PAPER READ BEFORE THE CHEMICAL SOCIETY.

XLIV.—*Notes on the Chemistry of Tartaric and Citric Acid.*

By Robert Warington.

CONTENTS.

PAGE

Citric acid :—

Lemon, bergamot, and lime-juice :—

Citrate of calcium :—

Citric acid liquors :—

Tartaric acid :—

PAGE

Tartrate of calcium :—

Solubility of bitartrate of potassium :—

Lees, argol, and tartar :—

Determination of tartaric acid in tartar, argol, and lees :—

Analysis of tartaric acid liquors :—

As chemist for several years to the Citric and Tartaric Acid Factory of J. B. Lawes, Esq., I have had considerable opportunities of studying the chemistry of these acids in their commercial aspect. I propose, by Mr. Lawes' kind permission, to lay before the Society the results of the experience thus acquired. Chemical literature furnishes at present very scanty information as to methods of analysis of the various materials with which the manufacture of tartaric and citric acid is concerned. I propose therefore to treat this part of the subject somewhat fully. In doing so I shall doubtless state some facts which will appear as familiar truths to those chemists who are habitually engaged with the manufacture in question. I believe, however, that these facts have not before been published, and they will in this case at least be the result of an independent experience. With regard to the researches to be narrated, I would ask the Society to bear in mind that they were carried out in a commercial laboratory, where the object is a practical rather than a scientific one, and where time can seldom be given to an investigation after the practical object in view has been sufficiently attained.

As many of the analytical operations I have to describe are based on alkalimetrical reactions, I will begin with a notice of the materials employed in such determinations.

Standard Alkali and Acid.—The standard alkali I make use of is a dilute solution of caustic soda, containing in 100 c.c. about half a gram of pure hydrate of sodium. The sharpness of the final reaction in alkalimetrical operations depends greatly on the purity of the solutions; alkali made with soda prepared from sodium, gives a much sharper reaction than alkali made with other soda.

I employ as standard acids a dilute sulphuric, and a dilute hydrochloric acid; 20 c.c. of each of these are equivalent to about 100 c.c. of the alkali. The sulphuric acid is preferred as non-volatile, but when much carbonate of calcium has to be acted on, the hydrochloric acid should be employed. Hydrochloric acid of the strength here described (about 1 volume of strong acid to 12 volumes of water) may be gently boiled in a covered beaker without loss of acid.

The dilute sulphuric acid is prepared from distilled oil of vitriol, its strength is accurately determined by precipitation with chloride of barium. From the relation of the sulphuric acid to the alkali all the required values of the alkali are calculated, except its value in free citric acid, which should be determined by experiment. As the point of neutralisation will have to be determined in most cases with litmus paper, this should also be used for the final reaction in the experiments made to determine the value of the alkali.

Litmus Paper.—The exactness attained in alkalimetrical work, depends very much on the quality of the litmus paper used. Being unable to procure litmus paper of sufficient delicacy, or of constant tint, we have been obliged to make it for ourselves. After many unsuccessful efforts the following plan was adopted. A strong solution of litmus in cold water is rendered pretty clear by subsidence and filtration, it is then treated with nitric acid in slight excess, and brought to boiling to destroy carbonates. The solution is then filtered through Swedish paper, and pure caustic soda added till the desired tint of violet is reached, which is known by making a trial piece of litmus paper. Sheets of thin demy paper are then painted on one side with the litmus solution; the paper is finally flooded with the liquor, and kept in motion between the hands for a few minutes so as to pass the flood frequently to and fro over the surface. The paper is then hung up to dry. If tincture of litmus is employed, the paper changes its tint when moistened. If the long-continued flooding be omitted, the colour washes out when the paper is used; this also happens if the solution of litmus has been too strong. The tendency of the colour to wash out may be entirely prevented by adding a little gelatin to the litmus solution, as recommended by Mr. Vacher; but paper thus made, so far as my experience goes, turns reddish when moistened. It is convenient to have litmus paper of more than one tint; we employ three tints of violet in our laboratory. Extreme delicacy is attained when the paper is not too deeply coloured, and when its tint approaches neutrality; pale or neutral paper is however worthless. The limit of distinct reaction of our most delicate paper with various acids is about as follows, the paper being held half a minute in the solution:—

1 part of dry hydrochloric acid in 220,000 of water.
1 part of oil of vitriol in 190,000 of water.
1 part of crystallised tartaric acid in 90,000 of water.
1 part of crystallised citric acid in 70,000 of water.

Citric Acid.—The amount of water in crystallised citric acid is a point on which there has been a good deal of difference of opinion. Manuals of chemistry now generally state that the commercial acid contains one molecule of water of crystallisation, and that the acid has this composition whenever crystallised from cold solutions; but that when citric acid is crystallised from hot saturated solutions it contains only half a molecule of water. In the citric acid trade, however, the crystallised acid is reckoned as containing only half a molecule of water, and all analyses of lemon-juice and citrate of calcium are reckoned on this assumption. As it is clearly of great importance to the manufacturer to have a correct knowledge of the amount of water in the citric acid he produces, I have determined from time to time the amount of water in the citric acid made in our factory, the trials extending over several years, and being made on wholly different bulks of acid. I have also lately examined the citric acid of other London makers. The water expelled at 100° has varied from 8·46 to 9·35 per cent. as its extreme ranges, the mean of 17 determinations was 8·72 per cent. Theory requires for one molecule of water 8·57 per cent. There can be no doubt, therefore, that the commercial acid contains one molecule of water of crystallisation, corresponding with the formula—

$$C_6H_8O_7,H_2O.$$

The citric acid liquors in our factory do not begin to crystallise till they have nearly reached the temperature of the air.

The best way of determining water in citric acid is to heat the powdered acid for some hours at 50°—60°, and gradually raise the temperature to 100°. If this precaution be neglected, the acid partially melts, and has to be kept many days in the water-bath before it ceases to lose weight; the acid in this case darkens a little, and high results for water are obtained. The high results mentioned above are apparently due to this cause.

In making the determinations of water just mentioned, I have observed a difference in the facility with which citric acid parts with water, which I am unable to explain.

According to Berzelius, the ordinary crystals of citric acid remain unchanged in the air, but lose 9 per cent. of water in dry air at from 28°—35°. According to Marchand, the crystals lose the whole of their water in a vacuum over oil of vitriol at 16°. In the first determination I made, in December, 1868, the powdered acid lost the whole of its water by standing a few days over oil of vitriol. In September, 1871, powdered citric acid was again placed over oil of vitriol, and this time in a vacuum; it lost in several days but ·10 per cent., and in a duplicate experiment by Mr. Grosjean nothing was lost. This acid heated to 100° lost the normal amount of water. In February, 1873, the citric acid operated on lost, in four experiments, from nothing to ·20 per cent. in 5 days over oil of vitriol, but at 100° parted with the normal amount of water. In May, 1875, in complete contradiction to the latter results, samples of our own acid, and of other London makers, lost the whole of their water (8·57 per cent.) by standing 4—6 days over oil of vitriol at 17°—18.° In all the above experiments different specimens of citric acid were employed. The difference in the results can hardly be owing to difference of temperature, as the citric acid lost water in December, and did not lose in September. I propose, however, to put this question beyond doubt, by keeping the last-named specimens, and placing them again over oil of vitriol in winter time.

A strong solution of citric acid, like many other solutions, suffers considerable contraction when mixed with water. 500 volumes of a solution of 1·2709 sp. gr. (bright liquor of the factory), required the addition of 503·61 vols. of water to produce 1,000 vols. after mixing. 250 volumes of the same solution required 753·24 vols. of water to produce 1,000 vols. No rise in temperature was observed in either of the mixings; the rise, if any, could not have exceeded ½° C.

Free citric acid cannot be very exactly determined by neutralisation with standard alkali, as it gives no sharp reaction either with litmus, cochineal, or logwood. When litmus solution is mixed with citric acid, and standard alkali is slowly added, the colour, towards the conclusion of the reaction, changes in a perfectly gradual manner, comparatively large additions of alkali being required to produce small changes in colour. When the point is reached at which litmus paper is no longer affected, it will be found that the amount of alkali used is a little less than that required by theory to form trisodic citrate. The more delicate the litmus paper, the nearer does experiment approach theory, but I have never found the theoretical quantity of alkali to be quite reached even with the most delicate paper. For the above reason, the value of the alkali in citric acid should always be determined by experiment with the litmus paper that is to be subsequently used. For this purpose, the crystallised acid is to be powdered, water determined in one portion, and an experiment made with alkali and litmus in another portion.

Lemon, Bergamot, and Lime Juice.—Nearly the whole of the citric acid manufactured in this country is made from concentrated lemon-juice exported from Sicily and South Italy. Concentrated bergamot-juice from South Italy is also exported for this purpose. The lime-juice of the West Indies is chiefly used as a beverage; small quantities of concentrated lime-juice are exported from Montserrat and Dominica for the manufacture of citric acid.

All the fine and perfect fruit of the Italian lemon orchards is exported as lemons; the windfalls, and the damaged fruit are used for the production of essence and juice. About 13,000 lemons are required to make one pipe (108 gallons) of raw juice. The lemons are most acid at the beginning of the season. Sicilian lemon-juice pressed in November will contain about 9 ozs. of free citric acid per gallon;* this amount will gradually diminish as the pressings proceed, so that the juice obtained at the end of the following April will contain only about 6 ozs. per gallon. Three samples of Sicilian juice gave me 9·33, 8·82, and 8·21 ozs., and a sample of Naples juice 8·75 ozs. of free citric acid per gallon. The quantity of free acid in lemon-juice pressed in England is much higher. Various samples of English pressed juice have given me 13·03, 12·77, 11·84, and 10·91 ozs. of free acid per gallon; the last-mentioned sample was pressed at the end of May. The greater acidity of the English pressed juice is probably due to its being obtained from fine fruit: we shall shortly have to remark other differences between English and Italian pressed juice. The specific gravities of the first and third samples of English juice were 1·040, and 1·033 respectively.

Lemon-juice is imported for citric acid manufacturers in a concentrated state. It is boiled down in copper vessels over an open fire till it is supposed to mark when cold 60° on the citrometer; it is then a syrupy liquor of a dark brown colour, and is imported in this condition. The concentrated juice will occupy about $\frac{1}{9}$th or $\frac{1}{10}$th the bulk of the raw juice.†

In the early days of the citric acid manufacture, concentrated lemon-juice was purchased on the basis of its specific gravity as indicated by the citrometer. As to the origin of this instrument, or the values originally given to its scale, I have been unable to procure any information. On our own citrometer—

60°	correspond with	1·2394	sp. gr.
50°	,,	1·2003	,,
40°	,,	1·1598	,,

I conclude from these figures that 1° on the citrometer scale is intended to correspond with ·004 sp. gr., and consequently 60° are equivalent to a gravity of 1·240.

The purchase by specific gravity was open to many frauds; bergamot-juice, which has a high gravity but low acidity, was mixed with

---

* In all analyses contained in this paper in which quantities of citric acid are mentioned, the acid will be expressed as the crystallised acid, containing one molecule of water. The relation between the crystallised acid and the nominal acid, in terms of which commercial analyses are usually stated, is 70 : 67.

† For information respecting Sicilian lemon-juice, and its preparation in that country, I am indebted to Gardner, Rose, and Co., of Palermo; to H. T. Hodgson, Esq., and to my friend, Mr. Grosjean.

lemon-juice; sea-water was also added to the juice during the process of concentration. Lemon-juice is now generally purchased on the basis of its acidity. In the case of concentrated juice the acidity is conveniently determined by diluting 50 c.c. of the juice to 500 c.c., and then taking for experiment 30 c.c. of the solution. Standard alkali is added in quantity about $\frac{5}{6}$ths of that which will be required, the whole is then boiled for a few minutes, and when quite cold the titration is completed. With unconcentrated juice 10—20 c.c. of the original juice may be taken.* Owing to the want of sharpness of the reaction of citric acid with litmus paper, the determination does not admit of very great nicety; experiments with concentrated juice cannot be expected to agree nearer than $\frac{1}{4}$ oz. of citric acid per gallon.

Concentrated lemon-juice is considered to be of standard quality when it contains free acid equal to 64 ozs. of nominal citric acid per gallon (66·87 ozs. crystallised). In bygone years the acidity was usually as high as 71 or 72 ozs. of the crystallised acid, it is now often under 62 ozs., the juice being probably less boiled than formerly. The extreme ranges I have met with are from 56·6 to 72·6 ozs.

Concentrated bergamot-juice is far less acid than lemon-juice; it usually contains about 51 ozs. of free acid per gallon, the range I have noticed has been from 49·4 to 55·5 ozs.

The acidity of raw lime-juice is about equal to that of English pressed lemon-juice. Two samples from Montserrat gave me 12·46 and 11·91 ozs. of free acid per gallon. Another sample, representing 11,000 gallons from the Sandwich Islands, gave 12·24 ozs. Concentrated lime-juice is a thick viscid fluid, exceeding concentrated lemon-juice both in density and acidity.†

Besides the acids in a free state, lemon-juice contains organic acids as salts of the alkalis and alkaline earths. The quantity of combined acid which a sample of juice contains may be ascertained very simply

---

* In calculating analytical results for commercial purposes, it is a golden rule to remember that grams per 10 c.c. are the same as pounds per gallon.

