	0.677	0.372	0.640	0.637
Rochelle Salt	1.000	0.555	...	...

FOR GRAPE JUICE—Take 50 cc. of the filtered juice and neutralize with *N* NaOH. After neutralizing make to 100 cc. volume with distilled water. From this point on, the H.-E. procedure as described under wine is followed, using 20 cc. instead of 15 cc. of

95 per cent alcohol. The occlusion of other organic acids with precipitated pectin bodies and cream of tartar makes the use of only 50 cc. of grape juice advisable for the determination.

In case of syrups, fermentation of sugar or a separation of the acid therefrom as the lead salt¹ is advisable. It may be of interest to mention that Halenke and Möslinger advise a double precipitation in the case of grape juices.

FOR ARTIFICIAL PRODUCTS CONTAINING FREE PHOSPHORIC ACID AND ALCOHOL—While experimenting with synthetic solutions, containing tartaric acid, free phosphoric acid and alcohol, it was found that neither the Halenke-Möslinger method nor the Hartmann and Eoff method gave satisfactory results. Further, it developed that these two methods became less reliable as the solutions under discussion aged. This condition was found to be brought about by the formation of ethyl esters of tartaric acid, the amount of ester formed increasing with the time allowed for the reaction. This was shown by saponifying the solution with an excess of alkali before determining the tartaric acid, a complete recovery of the theoretical amount of acid being thereby obtained. It was also observed that in cases where much free phosphoric acid was present the Halenke and Möslinger method failed to give any precipitate of potassium acid tartrate whatever, notwithstanding the presence of considerable tartaric acid in the solution. These two points, the loss of tartaric acid through esterification and the failure of the Halenke-Möslinger method to give even approximate results in presence of free phosphoric acid, were made the subject of investigation in 1914 by the Associate Referee on Wines of the Association of Official Agricultural Chemists. The heretofore unpublished work of five collaborators was very satisfactory and fully substantiates the findings recorded above.

The behavior of alcohol and tartaric acid in the presence of other free organic acids (formation of esters) is a well-known phenomenon and was pointed out by Berthelot and Fleurieu in their original paper describing the alcohol-ether method. Esterification in part may explain why very old wines, when employing the customary methods for determining the total tartaric acid, very often show an exceedingly small amount of this constituent.

It is very important to know the extent of esterification in artificial products containing free phosphoric acid, alcohol, and tartaric acid, since the ordinary methods may not reveal the tartaric acid that is present even in amounts as high as 3 g. per 100 cc. of solution.

It was found that by adding 5 cc. *N* NaOH in excess of neutralization to 50 cc. of the solution under examination, bringing to a boil and allowing to stand over night, a complete saponification could be obtained. The addition of the required amount of tartaric acid, dilution to 100 cc. with water and then proceeding as detailed for wines, yielded quantitative results for total tartaric acid.

¹ C. Schmitt and C. Hiepe, *Z. anal. Chem.*, **21** (1882), 534-41.

Solutions indicated in Table V were analyzed by different analysts on different dates with the results given.

TABLE V—(Results in Grams per 100 cc.)

DETERMINATION	HALENKE AND MÖSLINGER METHOD	HARTMANN-EOFF METHOD	
		Half Neutralized	Completely Neutralized
Acidity as Tartaric.....	4.92	2.52	1.96
Total Tartaric Acid.....	2.00	1.80	1.89
Phosphoric Acid.....	1.91	0.48	0.048
Caramel.....	1.20	1.20	1.20
Amaranth.....	0.024	0.024	0.024
Cane Sugar.....	5.00	5.00	5.00
Alcohol.....	5.00	5.00	5.00

Table VI presents results obtained on three synthetic solutions, on the dates indicated.

TABLE VI—RESULTS (G. per 100 cc.) ON THREE SYNTHETIC SOLUTIONS

Solution Number	DATE 1914	HALENKE AND MÖSLINGER	HARTMANN AND EOFF METHOD	
			Neutralization	Preliminary Complete Saponification
I.....	7/20	0.74	1.88	1.90
	8/12	0.64	1.69	1.84
	8/24	0.06	1.54	1.76
	8/26	0.63	1.66	1.67
	10/30	0.00	1.61	1.65
II.....	7/20	1.03	1.76	1.76
	8/12	0.90	1.62	1.68
	8/24	0.67	1.51	1.62
	8/26	0.91	1.57	1.58
	10/30	0.65	1.51	1.63
III.....	7/20	1.23	1.87	1.87
	8/12	1.18	1.77	1.77
	8/24	1.00	1.68	1.77
	8/26	1.22	1.72	1.71
	10/30	0.92	1.63	1.67

The low results obtained by the Halenke and Möslinger method show the necessity of starting the precipitation by stirring as illustrated by the results obtained on August 24th, and October 30th. The gradual esterification of the free tartaric acid is shown by the lower results obtained as the solutions aged.

BUREAU OF CHEMISTRY, WASHINGTON

THE DECOMPOSITION OF THE ORGANIC MATTER OF KELP IN THE SOIL¹

By A. W. CHRISTIE

Received November 15, 1915

Considerable interest has been evinced of late in the possible use of kelp as a commercial fertilizer. Burd² has shown that probably the most practical and profitable way of utilizing kelp would consist in drying at a low temperature and grinding. The resulting product, in addition to the valuable potash (11.45 per cent K_2O in air-dried kelp (*Macrocystis*)), contains all the nitrogen and organic matter. Stewart³ has shown that the nitrogen (1.18 per cent N in air-dried kelp (*Macrocystis*)) becomes slowly available in the soil. In connection with the probable use of dried and ground kelp as a commercial fertilizer or as a filler for mixed fertilizers, it becomes of interest to learn the fate of the organic matter and whether any agricultural value may be assigned to it. The extent and rate of decomposition of kelp in soil were compared with the following materials which are common sources of organic matter in the soil, *viz.*, manure, straw and alfalfa.

PLAN OF EXPERIMENT

In each of 14 glass jars were placed 300 g. of air-dried soil (fine sandy loam from Anaheim, California),

¹ See also work of U. S. Department of Agriculture on Kelp. [EDITOR'S NOTE.]

² "Economic Value of Pacific Coast Kelps," *Bull.* **248**, California Agricultural Experiment Station.

³ "Availability of Nitrogen in Pacific Coast Kelps," *J. Agr. Research*, **4**, No. 1 (1915), 21.