Amyl alcohol	129°	and ethyl butyrate	120.6°
Amyl alcohol	129°	and bromoform	147.1°
Amyl acetate	137.5°	and ethylene bromide	129°
Amyl acetate	137.5°	and amyl bromide	118°
Amyl acetate	137.5°	and amyl iodide	146.5°
Amyl acetate	137.5°	and bromoform	147.1°
Amyl acetate	137.5°	and ethyl butyrate	120.6°
Amyl bromide	118°	and ethyl butyrate	120.6°
Amyl bromide	118°	and toluene	109.5°

Of the 16 pairs of liquids investigated, 5 gave mixtures having well-defined minimum boiling-points, while 2 showed no relative elevation or depression of the boiling-point.

The chemical constitution of the constituents exercises a greater influence in the formation of mixtures with minimum boiling-points than the close proximity of the boiling-points of the constituents. One constituent remaining the same, or with constituents closely related, mixtures with substances of similar chemical constitution yield similar boiling-point curves.

In the next paper the writer hopes to present the results obtained with propyl and isobutyl compounds.

UNIVERSITY OF MAINE.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE VOLUMETRIC ESTIMATION OF ALUMINA, AND FREE AND COMBINED SULPHURIC ACID IN ALUMS.

BY ALFRED H. WHITE.

Received January 25, 1902.

IN judging the quality of an alum, among the important determinations are those which give the amount of soluble alumina and the amount of sulphuric acid in combination with it or existing as free acid. The alumina may be satisfactorily estimated gravimetrically, but the method is tedious. A gravimetric estimation of the sulphuric acid gives not only that combined with aluminum plus that present as free sulphuric acid, but also that present as sodium sulphate, etc., and the amount of alkalies must be known before the amount of sulphuric acid combined with aluminum can be determined.

The determination of free sulphuric acid in alums by volumetric means has been repeatedly attempted. The hydrolysis of aluminum sulphate prevents direct titration with an alkali, since as fast as the free acid present is neutralized, more is formed by hydrolysis, so that the solution will not remain neutral for an appreciable length of time until nearly all the acid originally combined with the aluminum has been neutralized, and most of the aluminum hydroxide precipitated. This cannot be made into a practicable quantitative method for the estimation of free and combined acid, as the formation of aluminate with alkaline reaction begins before all the hydroxide has been precipitated. Further if phenolphthalein is used as indicator the precipitated hydroxide obstinately holds, by adsorption, the pink color even when the solution is no longer alkaline so that the method, though perhaps giving in the hands of works chemists in constant practice results which are fairly concordant, is, because of these various errors, not to be considered a practicable analytical method. The following paper results from an attempt to work out a practicable method.

A standard solution of barium hydroxide was used instead of caustic soda to avoid any trouble caused by carbon dioxide in the caustic affecting the phenolphthalein used as indicator. It was found later that the barium hydroxide possessed other advantages. To prevent the adsorption of pink color by the precipitated aluminum hydroxide obscuring the end reaction, an addition of neutral potassium sodium tartrate (Rochelle salt) was made to hold the alumina in solution. The modification proved a good one. Duplicate results checked closely. There was no precipitation of alumina during the titration, nor even of barium sulphate. The solution remained perfectly clear and colorless until the end reaction, which was sharp. After standing a short time the solution became opalescent, and then milky, but no precipitate settled out. This marked retardation of the precipitation of barium sulphate was unexpected, and the conditions under which it occurs are undergoing further investigation.

To determine that the results thus obtained were accurate, a solution of aluminum sulphate was made by precipitating aluminum hydroxide from a solution of aluminum chloride with ammonia, washing the precipitate thoroughly and then dissolving in standard sulphuric acid which was afterward diluted to a liter (Solution A). The solution thus obtained was almost fifth-normal, and the amount of acid was slightly in excess of the amount theoretically necessary to form the normal aluminum sulphate. A duplicate solution of acid alone, carefully standardized gravimetrically, was used to check the results.