† The following data have been kindly furnished by friends:—Mr. G. H. Ogston informs me that the average of his analyses of concentrated lemon-juice, representing 3,288 pipes sold in 1873–75, is sp. gr. 1·2376 (extremes 1·2059—1·2569); acidity 63·2 ozs. (extremes 58·8—70·6). The average of 531 pipes of bergamot-juice was, sp. gr. 1·2616 (extremes 1,2239—1·2516); acidity 51·3 ozs. (extremes 47·4—55·0). Messrs. Sturge (to whom I am indebted for much information), have supplied me with the analyses made by Messrs. Evans, Sons, and Co., of the raw lime-juice exported from Montserrat, 1870–74. The mean sp. gr. was 1·0365 (extremes 1·035—1·040); the mean acidity 12·34 ozs. (extremes 10·63—13·48). The concentrated lime-juice from Montserrat, 1870–75, has averaged, according to Mr. Ogston's analyses, sp. gr. 1·3249 (extremes 1·2840—1·3792); acidity 93·6 ozs. (extremes 82·6—112·7)

by evaporating in a platinum basin the portion of juice which has already been used for the determination of the free acid, and which is consequently exactly neutralised with caustic soda. The residue left on evaporation is heated gradually, and at last reduced to charcoal at a low red heat. The ignited mass is treated with water and removed to a beaker, a known quantity of standard sulphuric acid added from a pipette with the proper precautions, the whole boiled and filtered, and the unneutralised sulphuric acid in the filtrate determined by standard alkali. We have now the neutralising power of the ash in terms of alkali; by deducting from this the amount of alkali used in neutralising the free acid of the juice, we obtain the alkali corresponding with those bases of the juice which during ignition became carbonates; the equivalence of this alkali in citric acid can then be calculated. In making this calculation the theoretical value of the alkali in citric acid must be used, and not the value obtained by experiment with the free acid. The method here given is more accurate than if the original juice were burnt, and the carbonates of the ash determined, as the free citric acid would in this case decompose during evaporation the chlorides present, and produce citrates which the original juice never contained.

Two samples of English pressed lemon-juice gave in each case ·30 oz. of combined acid per gallon, amounting respectively to 2·31 and 2·70 per cent. of the total organic acids (free plus combined) present. In a sample of concentrated juice, prepared in the laboratory from English pressed lemons, the combined acid was 2·25 ozs., or 3·17 per cent. of the total acids. The amount of combined acid in the less acid lemon-juices pressed in Italy is however much greater. The sample of raw Naples juice already mentioned contained ·85 oz., or 8·95 per cent. of combined acid, and a sample of raw Sicilian juice ·60 oz., or 6.73 per cent., and the quantity found in the latter case must have been below the truth, as the juice had been heavily sulphured in order to preserve it. When we turn to the concentrated lemon-juice exported from Sicily, we find it agrees in character with the two analyses last quoted, and not with English pressed juice. In the following table the quantity of the free and combined organic acids, and the relation of the latter to the total acid, is shown for sundry samples of concentrated juice belonging to the seasons 1870–71 and 1872–73. Both free and combined acid are here reckoned as citric acid, the question of the nature of the acids will be discussed presently.

Organic Acids in Concentrated Lemon-juice (ounces per gallon).

Season 1870–71.			Season 1872–73.		
Free acid (ounces).	Combined acid (ounces).	Combined per 100 of total acid.	Free acid (ounces).	Combined acid (ounces).	Combined per 100 of total acid.
60·20	7·81	11·47	63·64	8·01	11·17
65·43	8·33	11·29	63·81	7·94	11·06
64·90	7·98	10·94	63·81	7·53	10·55
65·96	8·04	10·85	64·11	7·42	10·37
67·05	7·53	10·09	63·80	7·36	10·33
65·43	7·16	9·86	65·61	7·52	10·28
66·73	7·04	9·54	65 61	6·17	8·59
67·86	4·56	6·30	62·91	5·74	8·37
70·41	1·93	2·67	—	—	—

The quantity of combined organic acid in concentrated lemon-juice is seen to be very uniformly 7—8 ozs. per gallon. The mean proportion of the combined to the total acids is 10·06 per cent., if we omit the analysis at the foot of the table. This proportion is far higher than that found in English pressed lemon-juice. It is certainly puzzling to find that the English and Italian pressings of lemons coming, as we believe, from the same districts, should exhibit so great a difference in character; the evidence seems to show that the juice obtained in Italy by pressing inferior fruit is both considerably poorer in free acid, and richer in combined acid, than the juice obtained in England from fine lemons. The analysis given at the bottom of the table agrees, however, with English juice; we may suppose that in this instance fine lemons had been used.

During the process of concentrating juice, the proportion of combined acid must somewhat increase, as in this process there is some loss of free acid, but no loss of bases. If ordinary concentrated juice be long kept, a white deposit, sometimes considerable, of citrate of calcium is produced; such juice will be found to have decreased considerably in specific gravity, and in the amount of combined acids present, while the free acid remains unchanged. When the price of juice is rising, pipes of juice may be stored for a considerable time before they come to market, during this time citrate of calcium may be deposited, and thus differences in the composition of juice may arise.

Concentrated bergamot-juice contains about the same quantity of combined acid per gallon as lemon-juice; three samples gave 7·77, 7·69, and 7·54 ozs. respectively; the proportion of combined to total acid is, however, higher, owing to the low acidity of bergamot-juice; the proportion in these cases was 13·01, 12·90, and 12·12 per cent.

Raw lime-juice appears to contain about the same quantity of combined acid as lemon-juice, the quantity being variable, as in lemon-juice. The sample from the Sandwich Islands, already referred to, gave ·41 oz., and the two samples from Montserrat, ·63 and ·66 oz. per gallon, or, respectively, 3·21, 5·01, and 5·04 per cent. of the total organic acids present. Three samples of concentrated juice from Montserrat gave a mean of 8·60 ozs. per gallon of combined acid, or 7·36 per cent. of the total acids. A sample of very acid concentrated juice from Dominica contained only 4·61 ozs. of combined acid, or 3·93 per cent. We have evidence in these figures that, as in the case of lemon-juice, a distinct increase in the proportion of combined acid results from concentration.

The direct determination of citric acid in lemon-juice is clearly a great desideratum to the manufacturer. I am not acquainted with any general method by which citric acid can be separated from other organic acids; there is, however, no difficulty in determining the amount of insoluble organic lime salt which can be obtained from lemon-juice; and as the lime salts of malic and aconitic acid are readily soluble, and the same is true of the lime salts of the volatile acids of the acetic series, such a determination will probably give with sufficient exactness the quantity of citric acid present. The mode of operating is very simple. 15—20 c.c. of unconcentrated lemon-juice, or a quantity of concentrated juice equal to about 3 c.c., is exactly neutralised with pure caustic soda; the solution, which is about 50 c.c., or is concentrated to that bulk, is brought to boiling in a salt-bath, and so much solution of chloride of calcium added as is known to be rather more than sufficient for the total organic acids present; the whole is then boiled for half-an-hour. The precipitate is collected and washed with hot water. As citrate of calcium is rather soluble in water, the filtrate and washings are to be concentrated in the salt-bath to about 10—15 c.c., the solution being finally neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is to be collected on a very small filter, the filtrate being used to transfer the precipitate to the paper, and the precipitate receiving only five or six washings with hot water. As a matter of precaution, the filtrate and washings may be evaporated a third time in the salt-bath. The precipitates, with their papers, are then burnt at a low red heat in a platinum basin, and the neutralising power of the ash determined by appropriate treatment with standard hydrochloric acid and alkali. This alkalimetric determination of the lime-salt is more accurate than if the precipitates were weighed, since, for the purpose of weighing, all the precipitates must be thoroughly washed, and consequently citrate of calcium lost, while, on the present plan, the last precipitate need not be thoroughly washed, the chloride of sodium remaining in it having no influence on the neutralising power of the ash. Precipitated vegetable matter is also clearly without influence on the result. Working in this way, and calculating the precipitated calcium salt into its equivalent in citric acid, the following results were obtained :—

A sample of English juice, pressed in January, yielded citric acid equal to 99·60 per cent. of the total organic acids (free acid plus combined) present. Another sample, pressed in May, yielded 98·97 per cent. A sample of concentrated juice, prepared in the laboratory some years before from English pressed juice, gave 97·06 per cent. A sample of Sicilian unconcentrated juice gave only 91·71 per cent. Two samples of Sicilian concentrated juice of the season 1871–72 gave, respectively, 92·98 and 94·57 per cent. Three samples of the season 1872–73 gave 88·75, 89·36, and 91·91 per cent. It appears, then, that in English pressed juice the organic acids other than citric do not amount to more than 1 per cent. of the total organic acids present; while in concentrated juice from Sicily they amount to 5—11 per cent. The single specimen of unconcentrated Sicilian juice agreed with the concentrated Sicilian juices, containing 8·29 per cent. of organic acids other than citric. The Italian juice, which we have seen to be so much richer in combined acid, is thus also richer in certain organic acids yielding soluble calcium salts, than the juice pressed in England from fine lemons.

Two samples of concentrated bergamot-juice contained 87·24, and 88·95 of precipitable acid, for 100 of total organic acid.

The raw lime-juice from the Sandwich Islands gave 92·31, and the two Montserrat juices 91·75 and 89·64 per cent. of precipitable acid. Three concentrated juices from Montserrat, of the same season as the raw juice just mentioned, gave 86·98, 88·16, and 90·40, and the Dominica concentrated juice 89·12 of precipitable acid for 100 of total organic acid.

It appears, then, that in all these juices, there is a far greater quantity of non-precipitable acid than exists in English pressed lemon-juice. Another point brought out is that the proportion of non-precipitable acid is very similar in raw and concentrated juice, and is apparently but slightly increased by the process of concentration.

It is important to compare the citric acid found by the method of precipitation with the citric acid calculated by the ordinary method from the acidity of the juice. The following table gives the proportion of precipitable acid to that calculated from the acidity :—

Nature of Juice.	Precipitable for 100 of acidity.	Nature of Juice.	Precipitable for 100 of acidity.
Lemon-juice.		*Bergamot-juice.*	
Raw, English..........	102·0	Concentrated, Italian....	101·2
,, ,, ...	101·7	,, ,, ...	100·2
,, Sicilian..........	98·3	*Lime-juice.*	
Concentrated, English...	100·2	Raw, Sandwich Islands..	95·4
,, Sicilian...	103·7	,, Montserrat.......	96·6
,, ,, ...	103·0	,, ,, ...	94·4
,, ,, ...	102·5	Concentrated, Montserrat	97·2
,, ,, ...	99·7	,, ,,	95·5
,, ,, ...	99·2	,, ,,	93·9
		,, Dominica.	92·8

It appears from these figures that the ordinary method of determining the value of juice from its acidity gives tolerable results in the case of lemon and bergamot juice, but that with lime-juice such results are too high.

Having thus limited the amount of the other organic acids present in lemon-juice, we pass next to a consideration of their nature. It is well known that lemon-juice suffers loss of acidity by concentration. In 1868 some English pressed juice was concentrated in the laboratory to one-sixth its bulk over a water-bath; it lost in this operation 3·5 per cent. of its acidity.* We must not conclude, however, that the whole of this loss is due to the presence of volatile organic acids, as hydrochloric acid is doubtless expelled by the action of citric acid upon chlorides.

That concentrated juice should contain any considerable amount of volatile acids seems unlikely from the mode of its preparation. Some concentrated Sicilian juice was mixed with water, and distilled in the salt-bath till the juice was reduced to about 70 per cent. of its original volume. The juice was again diluted with water, and again reduced by distillation to the same volume, and this operation was repeated four times. The last distillate contained only one-fifth the acidity of the first distillate. If we assume that the amount of acid in the distillate would have continued to diminish in the same ratio, it is easy to calculate the amount of the volatile acid present. Calculating on this assumption, the amount of volatile acid was 1·25 per cent. of the acidity of the juice, or about 1·12 per cent. of the total organic acids present.

The distillates were purified by redistillation, and then examined

---

* The concentrated juice thus obtained was of excellent quality, containing 68·91 ozs. of free acid per gallon; it marked the exceedingly low gravity of 49° on the citrometer. This juice deposited nothing in five years.

qualitatively. Formic acid was at once detected by the speedy reduction of nitrate of silver even in the cold. The weak acid solution was neutralised with oxide of silver, the formate destroyed by boiling, and the filtered solution concentrated and allowed to crystallise over oil of vitriol. Star-like groups of opaque white crystals were first formed; afterwards the deposit consisted merely of white crusts. These silver salts treated with sulphuric acid gave the characteristic odour of acetic acid, but not in its purest form. A little propionic acid was probably present.

It is clear from the facts now stated, that the organic acids other than citric which occur in concentrated juice are chiefly non-volatile, and have soluble calcium salts. I have spent some time in endeavouring to determine the nature of the acid or acids in question, but from the short supply of material, and the difficulty of the subject, I did not obtain more than qualitative indications. I am happy to say that Dr. Armstrong has very kindly undertaken the further investigation of the subject, which I have no doubt will, in his hands, be brought to a successful issue.

Before leaving the subject of lemon-juice, we may refer to the fact of its not being neutralised by chalk. There is no difficulty in neutralising pure citric acid with chalk, but lemon-juice, and especially commercial concentrated juice, remains unneutralised even after long boiling with chalk. The neutralisation is more perfect when chalk is added in excess to cold juice than when it is added to hot juice; in the former case a part of the chalk is dissolved by the carbonic acid set free, and probably acts more energetically than solid chalk. English pressed juice can generally be perfectly neutralised by chalk in the cold, but not at a boiling heat.* The neutralisation in the cold is not destroyed by subsequent boiling. With commercial concentrated juice neutralisation cannot be effected, even in the cold, but there is a nearer approach to neutralisation under this condition. In nine cases in which the unneutralised acidity was determined, which remained when diluted concentrated juice was heated with excess of chalk on a manufacturing scale, the amount varied from 1·11 to 2·52 per cent. of the original acidity of the juice. I believe, however, that the unneutralised acidity is sometimes less than this minimum.

The fact of the imperfect neutralisation by chalk has been variously explained. In Richardson and Watts's *Chemical Technology* it is stated to be owing to the presence of alumina in the juice. I have not, however, been able to detect alumina in lemon-juice. Moreover, when alumina or ferric oxide is dissolved in citric acid, the solution can be easily neutralised with chalk. I find, however, that if phosphoric acid, or phosphate of iron or aluminium, be dissolved in citric acid, the solu-

---

* I have known a few samples which neutralised at a boiling heat.

tion is not neutralised by chalk. We shall consider this reaction more fully by-and-bye. It suffices at present that juice contains a good deal of phosphoric acid and a little iron. It is probable, therefore, that a part of the unneutralised acidity may be due to their action. Several other explanations are possible. It has been noticed by several chemists that malic acid is not neutralised when boiled with chalk. I am able to confirm this statement. Malic acid after long boiling with excess of chalk is still strongly acid. Aconitic acid appears to have a similar property, though I do not find the fact mentioned in the manuals. If citric acid be slowly heated to 170°, and kept for some time at that temperature, it loses water, and aconitic acid is produced. If the resulting mass is dissolved in water and boiled with excess of chalk the solution remains strongly acid, though the original citric acid could be perfectly neutralised by chalk. Since, according to Dessaignes, some aconitic acid is formed when solution of citric acid is long boiled, it may clearly be produced during the rough concentration of the juice in Sicily; or aconitic acid may occur in lemons ready formed, as it is known to do in aconite.

Citrate of Calcium.—The formula of citrate of calcium dried at ordinary temperatures is, according to *Gmelin's Chemistry*, $C_{12}H_{10}Ca_3O_{14}$, $4H_2O$, and when dried at 100°, $C_{12}H_{10}Ca_3O_{14},H_2O$. On igniting some specimens of citrate of calcium dried at 100°, I found that they always gave less lime than is required by the above formula. The lime determinations given in *Gmelin* are also below the amount required by theory. With the object of explaining these facts, my friend Mr. B. J. Grosjean and myself have made a number of water determinations in citrate of calcium artificially prepared. We find that the amount of water in different samples of citrate dried at 100° varies very considerably, apparently according to the conditions under which the specimen has been prepared. The particulars of three of the citrates examined are as follows:—

I. Neutral citrate of sodium was treated in the cold with chloride of calcium, in quantity slightly insufficient for the citric acid, and the mixture made faintly alkaline with ammonia. Precipitation commenced in about twenty minutes, and was complete in two hours. The precipitate was washed with cold water, and dried at a low temperature.

II. A solution of neutral citrate of sodium was brought to boiling, and an equivalent quantity of chloride of calcium in solution slowly added. The precipitate was washed with hot water and partially dried.

III. A dilute solution of citric acid was neutralised with lime-water, the whole brought to boiling, the liquor decanted from the precipitate, which was partially dried without washing.

The citrates thus prepared were heated in the water-bath till they ceased to lose weight, were next dried at 200°, and finally burnt, and the lime determined with standard hydrochloric acid and alkali. The percentage results obtained were as follows:—

	Water retained at 100°.	Lime at 100°.	Lime at 200°.
Citrate of calcium I................	5·91	—	—
,, ,, ...	5·90	31·16	33·11
Citrate of calcium II................	7·68	30·96*	33·53
,, ,, ...	7·66	31·07	33·65
Citrate of calcium III................	6·25	31·46	33·56
,, ,, ...	6·38	31·65	33·80

The percentage of lime at 200° proves the samples to be normal citrates, anhydrous tricalcic citrate containing 33·73 per cent. As the first two citrates might possibly contain some soda in place of lime, one lime determination was made with oxalate of ammonium. Tricalcic citrate with one molecule of water would contain 3·49 per cent., with two molecules 6·74, and with three molecules 9·78 per cent.

It is seen that in no case does the water existing in citrate of calcium dried at 100° fall as low as one molecule, nor does it in any case reach three molecules; and this is true of several determinations of water made in other citrates not here recorded. In the case of the citrate prepared directly with citric acid and lime-water, the percentage of water is very nearly two molecules. The cause of the variations here indicated demands further investigation.

That citrate of calcium is more soluble in cold than in hot water has been generally noticed, but I do not know that any quantitative determinations of its solubility have been made. Crystalline citrate of calcium, prepared by neutralising citric acid with lime-water and boiling, gave at 14° a solubility of 1 part (dried at 100°) in 1,133 of water, and at a boiling heat a solubility of 1 in 1,754. Another specimen of citrate prepared by slowly adding pure carbonate of calcium to a hot solution of citric acid, gave at 14° a solubility of 1 in 1,223, and at 90° a solubility of 1 in 1,784. A third specimen of citrate, prepared by slowly adding citric acid to carbonate of calcium diffused in hot water, gave at 14° a solubility of 1 in 1,183, and at 90° a solubility of 1 in 1,652. A fourth specimen of citrate, prepared in the factory in the ordinary process of adding lemon-juice to chalk, gave at 18° a solubility of 1 in 707, and at a boiling heat a solubility of 1 in 1,123. The first three specimens give fairly accordant results; the mean solubility is 1 in 1,180 at 14°, and 1 in 1,730 at 90°—

* Determined as oxalate.

100°. The fourth specimen has a decidedly higher solubility, and illustrates Liebig's remark that amorphous citrate is more soluble than crystalline citrate.

It is stated in *Gmelin's Chemistry*, and the remark reappears in recent manuals, that the solubility of citrate of calcium in ammonium salts is so great, that if the citrate be dissolved in hydrochloric acid and ammonia added, no precipitate takes place unless the solution is boiled. The fact however is that the citrate of calcium is precipitated very perfectly in the cold, if sufficient time is allowed, and even when considerable quantities of chloride of ammonium are present. If citrate of calcium be dissolved in dilute hydrochloric acid, and ammonia added in excess, precipitation will commence in a few minutes if the solution is pretty strong, but takes many hours to complete. With large quantities of ammonium salt the precipitate may not commence for some hours, and takes several days to complete. The citrate falls under these circumstances in curious curled crusts and arborescent forms. Citrate of calcium is never precipitated immediately on the addition of ammonia, as is often the case with tartrate of calcium.

For many years citrate of calcium has from time to time come into the market as a material for the manufacture of citric acid; it is prepared by adding chalk or lime to lemon-juice, the chalk or lime being usually added in excess. Besides the excess of carbonate or hydrate of calcium thus introduced, the citrate may contain carbonate due to the decomposition of the citrate; this decomposition readily takes place if more than 12 per cent. of water is present.

Commercial citrate may be conveniently analysed by an alkalimetric method. The excess of chalk or lime is first determined by adding to about 4 grams of the citrate a known quantity of standard hydrochloric acid, boiling gently in a covered beaker, and when the whole is quite cold, determining the excess of acid remaining with standard alkali. It seems safer to add the alkali till delicate-red litmus paper assumes a decided blue tint, and then to deduct the amount of alkali necessary to produce the same tint on the paper in a similar bulk of water; by this precaution we insure the citrates returning to the tribasic state. Two grams of the citrate are next gently ignited in a covered platinum crucible, the ash obtained is boiled in a covered beaker with standard hydrochloric acid, filtered when quite cold, and the excess of acid determined with alkali. The neutralising power of the ash in units of alkali is thus ascertained; by subtracting from this figure the alkali corresponding with the excess of chalk or lime in two grams of the citrate, we obtain the amount of alkali which corresponds with the citrate of calcium present. This method is very speedy and convenient, but of course assumes that citric acid is the only organic acid present.

If it is desired, one can ascertain, as in the case of juice, the amount of organic acid forming insoluble lime salt. For this purpose the citrate is dissolved in a small quantity of hydrochloric acid, filtered, the filtrate exactly neutralised with caustic soda, and boiled in the salt-bath, the further operation being conducted as already described under the head of juice. If it is uncertain what bases are present, and citrate from Sicily is sometimes prepared with lime burnt from dolomite, this is no obstacle to the alkalimetric method; but if the insoluble lime salt is to be determined, the citrate must in this case be first decomposed by boiling with carbonate of sodium, the solution filtered, neutralised with hydrochloric acid, and precipitated with chloride of calcium in the salt-bath; this method is, however, not so good as the two preceding.

The best sample of commercial citrate I have met with has contained 72 per cent. of citric acid, and this is about the highest percentage that can be reached when the citrate contains no excess of chalk, and has also been thoroughly dried. Commercial citrate that has been insufficiently dried may contain scarcely any citric acid, as citrate of calcium prepared from juice rapidly decomposes when in a moist condition.

Citric Acid Liquors.—The analysis of the solutions of citric acid met with in a citric acid factory is generally performed by determining the acidity, and the amount of sulphuric acid present, then subtracting the acidity due to the sulphuric acid, and calculating the remaining acidity as citric acid. This method plainly assumes that citric and sulphuric acids are the only acids present; this is certainly not true of all liquors, but the method in question, when applied to the better class of liquors, certainly gives results which the practical working of the solutions amply confirms.

To perform the analysis correctly, it is clearly necessary to determine the free sulphuric acid, and not the total sulphuric acid present. For this purpose 10—20 c.c. of the liquor are poured into five times their volume of strong alcohol, thoroughly mixed, and left at rest for twelve hours. A portion of the clear liquor is then treated with more alcohol, and if opalescence is produced, the whole is treated in the same way. When a further addition of alcohol produces no change, the whole is filtered, and the precipitate washed with spirit. The filtrate and washings are then precipitated with an alcoholic solution of chloride of calcium. The sulphate of calcium thus obtained is exceedingly troublesome to filter; at first it passes through Swedish paper, and finally chokes the filter so that it can scarcely be washed. By a simple artifice, however, this precipitate may be converted into a highly crystalline substance. For this purpose the precipitate is allowed completely to subside, the supernatant liquor poured away, and the precipitate and small quantity of remaining liquor gently warmed. When the whole has become pasty, a little water is added; when this has evaporated, a little more water is added, and warming continued. The alcohol being thus gradually replaced by water, the precipitate soon becomes highly crystalline, changing into gypsum; when this is accomplished, alcohol is added and the precipitate collected. The operation should be carried out at a very gentle heat, and the mass never allowed to become dry.

Another method of analysing citric acid liquors is to neutralise with pure soda, evaporate in a platinum basin, ignite the residue, and determine the neutralising power of the ash with standard sulphuric acid and alkali. This method gives all the organic acids calculated as citric. In order to be perfectly accurate, it is necessary that the *whole* of the ash should dissolve in the sulphuric acid, and if iron or aluminium be present, sufficient neutral citrate of sodium should be added to the sulphuric acid solution to prevent any precipitate being formed on neutralisation with standard alkali: see determination of total organic acids in tartaric liquors. The two methods here described have agreed perfectly in their results when applied to the ordinary liquors of the factory.

In determining the amount of citric acid present in old liquor, the citric acid should undoubtedly be separated in the form of calcium salt, as in this case other organic acids are most probably present. The liquor is for this purpose exactly neutralised with soda, and precipitated with chloride of calcium in the salt-bath, as directed in the analysis of lemon-juice. The mixed precipitate of sulphate and citrate of calcium is ignited at a low temperature, and the citric acid calculated from the neutralising power of the ash.

Tartaric Acid.—Crystallised tartaric acid is allowed by all to have the formula $C_4H_6O_6$, it suffers no loss at 100°. In reporting analyses of tartar, &c., it is usual to express the tartaric acid in terms of the crystallised acid.

Strong solutions of tartaric acid contract on mixing with water even more than citric acid liquors. 500 volumes of a solution of sp. gr. 1·338 (bright liquor of the factory) required 505·508 volumes of water to produce 1,000 volumes. 250 volumes of sp. gr. 1·3387 required 754·472 volumes of water to produce 1,000. As in the experiments with citric acid no rise in temperature was observed on mixing, the rise at least did not exceed $\frac{1}{2}$° C.

Free tartaric acid can be determined without difficulty by titration with caustic alkali, the final reaction with litmus being much sharper than is the case with citric acid, though distinctly less sharp than with hydrochloric or sulphuric acid. The value of alkali in tartaric acid may be determined indifferently by direct experiment with tartaric acid, or by calculation from the value in sulphuric or hydrochloric acid.