The method of procedure was as follows: To 25 cc. of the fifth-normal alum solution was added 50 cc. of 10 per cent. neutral potassium sodium tartrate, and the mixture was titrated cold with barium hydroxide solution, using phenolphthalein as indicator. This amount of tartrate was sufficient to prevent anything more than a slight opalescence in the solution before the end reaction. Duplicate titrations required 25.85 and 25.80 cc. of fifth-normal barium hydroxide. To determine the effect of the amount of tartrate, another titration was made, using 100 cc. of tartrate instead of 50. The amount of barium hydroxide solution used was 25.85 as before. The check solution of sulphuric acid required 25.65 cc. barium hydroxide, no difference being apparent whether no tartrate, 50 cc., or 100 cc. of tartrate were present. The solution containing the aluminum sulphate therefore requires slightly more barium hydroxide than that containing the sulphuric acid alone. A possible explanation is that the ionization of the barium hydroxide is lessened to such an extent by the aluminum tartrate complex that it requires an appreciably large excess of barium hydroxide to bring about the end reaction. If, however, the barium hydroxide is standardized against a solution of aluminum sulphate made from precipitated alumina and sulphuric acid as described, the results will be constant and give accurate results when extended to other alums. The addition of sodium sulphate in amount equivalent to the amount of sulphuric acid combined with the aluminum does not affect the result; the addition of standard sulphuric acid increases the amount of barium hydroxide used by the theoretical amount. The addition of neutral tartrate and titration with barium hydroxide, therefore, affords an accurate method of determining the total sulphuric acid combined with the aluminum plus the excess of free acid, irrespective of the amount of sulphuric acid combined with alkalies.

As it is well known that the hydroxy-organic acids in general have the power of preventing the precipitation of alumina, salts of other acids than tartaric were tried, among them neutral sodium citrate. Sodium citrate prevented the precipitation of alumina, retarded the precipitation of barium sulphate, and allowed a perfectly sharp end reaction, as did the tartrate, but the amount of barium hydroxide used was only a little over two-thirds of that required when titrating in the presence of the tartrate. Solution A, with neutral sodium citrate added, required only 17.95 cc. barium hydroxide instead of 25.84 when tartrate was used. Experiment showed that the addition of sodium sulphate did not affect the result and that an addition of standard sulphuric acid caused the theoretically calculated increase in the barium hydroxide used. It seemed that the result obtained when titrating in the presence of citrate could be due only to the formation of a complex aluminum ion and that this might furnish the basis of a method for the estimation of the aluminum. If we assume that the barium hydroxide used when titrating in presence of tartrate, represents free acid plus acid combined with alumina, while the barium hydroxide used when titrating in presence of citrate represents free acid, plus two-thirds of acid combined with alumina, the difference represents one-third of the sulphuric acid combined with the alumina, or one-third the alumina. In the above instance, 25.84 — 17.95 = 7.89 cc. fifth-normal barium hydroxide, and calculating the alumina on the assumption that this is equivalent to one-third of it we find that we get 0.0805 gram of alumina as compared with 0.0831 gram obtained gravimetrically. The volumetric result is too low. It seemed entirely possible that partial hydrolysis of the alum in the citrate solution might cause more barium hydroxide to be used than called for by the above supposition and that this might account for the low result. Accordingly, among other variations, the solution of aluminum sulphate was evaporated to dryness on the water-bath and dissolved in 50 cc. of 10 per cent. sodium citrate, and titrated. There were required only 17.58 cc. barium hydroxide instead of 17.95 cc., and the alumina calculated from this is 0.0842 gram instead of 0.0831 gram obtained gravimetrically. Using a saturated solution of citrate to redissolve the alum did not give an appreciably different result. Thus, the first method gives results considerably low while the second gives slightly high results. Some further experiments upon the influence of concentration and time follow, made upon a C. P. aluminum sulphate in a solution of 30 grams per liter (Solution B).

B.	Volume. Aluminum sulphate.	Water added.	Citrate added.	Barium hydroxide.	Remarks.
1	25	0	50	21.75	Titrated at once.
2	25	25	50	21.76	Titrated at once.
3	25	50	50	21.67	Water added; stood fifteen minutes; then citrate added, and titrated.
4	25	100	50	21.70	Water added; stood fifteen minutes; then citrate added, and titrated.
5	25	200	50	21.72	Water added; stood fifteen minutes; then citrate added, and titrated.
6	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate; stood ten minutes before titrating; required 21.62 cc. barium hydroxide.			
7	0.750 gram (25 cc.) of solid salt, dissolved in 50 cc. 10 per cent. citrate and titrated at once, required 21.90 cc. barium hydroxide.				