Qualitative reactions of Tartaric, Metatartaric, and Ditartaric Acid.—With the view of distinguishing between tartaric acid, and the acids which it yields on the application of heat, some qualitative experiments were made with the fused acid.

When dry tartaric acid is carefully melted, a mixture of metatartaric and ditartaric acid is produced. I do not think it is possible to melt the dry acid without producing some ditartaric acid; the formation of this acid is readily shown by the alteration in the neutralising power of the mass. Half a gram of powdered tartaric acid, requiring 50 c.c. of alkali for its neutralisation, was spread on a watch-glass, dried at 100°, and then heated in an oil oven for six minutes at 172°, it had then just begun to fuse at the edges. Redissolved in water, it took 49·4 c.c. of alkali for neutralisation. Another half gram heated to perfect tranquil fusion, the temperature not exceeding 174°, required, when redissolved, 41·8 c.c. of alkali. A third half gram heated for half-an-hour at 176°—182°, swelled up a good deal, and when redissolved required only 31·3 c.c. of alkali for neutralisation.

When a solution of the fused acid* is neutralised with soda and boiled, it becomes powerfully acid; the acidification is more rapid when chloride of calcium is added. If the acidity is neutralised from time to time, and boiling continued, it will be found that the total alkali consumed by the fused acid is equal to that required previous to fusion, the whole of the ditartaric acid being reconverted into metatartaric or tartaric acid. In the second experiment mentioned above, the total acidity neutralised in an hour's boiling, after addition of chloride of calcium, was 7·8 c.c. (41·8 + 7·8 = 49·6).

A solution of fused tartaric acid is readily and completely neutralised by chalk in the cold, but at a boiling heat it is very difficult to neutralise, the continual splitting up of the ditartrate of calcium producing a fresh acidity.

If acetate of calcium is added to a pretty strong solution of fused tartaric acid, a flocculent precipitate is formed, which, on heating, agglutinates, becomes perfectly plastic, and in its purest form can be drawn out into transparent threads. If the solution of the acid be weak, acetate of calcium produces no immediate precipitate, but if alcohol is added a bulky precipitate is produced, which on heating agglutinates and becomes plastic as before. Solutions of fused tartaric acid, treated with excess of calcium acetate, also produce on standing a crystalline precipitate of calcium metatartrate.

---

* The acid employed in all these experiments was powdered tartaric acid, heated till complete tranquil fusion was attained, and no longer; tartralic acid was therefore probably not formed.

The plastic precipitate is, I believe, ditartrate of calcium. It is easily soluble in cold water, and the solution neutralised with soda and boiled becomes strongly acid. A further proof is afforded by the fact, that if a pretty strong solution of fused tartaric acid is treated with excess of potassium acetate, and the metabitartrate precipitated and filtered off, the filtrate gives the reaction of the plastic salt quite plainly, but the metabitartrate dissolved in dilute nitric acid gives with acetate of calcium only a crystalline precipitate of calcium metatartrate. The statement of Braconnot that metatartrate of calcium can be obtained as a "viscid mass" (*Gmelin's Chemistry in loco*), I am inclined to think is erroneous, and that it was the ditartrate which he had in view.

Ordinary tartaric acid treated with acetate of calcium yields, even in dilute solutions, a crystalline precipitate of calcium tartrate. Free tartaric acid is also precipitated by chloride of calcium in the presence of alcohol; the fused acid is less easily precipitated. Most books on qualitative analysis state that free tartaric acid is not precipitated by any calcium salt.

I have frequently observed a curious form of tartrate of calcium, which does not appear to be noticed in the books; it occurs when the tartrate crystallises from cold dilute solutions which are at rest. The first crystals are usually of the ordinary kind, then tufts of long fine needles begin to appear, and exquisite stars and parachutes of needles are seen floating in the liquid. The growth of these needles may become so great that the solution is changed into a magma by their interlacing. But this form is not permanent, the needles soon begin to diminish, and in a day have generally altogether disappeared, leaving in their place only a small bulk of the ordinary salt. These needles appear in a variety of solutions. As I have observed them when only tartaric acid and lime-water have been present, I have no doubt that they are really tartrate of calcium, and not a double salt containing alkali. With metatartaric acid I once observed a similar formation, but as metatartrate of calcium changes somewhat easily into tartrate, I cannot be certain that the crystals were really metatartrate. Racemate of calcium crystallises under similar circumstances in feather-shaped crystals, quite distinct from the needles of the tartrate.

Barium tartrate also assumes a very characteristic form. If chloride of barium be added to dilute sodium or ammonium tartrate, or if barium acetate be added to tartaric acid, the precipitate is at first generally bulky and flocculent, but in a few hours this precipitate disappears, and the sides of the vessel become coated with clear globular masses. In *Gmelin's Chemistry* this is given as a reaction of metatartaric acid. I have only once obtained this reaction with fused tartaric acid, but have never failed of the result when using ordinary tartaric acid. Acetate of barium produces this salt even in a 1 per cent. solution of tartaric acid.

When acetate of lead is gradually added to a boiling solution of tartaric acid, the precipitate at first redissolves, and then suddenly comes down as a heavy precipitate of microscopic needles. With a solution of fused tartaric acid, the reaction is very different. A curdy precipitate is produced, which speedily shrinks into a mass which is plastic while hot, and brittle when cold. The solution crystallises on cooling; small rectangular, or nearly rectangular plates, is a common form of the crystals. During cooling clear globular masses are also sometimes deposited on the sides of the vessel. The same globular salt is obtained when a hot solution of the fused acid is treated with carbonate of lead not in excess, and the filtered liquor allowed to cool. It may also be obtained by precipitating a solution of the fused acid with acetate of lead in the cold, saturating dilute nitric acid with the washed precipitate, and pouring the nitric solution into boiling dilute acetate of ammonium; on cooling the globular salt is deposited. The globular salt redissolved in nitric acid yields the plastic salt in perfection on the addition of lead acetate. The following facts seem to prove that neither of these salts is a metatartrate. The plastic body decomposed with sulphuric acid yields a solution which neutralised with soda and boiled becomes acid. A solution of metabitartrate of potassium in nitric acid yields a curdy precipitate with acetate of lead, but the precipitate is scarcely coherent. The globular body is formed most freely when the tartaric acid has been kept rather long in fusion. A specimen of the globular salt, obtained by the carbonate of lead method, was dried over oil of vitriol; heated to 120° it lost 4·04 per cent., at 150° the total loss was 4·67 per cent.; it had then become slightly brownish. The oxide of lead, determined as sulphate, was 55·05 per cent. of the original salt, 57·37 per cent. at 120°, and 57·74 per cent. at 150°. I do not pretend to found a formula on this experiment; the results agree best with Frémy's tartralate of lead ($C_{16}H_{16}Pb_3O_{23}$), containing 56·0 per cent. of lead oxide. Frémy's tartralates are intermediate in composition between metatartrates ($C_8H_8M_2''O_{12}$) and ditartrates ($C_8H_8M''O_{11}$).

A solution of fused tartaric acid gives with acetate of potassium a precipitate of acid potassium metatartrate; in dilute solutions this precipitate forms far more slowly than in the case of tartaric acid; the precipitate is also more bulky, and less crystalline. Both the potassium and ammonium acid metatartrates are decidedly more soluble than the corresponding tartrates.

Tartrate of Calcium.—The neutral tartrate of calcium is known to have the composition, $C_4H_4CaO_6,4H_2O$; it is stated in *Gmelin's*

Chemistry to have the same composition when dried at 100°, though two out of the three analyses quoted show a higher percentage of lime. Finding that some tartrate of calcium obtained from old liquor contained only 1—1½ molecule of water after drying in the water-bath, I was led to inquire if this was also the case with normal tartrate of calcium.

Rochelle salt was precipitated with chloride of calcium, and the washed precipitate dried over oil of vitriol. The tartrate of calcium thus obtained lost 17·78 per cent. of its weight in the water-bath, and had not then quite ceased to lose; when removed from the bath it contained 11·0 per cent. of water. At 200° the total loss of water was 26·83 per cent.; the formula, $C_4H_4CaO_6,4H_2O$, requires 27·69 per cent.

As the tartrate experimented with above contained a little alkali, it was redissolved in cold hydrochloric acid, a little chloride of calcium added, and then ammonia in slight excess. On stirring, the tartrate of calcium came down as a perfectly white highly crystalline salt; it was thoroughly washed, and dried over oil of vitriol. Placed in the water-bath this tartrate lost in six hours 14·45 per cent., at the end of 24 hours the total loss was 15·97 per cent., and it was still losing weight very slowly. The salt was then ignited, and the lime determined as sulphate. By calculation it appeared that the salt dried over oil of vitriol contained 21·66 per cent. of lime; the formula, $C_4H_4CaO_6,4H_2O$, requires 21·54 per cent.; the substance used was thus the normal tartrate of calcium. After 24 hours in the water-bath the salt would contain, lime 25·78, and water (assuming the normal formula for the original salt) 13·94 per cent. The nearest formula to these numbers is $C_4H_4CaO_6,1\frac{1}{2}H_2O$, which requires 26·05 per cent. of lime, and 12·56 per cent. of water. It is evident, however, from the slowness with which the water was given off, that tartrate of calcium has no definite composition at 100°.

Commercial tartrate of calcium is best analysed by the oxalate of potash method: see determination of tartaric acid in lees, page 972.

Solubility of Bitartrate of Potassium.—The solubility of bitartrate of potassium in water has been determined by several observers. In my own experiments a refined tartar was used containing 99·33 per cent. of real bitartrate, with a little tartrate of calcium; this, though not chemically pure, is much purer than any cream of tartar. The amount of bitartrate dissolved was determined with standard alkali.

100 parts of water dissolved:—

at 14°	·431	parts bitartrate,	or 1 in 232,
at 22°	·600	,,	or 1 in 167,
at 80°	4·027	,,	or 1 in 25.

These numbers agree with those obtained by Chancel, whose results are for 14° ·434, and for 22° ·598 of bitartrate in 100 of water, but are below those obtained by Alluard, namely, ·468, ·636, and 4·500, and are still further below the numbers obtained by Kissel for the first two temperatures, namely, ·479 and ·657.* Supersaturated solutions of bitartrate of potassium are obtainable by cooling without agitation.

The solubility of bitartrate of potassium is greatly affected by the presence of certain salts. If to a cold saturate solution of the bitartrate, crystals of chloride, sulphate, or nitrate of potassium are added, a considerable precipitation of the bitartrate speedily takes place. The same effect follows the addition of Rochelle salt; but acetate and citrate of potassium, and chloride of sodium, produce no precipitate. By adding 1·86 grm. of chloride of potassium to 50 c.c. of cold solution of bitartrate, the solubility of the latter, as determined by acidity, fell in 24 hours to 1 in 2,981. With 2 grms. of sulphate of potassium, the solubility fell under the same circumstances to 1 in 2,019. With 2 grms. of nitrate of potassium to 1 in 1,728. With 2 grms. of Rochelle salt, the bitartrate dissolved after 24 hours was 1 in 1,063.† The solubility of the bitartrate was thus diminished to from $\frac{1}{13}$ to $\frac{1}{5}$th of its solubility in pure water of the same temperature.

Different acids also very differently affect the solubility of bitartrate of potassium. In a series of experiments on this subject, various dilute acids of nearly the same acidity were digested with excess of powdered bitartrate, the solutions filtered, and the increased acidity of the filtered solutions determined. The solubility of bitartrate in acetate and citrate of potassium was at the same time ascertained. For this purpose, solutions of acĕtic and citric acid of known acidity were exactly neutralised with solid caustic potash, then digested with excess of bitartrate of potassium, and the acidity of the resulting solutions determined.

The solubility of the bitartrate in water was also determined for comparison. The data and calculated results are shown in the following table. All the experiments were made at 14° C.

---

* The figures here given are in some cases not the result of experiment, but have been obtained by intercalation.

† Experiments on this small scale can be made with considerable accuracy if the number of drops of standard alkali required for neutralisation is made the basis of the determination. With our burette 24 drops equal 1 c.c., and 1 drop would suffice for the final reaction.

	Grams of acid or salt in 100 c.c.	Original acidity of solution.	Increase of acidity after digestion with bitartrate.	Grams of bitartrate dissolved in 100 c.c.
Water	—	—	8·5	·422
Acetic acid ($C_2H_4O_2$)	·8106	51·2	8·5	·422
Tartaric acid ($C_4H_6O_6$)	1·0331	52·2	6·5	·322
Citric acid ($C_6H_8O_7$)	·8448	49·7	11·0	·546
Sulphuric acid (H_2SO_4)	·6853	53·0	34·3	1·701
Hydrochloric acid (HCl)	·5037	52·3	39·3	1·949
Nitric acid (HNO_3)	·8445	50·8	39·7	1·969
Potassium acetate ($C_2H_3KO_2$)	1·3875	[53·6]	15·0	·744
Potassium citrate ($C_6H_5K_3O_7$	1·3966	[51·5]	17·0	·843

It is seen from this table that acetic acid has no effect on the solubility of bitartrate of potassium, that tartaric acid diminishes the solubility, that citric acid produces a small increase of solubility, while with sulphuric, hydrochloric, and nitric acid, the increase of solubility is very considerable. If we take these acids in the proportion of their chemical equivalents, that is in quantities of equal neutralising power, nitric acid appears to exert the greatest solvent action; but if we take equal weights of each acid, hydrochloric acid has the greatest effect. These results agree with the general statements of Destouches quoted by Gmelin. The table also shows that neutral acetate and citrate of potassium have actually a greater solvent power for bitartrate than is possessed by equivalent quantities of their respective acids.