The above series of experiments shows that the addition of varying amounts of water and variation of time within short intervals makes but slight difference in the result. The hydrolysis is apparently a slow one. In twenty-four hours, however, equilibrium is practically complete, as is shown by another series of experiments on a commercial aluminum sulphate dissolved to a strength of 30 grams per liter (Solution C).

C.	Volume. Aluminum sulphate.	20 per cent. citrate added.	Barium hydroxide.	Remarks.
1	25	25	21.0	Titrated at once.
2	25	25	21.02	Stood fifteen minutes before titrating.
3	25	25	20.62	Stood sixteen hours before titrating.
4	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate.	20.53	Titrated at once.
5	25	Evaporated to dryness and redissolved in 50 cc. 10 per cent. citrate.	20.69	Stood ten minutes before titrating.
6	0.750 gram (25 cc.) solid salt dissolved in 50 cc. 10 per cent. citrate.		21.10	Stood ten minutes before titrating.

Nos. 3 and 5 show that if sufficient time is given to allow equilibrium to be established, the results are practically the same whether the 50 cc. solution is evaporated to dryness and dissolved in 50 cc. of 10 per cent. citrate (20.69 cc.) or 25 cc. of solution are treated with 25 cc. of 20 per cent. citrate, and the solution allowed to stand sixteen hours (20.62 cc.). No. 6 in this series, as well as No. 7 in Series B, shows that the same result is not reached when dissolving the solid salt in citrate (B 7 = 21.90) and titrating as when evaporating to dryness, and redissolving in the same amount of citrate (B 6 = 21.62). Commercial alum is evidently not a homogeneous body, and further combination between the alumina or basic sulphate and the sulphuric acid takes place after solution in water.

The analytical method as finally worked out is as follows: Dissolve 3 grams of alum in 100 cc. of water. Take 25 cc. sample, add 50 cc. strictly neutral 10 per cent. potassium-sodium tartrate and titrate with fifth-normal barium hydroxide, using phenolphthaleïn as indicator. This is equivalent to the sulphuric acid combined with the alumina plus the free acid. Evaporate a duplicate 25 cc. sample to dryness on the water-bath, dissolve in 50 cc. strictly neutral 10 per cent. sodium citrate, allow to stand ten minutes and titrate with barium hydroxide, with phenolphthaleïn indicator as before. The difference between these results is equivalent to one-third of the sulphuric acid combined with the alumina and hence to one-third of the alumina. The barium hydroxide solution should be standardized by a blank determination upon a solution of sulphuric acid in which approximately enough precipitated aluminum hydroxide has been dissolved to correspond to aluminum sulphate. The aluminum hydroxide may be best made by precipitation of the chloride to insure absence of sulphate. Caustic soda, even when freed from carbon dioxide by barium hydroxide, does not give such satisfactory results as the barium hydroxide. As examples of the practicability of the method the following results on two widely differing alums are cited.

Alum B, a C. P. aluminum sulphate:

30 grams per liter (25 cc.) sample = 0.750 gram sample.

		cc.
Fifth-normal barium hydroxide for tartrate titration . . .	32.50 32.55	32.52
Fifth-normal barium hydroxide for citrate titration	21.60 21.63	21.62
Difference		10.90

$10.90 \times 3 = 32.70$ cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina, and therefore equals alumina.

$32.70 \times 0.003407 = 0.1114$ gram alumina equals 14.86 per cent. alumina. Alumina determined gravimetrically equals 14.73 and 14.80.

The close agreement between the figures 32.52 cc. (free and combined sulphur trioxide) and 32.70 cc. (combined sulphur trioxide) show that the alum is almost exactly neutral with an excess equal to 0.18 cc. of fifth-normal alumina.

Alum C, a commercial aluminum sulphate:

30 grams per liter (25 cc.) sample = 0.750 gram sample.

		cc.
Fifth-normal barium hydroxide for tartrate titration	33.59 33.59	33.59
Fifth-normal barium hydroxide for citrate titration	20.64 20.74	20.69
Difference		12.90

$12.90 \times 3 = 38.70$ cc. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina and therefore equals alumina.

$38.70 \times 0.003407 = 0.1318$ gram alumina equals 17.58 per cent. alumina. Alumina determined gravimetrically equals 17.57 and 17.50.

$38.70 - 33.59 = 5.11$ cc. fifth-normal alumina equals 0.0174 gram alumina equals 2.32 per cent. alumina more than is sufficient to form aluminum sulphate.

Alum B, as shown by the above figures, is slightly basic, but a determination of free acid by the method of Beilstein and Grosset[1] gave 0.9 per cent free acid. This method of Beilstein and Grosset has been investigated by V. Keler and Lunge,[2] who state that it gives results which are uniformly slightly high but otherwise very accurate, and it therefore became necessary to explain the discrepancy. The method of Beilstein and Grosset is as follows: Dissolve 1 or 2 grams of alum in 5 cc. of cold water, add 5 cc. of a cold, saturated solution of ammonium sulphate, allow to stand, with frequent stirring, for fifteen minutes, and then add 50 cc. 95 per cent. alcohol. Filter, wash with 50 cc. 95 per cent. alcohol, evaporate to dryness on water-bath, dissolve in water, and titrate with tenth-normal potassium hydroxide, using litmus as indicator. All the alum is, in this process, supposed to be precipitated as normal ammonium alum together with most of the excess ammonium sulphate, and the free sulphuric acid re-

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[1] Bulletin de l'Academie Imperiale des Sciences in St. Petersburg, 1890, p. 147.

[2] *Ztschr. angew. Chem.* (1894), p. 669.

mains in solution together with a small amount of ammonium sulphate. Three determinations of free acid in alum B by this method gave 0.86, 0.88, and 0.89 per cent. free acid as sulphur trioxide—as good an agreement as could be desired. To test whether an error in Beilstein and Grosset's method due to hydrolysis might not be responsible for this apparent free acid, variations were made in amount of water and concentration of sulphur trioxide, with the following results :

Sample. Grams.	Water. cc.	Saturated solution $(NH_4)_2SO_4$. cc.	Alcohol. Per cent.	Free acid as SO_3. Per cent.
2	10	10	95	0.96
3	10	10	95	0.88
3	5	10	absolute	0.70
3	5	5 + 5 gram solid ammonium sulphate.	absolute	0.61

Blank determinations showed that the change in results was not due to impurities in the ammonium sulphate or alcohol. The results show that the decrease in the relative amount of water decreases the apparent amount of free acid, but although hydrolysis does thus play a part in influencing the results, there remains as the lowest figure, 0.6 per cent., which can hardly be attributed to an error in the method. Turning back to the series of results obtained by titrating alum B in presence of citrate, it was remarked that the figures obtained by dissolving the alum directly in citrate were higher than those obtained by dissolving the alum in water, then evaporating to dryness and redissolving in citrate which showed a greater amount of free acid in the original alum than after evaporation to dryness. If the results in B 7 are taken and calculation made we find that there are required

	cc.
Fifth-normal barium hydroxide for tartrate titration	32.52
Fifth-normal barium hydroxide for citrate titration when alum dissolved directly in citrate	21.90
Difference	10.62

$10.62 \times 3 = 31.86$ cc.

$32.52 - 31.86 = 0.66$ cc. $= 0.70$ per cent. free acid as sulphur troxide.

This result is in fair accord with the results obtained by the Beilstein and Grosset method of direct estimation, and probably corresponds closely to the amount of free acid actually present in the solid salt. It is entirely incorrect, however, to hold that the solution of this alum wlll have that amount of free acid, as the results on p. 463 show that the amount of alumina in solution is slightly greater than the amount necessary to form the normal salt. The solid salt is evidently not uniform. When dissolved in water to dilute solution, these inequalities disappear quickly. In concentrated solution, as in the Beilstein and Grosset method or when the salt is dissolved in citrate, equilibrium is attained much more slowly, and a titration of such a solution soon after solution is complete gives approximately the conditions prevailing in the solid salt. If the solution is allowed to stand a sufficient length of time, equilibrium is finally reached as shown by experiments C 3 and C 5, on page 461.