If crystals of chloride, sulphate, or nitrate of potassium are added to the acetic or citric acid solutions, a considerable precipitation of bitartrate speedily takes place. If the same salts are added to the hydrochloric, nitric, or sulphuric acid solutions, considerable precipitation also occurs, but rather more slowly; the sulphuric solution is perhaps the most difficult to precipitate. Nitrate of potassium has decidedly less efficacy as a precipitant than the chloride or sulphate.

When solutions of bitartrate in acetate or citrate of potassium are treated with crystals of sulphate of potassium, a very small precipitate is slowly formed. When similar solutions are treated respectively with acetic and citric acid a rather larger precipitate is produced; but the addition of sulphate of potassium together with these acids produces an immediate and very considerable precipitation of bitartrate.

These facts will be seen presently to have a direct bearing on the quantitative determination of tartaric acid, and the above trials were mostly made as test experiments with this object in view.

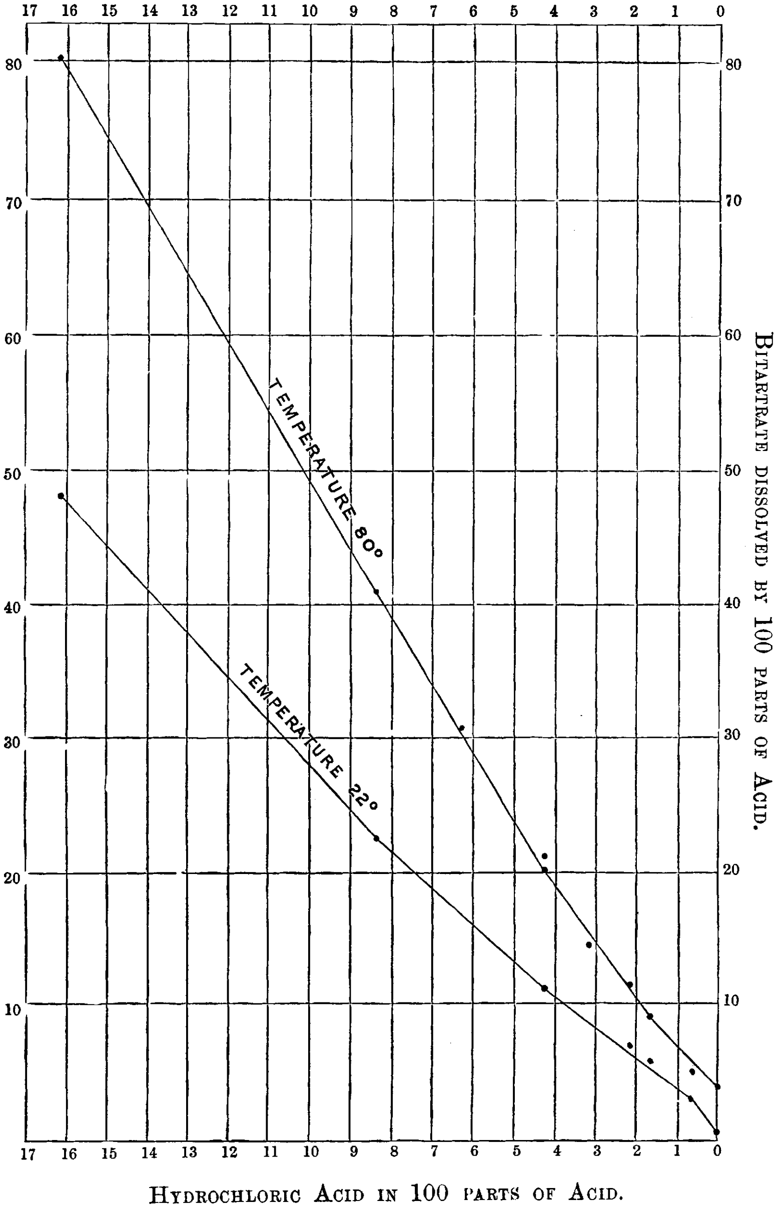
Some years ago I made a series of experiments on the solubility of bitartrate of potassium in hydrochloric acid of various strengths, and at two temperatures. The experiments were undertaken for a manufacturing purpose, and were not made with all the precautions necessary for scientific accuracy. As, however, the results will be substantially correct, I venture to append them. The bitartrate employed was the refined tartar already mentioned. The amount dissolved was ascertained by treating weighed portions of the solutions (previously concentrated when necessary) with acetate of potassium and some alcohol, washing the precipitate with alcohol, drying, and then titrating with standard alkali. The results were as follows; they are also graphically expressed in the accompanying chart (see next page).

Hydrochloric acid in 100 parts of the acid employed.	Bitartrate dissolved by 100 parts of acid.	
	At 22°.	At 80°.
·678	3·013	5·296
„	—	5·405
1·721	5·859	9·137
2·147	6 875	11·346
3·163	—	14·564
4. 255	11·186	20·226
„	—	21·220
6·240	—	30·709
8·358	22·747	40·932
16·134	48·311	80·116

Neither these experiments, nor the experiments with hydrochloric acid previously mentioned, confirm Ogston's statement that the solubility of bitartrate in very dilute hydrochloric acid is less than its solubility in water. He is, however, probably speaking of ordinary tartar, containing tartrate of calcium, with which I have made no experiments.

Lees, Argol, and Tartar.—The materials from which tartaric acid is made may be classed as lees, argol, and tartar. Lees is the solid matter collected from the bottoms of the fermenting vessels. Argol is the thin crystalline crust deposited on the sides of these vessels. Tartar is manufactured from the two former by a rough process of extraction with hot water and crystallisation. Italy is the great producer of the tartar exported to England; a smaller quantity comes from France. Other European countries export no tartar; but lees and argol are obtainable from all wine-producing countries having easy communication with the sea. The quantity of tartar exported by a country

Solubility of Bitartrate of Potassium in Hydrochloric Acid.



depends not only on the extent of its home consumption, but very greatly on the fact whether the wine is plastered or not. If the wine is plastered, the lees contain tartrate of calcium instead of acid tartrate of potassium, and consequently there is little material from which tartar can be made.

The influence of plastering on the composition of lees is very great. The analyses of lees in our laboratory books have been classified according to the countries from which they were exported, and the average composition of the lees of each country calculated.* The results are as follows:—

	Tartaric acid as		Total tartaric acid.
	Bitartrate of potassium.	Tartrate of calcium.	
Italian lees (33 samples)	24·1	6·1	30·2
Greek lees (14 samples)	19·9	11·8	31·7
French lees (9 samples)	17·3	6·0	23·3
Ditto (30 samples)	5·3	20·5	25·8
Yellow Spanish lees (59 samples)	8·7	18 2	26·9
Red Spanish lees (17 samples)..............	8·8	17·4	26·2

The tartaric acid in Italian lees is seen to exist almost entirely as acid tartrate. In the 33 samples of Italian lees there is only one in which the neutral tartrates exceed the acid tartrate, and the excess in this case is but small. In the 14 Greek lees there are two in which the neutral tartrates considerably exceed the acid tartrate; the remainder are similar in composition to the Italian lees, containing, however, rather more tartrate of calcium. Plastering is known to be practised in the island of Crete. The French lees have been divided into two classes. The first includes all in which the acid tartrate exceeds the neutral tartrates. The composition in this case is similar to that of the Italian lees, though the lees are poorer in tartaric acid. In the second, and larger class of French lees, the neutral tartrates greatly exceed the acid tartrate. These lees have undoubtedly resulted from plastered wines. It is probable that some of the lees in this second class are really Spanish lees reshipped from the south of France. It is well known, however, that in the southern districts of France plastering is largely practised. Of the 59 yellow Spanish lees there are only eight in which the acid tartrate exceeds the neutral tartrates; the excess of acid tartrate is in these instances but small, and only in one case equals the average excess in Greek lees. In the 17

---

* The analyses were by the method hereafter described as C.

red Spanish lees there are two instances of an excess of acid tartrate over neutral tartrates. Judging from these analyses of lees, we should conclude that plastering was all but universal in Spain, that it was common in the south of France, occasional in Greece, and unknown in Italy.

The amount of sulphates contained in lees of course depends very much on whether or not plaster has been used, and thus becomes another indication of this practice. We have made but few quantitative determinations of sulphuric acid in lees. For some time past, however, the hydrochloric solution of the lees ash, obtained in the ordinary course of analysis, has been treated with chloride of barium, and the bulk of the precipitate noted as "trace," "small," "considerable," or "very considerable." Of 12 Italian lees thus noted, 7 contained a "trace," and 5 a "small" quantity of sulphuric acid. Of 50 Spanish lees, 7 contained a "small," 18 a "considerable," and 25 a "very considerable" quantity of sulphuric acid. Few other descriptions of lees came under notice. Two Greek lees were noted, 1 as "small" and 1 as "considerable." Three French lees, 1 as "considerable," 2 as "very considerable." Three Sicilian lees were noted, 1 as "small," and 2 as "considerable."

Quantitative determinations of sulphuric acid were made in four Spanish lees; the amounts found were equal to 6·51, 12·32, 12·93, and 13·67 per cent. of gypsum.

Through the kindness of Gerard Clark, Esq., manager of La Andaluza Wine Company, I have fortunately been able to examine a sample of the "Yeso," or plaster, which is employed in Spain. The sample was in the condition of a coarse white powder. It had the following composition:—

Water (at 150°)	3·00
Matter lost at low red heat ..	·64
Lime	36·15
Magnesia	2·92
Ferric oxide	·30
Sulphuric acid	47·61
Carbonic acid	4·76
Sand	2·70
	98·08

The acids determined are not quite sufficient for the bases. In addition to the above ingredients, a small quantity of sulphuretted hydrogen was detected on treating the substance with an acid. The amount of carbonates is considerable, equivalent to 10·82 per cent. of carbonate of calcium.

According to the information kindly furnished by Mr. Clark, the "Yeso" is trodden with the grapes, about 10 lbs. being added to the quantity of grapes required to make a butt of wine (108 gallons). This proportion is nearly 1 per cent. Chancel mentions 1 per cent. (1 kilo per hectolitre) as being a usual proportion in the south of France. The "Yeso" is used equally for red and white wines, but is not employed in the preparation of the sweet wine, "vino dulce," made from over-ripe grapes for the purpose of tempering sherry.

The action of sulphate of calcium on wine has been thoroughly studied by Chancel (*Compt. rend.*, lx, 408), and by Bussy and Buignet (*Compt. rend.*, lx, 200; *J. Pharm.* [4], ii, 5). When an excess of gypsum, free from carbonates, acts either on an aqueous or alcoholic solution of bitartrate of potassium, the potassium parts with half its tartaric acid, taking sulphuric acid in its place, and a precipitate of tartrate of calcium is formed. The action of the gypsum ceases as soon as one-half of the tartaric acid has been removed. The resulting solution contains, according to Chancel, neutral sulphate of potassium and free tartaric acid; according to Bussy and Buignet the acids are distributed, and bitartrate and bisulphate of potassium are present in equal proportions. The weight of evidence seems to favour the latter view. The acidity of the solution is unchanged by the action of the gypsum. The action here described is that which must take place when pure calcium sulphate is added to wine after fermentation is completed.

When, however, gypsum is added to the must the effects produced are far more considerable. If a cold saturate solution of bitartrate of potassium is divided into two parts, one treated with gypsum, the other not, and alcohol is gradually added to each, so as to represent the change which occurs by fermentation, it will be found that the acidity of the solution containing no gypsum rapidly falls, from the precipitation of the bitartrate of potassium by the alcohol, while the acidity of the plastered solution does not fall till the amount of alcohol becomes considerable, and then only to a small extent, so that at the end of some days the plastered solution is found to be far more acid than the other. I will give one series of experiments on this point.

I. 100 c.c. of a cold nearly saturate solution of bitartrate of potassium, of which 10 c.c. = $44\frac{1}{2}$ drops of standard alkali, was treated with 25 c.c. of 91 per cent. alcohol, the alcohol being added at the rate of 5 c.c. a day. After 16 days the acidity had become 10 c.c. = 15 drops, and after 34 days 10 c.c = 13 drops of alkali.

II. 100 c.c. of the same bitartrate solution received 1 gram of pure gypsum, and then 25 c.c. of alcohol added as above. At the end of 16 days the acidity was 10 c.c. = $24\frac{1}{2}$ drops, and at the end of 34 days the acidity was still 10 c.c. = $24\frac{1}{2}$ drops of alkali. The acidity at the end of the experiment was thus nearly twice as great where gypsum had been employed.

It appears, then, that the addition of pure plaster to must saturated with bitartrate of potassium will produce a wine of much higher acidity than unplastered wine from the same grapes, and that this increased acidity will consist in great part of acid sulphate of potassium. The action of sulphate of calcium in increasing the acidity of a wine is, according to Chancel, carried still further, from the fact that grapes contain in their pulp undissolved bitartrate of potassium. When there is no plastering, this bitartrate can never come into solution, but when the plaster decomposes the bitartrate already dissolved, the liquid becomes capable of dissolving more, and a fresh action is set up.

We have at present considered only the reactions produced by pure sulphate of calcium; the results are modified when the plaster used contains carbonates. These will, of course, tend to diminish the acidity of the wine, and thus more or less counteract the acidifying effect of the sulphate of calcium. The carbonates in the yeso received from Spain are not easily attacked by a cold solution of bitartrate of potassium. On mixing 2 grams of yeso with 200 c.c. of a cold saturate solution of bitartrate of potassium, and stirring frequently for an hour, the neutralisation effected was equal to only one-sixth of the carbonates present; on boiling the mixture for ten minutes the neutralisation was equivalent to one-half the carbonates present. To ascertain more exactly the effect which these carbonates would produce on the acidity of a wine, a set of experiments was made similar to that just described, yeso being substituted for the pure gypsum then used.

I. 100 c.c. of a cold saturated solution of bitartrate of potassium, of which 10 c.c. = 65 drops of standard alkali (the 100 c.c. therefore contained ·6792 gram of bitartrate), was treated with 25 c.c. of 91 per cent. alcohol, the alcohol being added at the rate of 5 c.c. a day. Two days after the last alcohol had been added the acidity was 10 c.c. = $13\frac{1}{2}$ drops; after 25 days the acidity was 10 c.c. = $12\frac{1}{2}$ drops of alkali.

II. 100 c.c. of the same bitartrate solution was treated with 1 gram of yeso, in the state of coarse powder as received. After digesting in the cold for two days, 25 c.c. of alcohol were gradually added, as in the preceding experiment. After 2 days the acidity was 10 c.c. = 13 drops, after 25 days the acidity was 10 c.c. = 10 drops of alkali. The solid matter in the flask was then collected on a filter, and washed with alcohol till the washings were no longer acid, it then required 7 c.c. of alkali for neutralisation.

III. The experiment was performed as in II., but the yeso was finely powdered before being added to the bitartrate solution. After 2 days the acidity was 10 c.c. = 13 drops, after 25 days 10 c.c. = 9 drops of alkali. The washed solid matter required 5·5 c.c. of alkali for its neutralisation.

The neutralising power of 1 gram of yeso (as ascertained by an experiment with standard hydrochloric acid), was 15·5 c.c. of alkali. In experiment II the neutralising power actually exerted was 13·3 c.c. of alkali; in experiment III, where the yeso was finely powdered, the neutralisation was equal to 14·8 c.c. of alkali. It appears, therefore, that the carbonates of the yeso exercised nearly their full neutralising power. The acidity of the alcoholic fluid is, however, diminished far more than can be accounted for by the action of the carbonates. The acidity of the solutions treated with yeso is in both cases less at the close of the experiment than the acidity of the unplastered solution, and this not because the acid tartrate of potassium has been neutralised to this extent, but because it has been thrown out of solution, for a considerable quantity is found in the solid matter at the bottom of the flask. The presence of this precipitated bitartrate in solutions of such low acidity further shows, that the solubility of bitartrate in alcoholic solutions treated with yeso was less than in pure alcohol of the same strength. We have here the key to the greater neutralisation effected by the yeso. The carbonates of the yeso neutralise the acid sulphate of potassium formed by the action of the sulphate of calcium, neutral sulphate of potassium is thus produced, and the presence of this salt diminishing the solubility of bitartrate of potassium (as we have seen in an earlier section of this paper), the acidity of the solution is finally reduced to a lower point than that of the unplastered liquor. To prove that sulphate of potassium had the same effect in an alcoholic as in an aqueous solution of bitartrate, some powdered sulphate of potassium was added to the remaining solution of experiment I in the last series; in two days after this addition the acidity had fallen from 10 c.c. = 12½ drops to 10 c.c. = 2 drops of alkali.

It appears from the above, that the carbonates of natural plaster will have a greater effect in diminishing the acidity of a wine than is due to their own neutralising capacity, and that the nett result of plastering is probably in all cases the diminution of the acidity of the wine, and the introduction into it of neutral sulphate of potassium.

Besides plaster, other substances are sometimes added to wine, and affect the composition of the lees. "Spanish earth" is commonly employed in Spain for the purpose of fining the wine, it is sometimes used by English wine-merchants for the same purpose.

I have obtained samples of Spanish earth from various sources; it appears to be a tolerably uniform substance. Mr. Church has kindly furnished me with the following physical description:—"Earthy, more or less coherent, fragile; slightly soapy in feel; impressible by the nail, and yielding a polished streak; strongly adherent to the tongue; evolving an argillaceous odour when breathed upon; varying in colour from a pale warm grey in the more compact varieties, to a light buff in the less coherent [and more sandy] specimens; hardness 1 to 1·5." Some specimens contain many fragments of shells. When rubbed in the hands under water, Spanish earth is resolved into an unctuous paste, and is in this condition applied to the wine which it is desired to clarify.

The chemical characters of Spanish earth are very uniform, it consists of a hydrated silicate of aluminium, iron, and magnesium, with a variable quantity of sand. Lime is absent, or occurs only as a trace; a trace of carbonic acid is sometimes present. Boiled with dilute hydrochloric acid it is sufficiently decomposed to yield abundant evidence of magnesia.

A specimen of light colour and smooth texture, sent me by Mr. W. E. Halse, was submitted to quantitative analysis; it was decomposed with sulphuric acid; the sand and silica were separated with solution of sodium carbonate. The percentage results were as follows:—

Water, lost over oil of vitriol	7·69
Loss on ignition	9·84
Sand	11·01
Silica	47·92
Ferric oxide	5·24
Alumina	6·05
Magnesia	11·27
	99·02

This specimen of Spanish earth contained no lime or carbonic acid, also no phosphoric acid; a part of the iron was in the ferrous state. There was no blackening on ignition. At a white heat the substance fritted, and fused at the edges.

Resin is another substance which may occasionally be present in lees, it is applied in Greece as an internal coating to the wine casks. We have now and then had samples of lees possessing a distinct odour of pine-resin.

The general composition of the lees of various countries has been already given, as far as their contents in tartaric acid is concerned, the following analyses show the other ingredients present:—

	I. French Lees.	II. Spanish Lees.	III. Spanish Lees.
Tartaric acid as acid tartrate	4·48	5·27	22·66
Tartaric acid as neutral tartrates	21·34	19·13	11·67
Total tartaric acid	25·82	24·40	34·33
Water, at 100°	11·305	10·694	9·750
Sand	4·600	4·900	4·730
Silica	2·130	1·960	
Ferric oxide	·394	·351	·214
Alumina	·844	·832	·578
Phosphoric acid	·527	·486	·569
Lime	10·567	10·600	4·514
Magnesia	·327	·363	·209
Potash	1·868	2·123	[7·115]†
Soda	·100	·060	—
Sulphuric acid	4·566	5·729	—
Chlorine	·040	·042	—
Carbonic acid	·435	·388	—
Tartaric anhydride	22·721	21·472	30·210
Combined water*	5·904	5·552	4·159
Vegetable matter	33·672	34·448	[37·952]
	100·000	100·000	100·000

The French lees is so similar in composition to the first Spanish lees, that it seems probable that the French lees was really a Spanish lees re-shipped (as is the custom) from the South of France. The second Spanish lees (III) is of high quality, and must be the product of an unplastered wine. The lees I and II are undoubtedly plastered.

The sand, soluble silica, and alumina in lees, may arise from soil adhering to the grapes, or from the Spanish earth employed to clarify the wine. The magnesia may also arise, in part, from the employment of Spanish earth. The phosphoric acid is doubtless precipitated from solution as phosphate of iron or aluminium. Carbonates can hardly be original constituents of pure lees, but may arise from a subsequent admixture of dirt or soil, or from a decomposition of the tartrates, which readily takes place when the process of sun-drying is inefficiently performed. Carbonates may also possibly be a residue of yeso used in such coarse powder as to be only partially acted on. In some cases, however, carbonate of calcium is present in such large quantity, and in particles of such size and purity, that it must have been intentionally added, either to diminish the acidity of the wine, or as a direct adulteration.

* In calculating the combined water, it is assumed that the tartrate of calcium retained half its water, and the gypsum one-fourth its water at 100°.

† This figure is calculated from the acidity.

The vegetable matter of lees contains much nitrogen. Nitrogen was determined in the insoluble residue of a Spanish lees remaining after extraction with hot hydrochloric acid and water, the amount found was 3·24 per cent. of the dry matter. A similar residue from a French lees gave 3·07 per cent. of nitrogen. As these residues contained a good deal of sand, the percentage of nitrogen in the vegetable matter would really be much higher than these figures indicate. Wine lees have been commonly employed as manure in the countries where they are produced; they are well suited for this purpose from the considerable quantity of nitrogen and potash which they contain.

Argol exhibits a wide range of composition, containing from 40 to 70 per cent. of tartaric acid. Very low argols resemble superior lees, while first-class argols are equal to ordinary tartar. In argol, even of low quality, the tartaric acid is chiefly present as bitartrate of potassium. Small lumps of melted sulphur are not unfrequently found associated with argols. They probably arise from the sulphuring of the casks. Rather large quantities of sulphur are often burnt in wine-casks before the introduction of the wine; this fact should not be forgotten by analysts who look on the presence of sulphates in the wine as evidence of plastering.

Tartar, as already mentioned, is manufactured from lees or argol, by extraction with hot water and crystallisation. The highest quality tartars are those of south Italy and Messina, they contain about 76 per cent. of tartaric acid, and in some instances reach as much as 77* per cent. Of this tartaric acid $1\frac{1}{2}$—$3\frac{1}{2}$ exists as neutral tartrate of calcium. The good ordinary Italian tartars, as those of St. Antimo or Naples, contain 74—75 per cent. of tartaric acid, of which 3—$4\frac{1}{2}$ exists as calcium tartrate. Vinaccia tartar† is of poorer quality; it will contain 70—73 per cent. of tartaric acid, of which 5—7 per cent. will exist as neutral tartrates. Of French tartars I have but little experience, they appear to contain more tartrate of calcium than good Italian tartars. The following tolerably complete analyses by Mr. Grosjean of a Messina and St. Antimo tartar will serve to compare with the analyses of Lees already given. Sulphuric acid was unfortunately not determined.

---

* Pure bitartrate of potassium would contain 79·7 per cent. of tartaric acid.

† Vinaccia tartar is made in various parts of Italy and France, from the solid matter of the grape remaining after the must is expressed. This solid matter is fermented, distilled, and tartar made from the residue.

	Messina Tartar.	St. Antimo Tartar.
Tartaric acid as acid tartrate	74·05	69·34
Tartaric acid as neutral tartrates	2·60	4·66
Total tartaric acid	76·65	74·00
Sand	·140	·425
Silica	·055	·130
Ferric oxide	·053	·086
Alumina	·021	·092
Phosphoric acid	·041	·068
Lime	1·081	1·778
Magnesia	·025	·041
Potash	[23·236]	[21·773]
Tartaric anhydride	67·408	65·120
Combined water	5·688	6·396
Water, vegetable, and undetermined matter	2·252	4·091
	100·000	100·000

The potash in the above analyses is calculated from the acidity of the tartar.

Determination of Tartaric Acid in Tartar, Argol, and Lees.—In the methods of analysis commonly employed, tartaric acid is only indirectly determined, the methods merely giving the total amount of organic acid present, which is then reckoned as tartaric. These indirect methods may be briefly described as follows:—

A. The tartaric acid existing as acid tartrate of potassium is calculated either from the amount of potassium found by platinum, or else from the acidity of the sample. The tartaric acid present as neutral tartrate of calcium is calculated from the amount of calcium found. Both potassium and calcium are determined in the calcined tartar. This method, variously modified, is the one most commonly employed in this country.

B. The tartar is calcined, and exhausted with water; the neutralising power of the soluble potassium carbonate, and of the insoluble calcium carbonate, is then separately determined with standard acid and alkali, and the tartaric acid in combination with potassium and calcium calculated therefrom.

C. The tartaric acid present as bitartrate of potassium is determined from the acidity of the sample. Another portion of the tartar is calcined, and the neutralising power of the ash determined. By subtracting from the neutralising power of the burnt tartar that due to the potassium bitartrate previously determined, the amount of base corresponding to neutral tartrates is ascertained.

D. The whole of the tartaric acid present is converted into neutral tartrates by exact neutralisation with soda; the whole is then evaporated to dryness, calcined, the neutralising power of the ash determined, and the tartaric acid calculated therefrom.

In all these methods, save the last, the total tartaric acid present is found by adding together that existing as acid and as neutral tartrate. Methods C and D may be modified by determining the carbonic acid in the ash, in place of the neutralising power of the carbonates.

With a high quality tartar, consisting entirely of clean crystals, any of the above methods will give good results; but with low quality tartars sources of error are introduced which we must now consider.

Tartars of low quality contain, besides bitartrate of potassium, and neutral tartrate of calcium, small quantities of carbonates, sulphates, phosphates, and silicates, with vegetable matter.