SUMMARY.

If a solution of an alum to which has been added neutral potassium sodium tartrate (Rochelle salt) is titrated with barium hydroxide, the barium hydroxide used will correspond to the sulphuric acid combined with the alumina plus the free acid. The sulphuric acid combined with sodium or potassium is not estimated. If a duplicate solution of alum is evaporated to dryness, redissolved in neutral sodium citrate and titrated with barium hydroxide, a smaller quantity of barium hydroxide is required, and the difference between the amounts of barium hydroxide used in the two titrations is equivalent to one-third of the alumina. From these two titrations can be calculated the alumina and the sulphuric acid combined with it whether the alum be basic or acid, and if the alum is acid, the excess of acid over that necessary to form the normal sulphate. Commercial aluminum sulphate may, in its solid state, carry free acid, although in the solution such uncombined acid may disappear, combining with what had been basic portions of the solid salt. Such free acid may be estimated by dissolving the solid salt directly in citrate and titrating with barium hydroxide at once. This method gives results closely concordant with Beilstein and Grosset's method, but it does not show that the alum contains more acid than is sufficient to form with the alumina the normal salt.

When aluminum sulphate is titrated with barium hydroxide thus, in presence of neutral alkali tartrate or citrate, the precipitation of barium sulphate is retarded for a time, varying from a few minutes to several hours and when the precipitate does form it is in a very peculiar colloidal form which is undergoing further investigation. Consideration of this subject and also of the action of salts of other metals than aluminum and salts of other acids than tartaric and citric, as well as the theoretical points involved are reserved for a following paper.

ANN ARBOR, MICH.,
December, 1901.

THE ANALYTICAL CONSTANTS OF NEATSFOOT, TALLOW AND HORSE OILS.

BY AUGUSTUS H. GILL AND ALLAN W. ROWE.

Received February 3, 1902.

OF the commonly occurring oils, fewer data are to be found about these three than about any of the others ; this work was undertaken to supply this need.

The various tests were applied as described in a book published by one of us ;[1] that is, the specific gravity was taken with a correct Westphal balance at 15° C. or 100° C.; the Valenta test was done with an equal quantity of glacial acetic acid, proved to be 100 per cent. by titration ; the Maumené test was performed with 100 per cent. sulphuric acid, its strength also determined by titration, in a jacketed beaker, the acid being run into the oil drop by drop from a burette ; the iodine number, with the solutions after having been mixed twenty-four hours, and the oils allowed to stand for four hours with it. The titer test was carried out as prescribed by Lewkowitsch, the acid being melted in a 5″ test-tube held in a 100 cc. round-bottomed flask. The results given are usually the average of two closely agreeing determinations. The oils used were obtained from different dealers and guaranteed pure.

The constants are as follows :

	Sp. gr. 15° C.	Valenta. °C.	Maumené. °C.	Sp. temp. reaction.	Iodine. No.	Titer test. °C.	Iodine No fatty acid.
Neatsfoot oil, 1 ·	0.915	70.0	42.2	87.9	72.9	19–20	68.6
“ “ 2 ·	0.914	75.5	42.2	87.9	72.9	18–19	64.6
“ “ 3 ·	0.919	51.0	49.5	103.1	67.1	17–18	67.3
“ “ 4 ·	0.916	61.5	42.2	87.9	72.1	16	69.5
“ “ 5 ·	0.916	75.5	42.2	87.9	66.0	25.5–26.5	63.6
Usual figures ···	0.915	····	48.0	····	70.0	26.0	····
	100° C.						
Tallow oil, 1····	0.794	73.5	35.0	72.9	55.8	35–36	54.6
“ “ 2····	0.794	71.0	35.0	72.9	56.6	36.5–37.5	57.0
“ “ 3····	0.794	75.7	35.0	72.9	56.7	34.5–35.5	56.6
	15° C.						
Usual figures ···	0.916	47.0	43.0	····	57.0	39	····

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[1] Gill : “A Short Handbook of Oil Analysis.”