The carbonates are usually fragments of calcareous earth present as dirt,* but may arise from decomposition of the tartar if the latter is damp. If carbonates are present, and the tartaric acid existing as acid tartrate is determined from the acidity of the sample after boiling with water, the result obtained will be too low, a portion of the acid tartrate being neutralised by the carbonate. Crystalline carbonate of calcium is but little attacked by a solution of bitartrate, even when the solution is concentrated and hot; chalk, and other amorphous forms of calcium carbonate are, however, readily acted on by far weaker solutions. The insoluble carbonates present in lees and tartar are, as a rule, easily dissolved by a hot solution of bitartrate. It is possible by acting on the lees or tartar with excess of alkali, to determine the amount of bitartrate without the insoluble carbonates affecting the result; the method will be described further on.

If in method A the carbonate of calcium is allowed to act on the bitartrate, the total tartaric acid found will be too low; if on the other hand it does not act, the result will be too high. In method B the presence of carbonates must make the result too high. It is clear, therefore, that if either method A or B is employed, a determination of carbonic acid must be made if accuracy is desired.† With C, on the other hand, the presence of carbonates is without effect on the total tartaric acid found. If in determining the bitartrate by acidity the carbonates are allowed their full action, the tartaric acid as bitartrate is indeed estimated too low, and the tartaric acid as neutral tartrates too high, but the total tartaric acid is exactly given by this method.

---

* One argol we have received was largely adulterated with stalactitic carbonate of calcium.

† If carbonate of potassium is present, as well as carbonate of calcium, no determination of carbonic acid will serve to correct methods A and B, unless it can be ascertained in what proportion the carbonic acid is divided between the bases.

Employing the same precaution, the determination of total tartaric acid by method D in the presence of carbonates is also quite exact.

The presence of sulphates necessitates of course a determination of sulphuric acid if method A is adopted, the result must otherwise be too high; it must also be known with which base the sulphuric acid is combined. In method B the presence of alkali sulphates will have no ill effect, unless sulphides are produced during the ignition, but the presence of sulphate of calcium must lower both the tartaric acid calculated as bitartrate, and also the total tartaric acid found. In fact, if tartar is mixed with gypsum, and ignited, treatment with water at once causes the carbonate of potassium to react upon the sulphate of calcium, carbonate of calcium and sulphate of potassium being produced. With methods C and D the presence of sulphates is without effect on the result, provided no error is introduced by the formation of sulphides.

The phosphates in tartar are present as phosphates of iron and aluminium; they are very small in quantity, and have no practical effect on the analysis. The silicates in tartar are also comparatively unimportant. The action of silicates and phosphates will be noticed presently when considering the analysis of lees.

It is evident from the above considerations, that the accurate use of methods A and B is limited to the case of pure tartars, as the errors introduced by carbonates and sulphates cannot be certainly rectified by determining the quantity of carbonic and sulphuric acid present, but require further a knowledge of the manner in which these acids are combined, information which the chemist is unable to supply. Methods C and D, on the other hand, give reliable results in the presence of carbonates and sulphates, without any alteration in the plan of the analysis. Of these two methods, C gives the most complete results, as it includes a tolerable determination of acid tartrates; it is also very speedy; a powdered sample of tartar may be analysed by this method in 1½ hour. This plan of analysing tartar has been employed by me since 1867; I find, however, that a perfectly similar method was described by Brescius some years before. The details of the method are as follows.

Five grams of the finely powdered tartar are heated with a little water to dissolve any carbonates that may be present. If it is wished to guard against crystalline carbonates, 5 c.c. of standard hydrochloric acid are added in the first instance, and the heating is conducted in a covered beaker. Standard alkali is next added to the extent of about three-fourths of the amount required by a good tartar of the kind examined, plus that equivalent to the hydrochloric acid used, and the whole is brought to boiling; when nearly cold, the titration is finished. From the amount of alkali consumed, minus that required by the hydrochloric acid, the tartaric acid present as acid tartrate is calculated.

Two grams of the powdered tartar are next weighed into a platinum crucible with a well-fitting lid; the crucible is placed over an argand burner; heat is first applied very gently to dry the tartar, and then more strongly till inflammable gas ceases to be evolved. The heat should not rise above very low redness. The black ash is next removed with water to a beaker. If the tartar is known to be a good one, 20 c.c. of standard sulphuric acid are now run from a pipette into the beaker, a portion of the acid being used to rinse the crucible. The contents of the beaker are now brought to boiling, filtered, and the unneutralised acid determined with standard alkali. As the charcoal on the filter under some circumstances retains a little acid, even when well washed, it is advisable when the titration is completed to transfer the filter and its contents to the neutralised fluid, and add a further amount of alkali if necessary. From the neutralising power of a gram of burnt tartar is subtracted the acidity of a gram of unburnt tartar, both expressed in cubic centimeters of standard alkali, the difference is the neutralising power of the bases existing as neutral tartrates, and is then calculated into tartaric acid on this assumption.*

If the tartar is of low quality, 5 c.c. of solution of hydrogen peroxide (1 volume = 10 volumes of oxygen) are added to the black ash and water, and immediately afterwards the standard sulphuric acid; the rest of the analysis proceeds as already described; the small acidity usually belonging to the peroxide solution must, however, be known and allowed for in the calculation. By the use of hydrogen peroxide the sulphides formed during ignition are reconverted into sulphates, and the error of excess which their presence would occasion is avoided. This elegant method I owe to a suggestion of Mr. Valentin. I know of no other plan of oxidising sulphides which would not at the same time interfere with an alkalimetrical analysis.

The formation of sulphides is not apparently due to the reducing action of tartrates upon sulphates. Both tartrates and citrates may be mixed with sulphates, the solutions evaporated, and the dry matter ignited so as to convert all organic salts into carbonates, without the production of sulphides, or at most of a trace only; but if any nitrogenous organic matter be present, the formation of sulphides is under these circumstances abundant. On learning this fact, it seemed possible that the sulphides were derived from the organic sulphur of

---

* It is obvious that the neutralising power of the ash of an acid tartrate is exactly the same as the acidity of the same tartrate before burning. In making the calculations, it must be remembered that the value of the alkali in tartaric acid is twice as great in the calculation made from the acidity of the unburnt tartar, as in the calculation of the acid existing as neutral tartrates.

albuminous bodies, and not from the reduction of sulphates, in which case it would be a mistake to employ hydrogen peroxide as directed above. A test experiment in which white of egg and pure tartar were ignited together, gave however only a trace of sulphides, and thus negatived the idea. On repeating the experiment with the addition of gypsum, the production of sulphides was abundant. Gypsum and tartar alone gave, however, no sulphides at the low temperature necessary for converting tartrates into carbonates.

Sulphides will be formed in large quantity on ignition if the tartar or argol contained free sulphur; such sulphides cannot be oxidised into sulphates without vitiating the analysis. It is necessary therefore to remove all free sulphur before commencing the determination.

When nitrogenous organic matter is present in a tartar, cyanides as well as sulphides are produced on ignition. The hydrocyanic acid may be removed before titration by evaporating the sulphuric acid solution of the ash till all smell has disappeared.

The method now described does not, as already mentioned, give the separate amounts of acid and neutral tartrates with exactness in the presence of carbonates, but the total amount of tartaric acid is correctly given. The total acid is also correctly expressed in cases in which free tartaric acid is present, provided the final result shows some tartaric acid as neutral tartrates. When in using this method the acidity of the unburnt substance is found to be greater than the neutralising power of the ash, the method must be abandoned and method D employed.

In method D the tartar, freed from carbonates by heating with hydrochloric acid, is exactly neutralised with soda, the whole transferred to a platinum basin, evaporated, and ignited; the neutralising power of the ash is then ascertained as in method C. This method is the only one that will give exact results when the substance examined contains much free tartaric acid; it is also unaffected by the presence of free inorganic acids, if their salts are not altered by ignition with vegetable matter.

Methods C and D are not apparently affected by the presence of sand in the tartar, and the presence of clay has also little effect. Pure bitartrate mixed with 10 per cent. pipe clay, and ignited at the usual temperature, gave 99·44 per cent. of the tartaric acid present. On the other hand, these methods are very injuriously affected by the presence of certain silicates, as we shall presently see.

In place of the alkalimetrical determinations in C and D, determinations of carbonic acid in the burnt tartar, or in the burnt neutralised tartar, may be made. These determinations can be effected very speedily, and with tolerable accuracy, by means of Scheibler's well-known apparatus. The tartar, neutralised or not, according as method C or D is employed, is ignited at a low temperature in a platinum vessel, the black ash moistened with water, reduced to a smooth paste with a small agate pestle, and removed by means of water into the generating bottle of the apparatus. The quantity of water used must be exactly 5 c.c. The water is best supplied from a burette, and if used in washings of 1 c.c. each the quantity mentioned will be quite sufficient. In the hydrochloric acid used (10 c.c. of sp. gr. 1·12) a little mercuric chloride is dissolved, to prevent the evolution of sulphuretted hydrogen. The operation is performed as described in Scheibler's pamphlet, but the contents of the generating bottle should be shaken for three minutes in every case to ensure uniformity of result. The bottle should be wrapped in paper, and a glazed screen placed between the operator and the apparatus during the agitation, as a small rise of temperature would distinctly affect the result. The volume of gas obtained is to be increased by 7 per cent., to compensate for the amount of gas retained by the fluid in the generating bottle, this amount being proportional to the quantity of gas evolved, and not a constant quantity as stated by Scheibler (see *Chemical News*, xxxi, 253). To reduce the volume of gas into tartaric acid, first correct the volume for pressure, and then find the weight of carbonate of calcium it is equivalent to in Scheibler's table (Table VI). If a neutral tartrate has been operated on, as in method D, the weight of tartaric acid is 1½ times the carbonate of calcium; if an acid tartrate is the subject of experiment, the tartaric acid is three times the carbonate of calcium. If method C is used, calculate the tartaric acid as 1½ times the carbonate of calcium, and subtract one-half the tartaric acid previously found from the acidity of the sample, the difference will be the tartaric acid existing as neutral tartrates. Two grams of tartar, or one gram of tartar if neutralised with soda, is the maximum quantity for an experiment.

The following test experiments with pure bitartrate of potassium show the amount of accuracy which may be attained :—

Taken,	bitartrate	0·5 gram :	product	100·85	per cent.
,,	,,	1·0 gram :	,,	99·72	,,
,,	,,	1·5 gram :	,,	99·93	,,
,,	,,	2·0 grams :	,,	99·79	,,
,,	,,	2·0 grams :	,,	99·30	,,
,,	,,	2·0 grams :	,,	99·24	,,

1·5 gram of bitartrate of potassium, plus ·5 gram of sulphate of calcium and a little gelatin, yielded 100·66 per cent. of the tartaric acid taken, a little sulphuretted hydrogen being evolved. The experiment repeated, with the addition of mercuric chloride to the hydrochloric acid, gave 99·75 per cent., no sulphuretted hydrogen being evolved. 1 gram of tartrate of calcium, with ·5 gram of sulphate of calcium, yielded a product of 99·72 per cent.

As in the alkalimetrical method, no error is introduced by the presence of carbonates or sulphates, if the precautions already mentioned are employed. The presence of sand somewhat diminishes the result, and clay has a still greater effect. Pure tartar ignited with 10 per cent. of fine sand gave 98·53 and 98·43 per cent. of the tartaric acid present. With 10 per cent. of pipe-clay the product was 95·15 per cent.

We turn now to the determination of tartaric acid in lees. This has been hitherto done by indirect methods, the same as those employed for the analysis of tartar. A pretty long investigation of the application of these methods to lees has, however, convinced me that the tartaric acid present cannot be accurately determined by their means. Before describing the direct method by which I hope more accurate results will in future be obtained, I must point out the causes which prevent the successful use of the methods adopted in the case of tartar.

If it were possible to ascertain exactly the total amount of organic acid existing in a sample of lees, it would certainly be open to doubt whether the whole of this acid was in fact tartaric, since wine contains several organic acids besides tartaric, and lees itself is a substance which readily undergoes putrefactive change. This doubt has little place in the case of a crystalline tartar, to which, therefore, indirect methods of analysis may safely be applied. It is, however, I believe, not possible to determine with any exactness the total amount of organic acid existing in a lees.

In each of the indirect methods already described, with the exception of D, it is essential to determine separately the amount of acid and neutral tartrate present. If the determination of acid tartrate is founded on the amount of potash ascertained by platinum, the result can hardly fail of being too high, as every potassium salt is reckoned as bitartrate. For without assuming the presence of organic potassium salts other than tartrates, it is evident that, in the case of plastered lees, some small quantity of sulphate of potassium must be present. Since lees also frequently contain a rather considerable amount of carbonates, the conclusion seems unavoidable that neutral tartrate of potassium may be present as well as acid tartrate. If, on the other hand, the determination of bitartrate is founded on the acidity of the lees, the result is still less accurate and is open to great uncertainty.

When lees are boiled with water and neutralised with standard alkali, the acidity found is of course below the truth when carbonates have been present; in some lees, in fact, the carbonates are more than sufficient to neutralise the whole acidity. This error may to a great extent be avoided by treating the finely-powdered lees in the cold with a moderate excess of standard alkali, and after stirring for some minutes, neutralising the solution by the cautious addition of standard acid. The insoluble carbonates on this plan remain untouched, and only the soluble carbonates can affect the acidity. The results are, however, by no means sharp. The vegetable matter, silicates, or phosphates of the lees, appear to have the power of appropriating caustic alkali, especially on heating, which must therefore be avoided. The addition of caustic alkali probably produces a number of basic salts not previously present; the standard acid is, therefore, best added to faint acid reaction to re-establish a normal condition. If the liquor is decanted after such a determination, the insoluble carbonates will be seen as white particles at the bottom of the beaker, which effervesce with acid.*

As a complete correction of the effect of carbonates in the determinations of acidity, the carbonic acid present in the lees may be determined, and its equivalent in acidity added to the acidity found after boiling with water or standard hydrochloric acid. By this means still higher results are obtained than by the previous method. Carbonic acid in lees is conveniently determined by placing 8—10 grams in a flask with a tube of hydrochloric acid, which is subsequently overturned. The flask is brought to boiling, and the gas passed by means of an aspirator into tubes containing baryta-water. The carbonate of barium is collected on a small filter, with careful exclusion of air, and washed till the drain water no longer affects turmeric paper. The filter and precipitate are then treated with standard hydrochloric acid, boiled, and the excess of acid determined with alkali. The value of the carbonates in terms of alkali is thus at once obtained. A similar experiment should be made with a fragment of calc-spar containing about the same amount of carbonic acid which is determined in the case of lees; the excess of the result over theory furnishes a correction to be applied to the experiments with lees. The elements of this method were suggested by my friend Dr. Flight.

A considerable difficulty is introduced into the determination of the acidity of lees by the fact that lees when neutralised become distinctly acid if once more boiled for a few minutes. If this new acidity be neutralised with alkali and boiling resumed, a further, though smaller amount of acidity is developed. By proceeding in this way till the production of acidity ceases, a much higher result is obtained than if the experiment was stopped after one or two boilings only. This production of acidity during repeated boilings is not observed in the analysis of tartar, and is certainly not due to any insolubility of the bitartrate present. The phenomenon could readily be explained by

---

* If the acidity of tartar is to be determined by treatment with excess of alkali, the tartar must be reduced to an impalpable powder. Crystalline bitartrate is very slowly attacked by cold alkali.

assuming the presence of ditartaric acid, but this is most unlikely. I believe it is, at least in part, owing to the decomposition of the phosphates present. If precipitated phosphate of aluminium or iron is diffused in water, and made neutral to litmus paper by careful addition of caustic alkali, the mixture when boiled becomes distinctly acid. If gypsum be also present the acidification is much intensified. The solutions neutralised and boiled again develop a fresh acidity. The same phenomena occur if bitartrate of potassium is present along with the other ingredients. Now phosphates of iron and aluminium with calcium salts are certainly present in all lees; it appears likely, therefore, that a part at least of the acidification is due to the reaction just described. The vegetable matter which forms a large part of lees may possibly take a part in the reaction, but of its properties nothing is known.*

We have now noticed four methods of ascertaining the amount of tartaric acid existing in lees as acid tartrates. The divergency between these methods is illustrated by the following table, which gives the percentage of tartaric acid as bitartrate found in three lees by the methods just described:—

Method.	I. Spanish Lees.	II. Spanish Lees.	III. French Lees.
Calculation from the potash present	7·20	6·76	5·95
Boiling (twice) with water	4·00	6·18	4·59
Treatment with excess of alkali in the cold	7·75	7·88	6·69
Boiling with hydrochloric acid, the neutralisation by carbonates being corrected from a determination of carbonic acid	8·83	8·57	8·18

The amount of tartaric acid present as acid potassium tartrate cannot possibly exceed that calculated from the potash found, and, as we have already stated, is pretty sure to fall below it; yet the tartaric acid calculated from the acidity of the lees is seen to be in every case greater than that equivalent to the potash found, except when the neutralisation effected by the carbonates is unchecked. The results calculated from the acidity of the lees become still higher if a number of boilings take place. With lees II five boilings with water increased the tartaric acid found from 6·18 to 7·28 per cent.; with lees III the increase was from 4·59 to 6·28 per cent. If these numbers were corrected for carbonates, as in the fourth line of figures, the results would be higher than any in the table.

---

* For another possible explanation, see page 984.

The presence of free acids in lees would of course explain the higher results obtained by acidity than by calculation from potash. Grape-juice, according to Dupré, contains a good deal of free malic, and also some free tartaric acid; and wines, on the same authority, also contain free acid. A red and white Spanish, and an Italian lees, were extracted with strong alcohol, the solutions treated with water became turbid; evaporated on a water-bath they left in every case a green fat and a small quantity of a syrupy acid. In the case of Lees I in the preceding table, the amount of the free acid extracted by alcohol was determined; it was equivalent to only ·30 per cent. of tartaric acid, a quantity quite insufficient to account for the difference between the acidity of the lees and the potash present. As all the ingredients of lees have been formed and precipitated from an acid solution, it seems very likely that many of these ingredients are capable to some extent of neutralising caustic alkali, and that the acidity of a lees will consequently always be in excess of the quantity of bitartrate really present.

As an appendix to the above remarks on the acidity of lees, I would mention that in some cases lees appear to increase in acidity by keeping. Mr. Grosjean having observed a distinct increase of acidity in the case of a Greek lees re-analysed after 14 months, several other lees which had been long in the laboratory were re-analysed. Of 11 lees preserved more than a year in the state of powder, 9 had increased, 1 remained unchanged, and 1 had diminished in acidity. Of the 9 cases of increase, 6 exceeded the ordinary errors of experiment, and in two instances the increase of acidity was equal to 1—2 per cent. of tartaric acid. Lees which have been long kept in powder are frequently found caked together, apparently from the growth of fungus.

It has been supposed by Patterson (*Chem. News*, xxv, 149) that tartaric acid in alkaline solutions gradually splits up into simpler acids of greater neutralising power; such a decomposition would at once explain the increase in acidity of lees just mentioned. Solutions of bitartrate of potassium, and of Rochelle salt, both with and without the presence of gypsum, were set aside to ascertain the effect of fungoid growth upon their composition. A drop of phosphoric acid being added to each solution, an active growth of mould was started in a few days. The bitartrate solutions at once began to diminish in acidity, and at the end of six months (chiefly winter) had become neutral, and, indeed, when boiled, slightly alkaline. The solution containing gypsum changed somewhat more speedily than the other. The solutions of Rochelle salt became slowly slightly alkaline, but this alkalinity did not appear to increase; it would seem, indeed, that the presence of alkali checks the action of the fungus. It appears, then, that as far as the action of fungus is concerned, a diminution rather than an increase of acidity is to be expected.

If the acidity of lees is in excess of the acid tartrates and free acid present, it is evident that methods C and D must give results that are too high. These methods are, however, open to a still greater error on the side of excess, owing to the presence of silicates in the lees.

The adulteration of a parcel of lees with lumps of Spanish earth, induced me to ascertain its influence on the method of analysis (C) hitherto adopted. Spanish earth, as already mentioned, is a silicate of aluminium, iron, and magnesium. Boiled with the dilute sulphuric acid used for alkalimetric purposes, it is sufficiently decomposed to neutralise partially the acid; if heated to low redness before treatment with acid, the neutralisation of the acid is greater than when the fresh earth is employed. Spanish earth boiled with a solution of bitartrate of potassium is but little attacked, and the acidity of the bitartrate is consequently but little diminished. If, however, the bitartrate is ignited with Spanish earth, even for the short time and at the low temperature sufficient for the destruction of the tartrate, the bases of the Spanish earth become very soluble, and on boiling with standard acid the acid is neutralised to a much greater extent by the Spanish earth than when boiled with the earth ignited *per se*. The result of these reactions is, that the amount of tartaric acid found by methods C and D is, in the presence of Spanish earth, much above the truth. The error may be diminished by boiling the material with as large an amount of hydrochloric acid when determining its acidity, as when acting on the ignited substance, but the error is by no means wholly eliminated. The following analyses of mixtures of 2 grams of refined tartar with 1 gram of Spanish earth will illustrate these facts. Spanish earth I was a sandy variety; II was much freer from sand, and had a much greater effect on the analysis. The figures express the percentage of tartaric acid in the 3 grams of substance taken.

Tartar with Spanish Earth I.

	Tartaric acid really present.	Tartaric acid found.	
		Acidity by boiling with water. Ash treated with 20 c.c. HCl.	Acidity by boiling with 20 c.c. HCl. Ash treated with 20 c.c. HCl.
As acid tartrate..............	53·27	52·87	48·88
As neutral tartrate...........	None	4·32	6·32
Total tartaric acid..........	53·27	57·19	55·20

Tartar with Spanish Earth II.

	Tartaric acid really present.	Tartaric acid found.	
		Acidity by boiling with water. Ash treated with 20 c.c. HCl.	Acidity by boiling with 20 c.c. HCl. Ash treated with 20 c.c. HCl.
As acid tartrate	50·88	48·55	45·21
As neutral tartrate	1·32	10·14	11·80
Total tartaric acid..........	52·20	58·69	57·01

The product, in presence of the first Spanish earth, was thus 103·6, and in the case of the second Spanish earth 109·2 per cent. of the tartaric acid really present, even when the method was corrected by the employment of much hydrochloric acid in determining the acidity. In another experiment with the second Spanish earth, in which tartrate of calcium equivalent to 2 grams of bitartrate was mixed with 1 gram of the earth, the product was 107·4 per cent. of the tartaric acid taken.

The errors introduced by the presence of Spanish earth are not mended by substituting a determination of carbonic acid for the alkalimetric method. 1·5 gram of bitartrate, with ·75 gram of the second Spanish earth, ignited at the usual low temperature, gave in Scheibler's apparatus carbonic acid equal to only 65·1 per cent. of the tartaric acid taken. In a duplicate experiment the product was 64·5 per cent. One gram of tartrate of calcium, with ·5 gram of Spanish earth, gave a product of 96·3 per cent. of the tartaric acid present. The error is thus in the opposite direction to that which occurs in the alkalimetric method. The silicate, in fact, when ignited with carbonate of potassium or calcium, expels a portion of the carbonic acid from these salts, and is at the same time broken up so as to yield its bases readily to the action of acids; the quantity of base available for neutralisation is thus increased, and the amount of carbonic acid diminished.

We see, then, that the alkalimetrical methods (C and D) err on the side of excess, both from the presence in lees of acidifying matter other than bitartrate, and from the presence of decomposible silicates; while determinations founded on the estimation of carbonic acid are too low, from the decomposition of the carbonates by silica already mentioned. The following table shows the results obtained when these two methods are applied to the same lees and tartar. The total tartaric acid was in all cases determined by method D.

	I. Red Italian Lees.	II. Red Italian Lees.	III. Red Spanish Lees.	IV. Yellow Spanish Lees.	V. Yellow Spanish Lees.	VI. Argol.	VII. Tartar.
Alkalimetric Method.							
As acid tartrate	26·3	20·7	4·5	7·9	9·6	34·8	73·9
As neutral tartrates..........	7·1	5·6	18·9	18·1	17·7	14·5	2·1
Total tartaric acid	33·4	26·3	23·4	26·0	27·3	49·3	76·0
Carbonic Acid Method.							
Total tartaric acid	27·1	19·7	19·9	22·8	23·2	46·1	75·1

We have seen that both the alkalimetric and carbonic acid method give perfectly accurate results with pure tartrates; here, too, we see that with a high quality tartar the results of the two methods are near together; with argol there is less agreement, and with lees the difference is very considerable. the carbonic acid method giving much the lower result.

Higher results are obtained by the carbonic acid method, if the black ash obtained from the ignition of the tartrate is treated with carbonate of ammonium, and re-ignited before determining carbonic acid. Thus Lees I gave 28·9 per cent. of tartaric acid when thus treated, and Lees V 24·1 per cent. This treatment is certainly useful as converting cyanides into carbonates, and as exercising the same function on caustic lime, if that be present, which, however, seems unlikely. On the other hand, treatment with carbonate of ammonium also converts sulphides into carbonates,* and has partially the same effect on sulphate of calcium, unless a great quantity of alkali carbonate be present, thus introducing serious errors of excess. Solution of carbonate of ammonium, as is well known, converts sulphate of calcium into carbonate of calcium and sulphate of ammonium; when the mass is dried and ignited the reconversion is not complete, and some sulphate of ammonium is volatilised.† One gram of tartrate of calcium mixed with ·5 gram of gypsum, was ignited at the usual low tempera-

---

* Cyanide of potassium, and sulphide of sodium, if evaporated to dryness with excess of carbonate of ammonium and heated, contain no longer either cyanides or sulphides.

† These facts should be remembered by those chemists who are in the habit of treating ashes with carbonate of ammonium before analysis.

ture, treated with carbonate of ammonium, and re-ignited; the carbonic acid found was equivalent to 107·10 per cent. of the tartaric acid taken. A duplicate experiment gave a product of 106·8 per cent. One and a-half gram of bitartrate of potassium, with ·5 gram of gypsum, treated with carbonate of ammonium as above, gave a product of 99·76 per cent. When, however, the alkali carbonate was reduced by taking ·5 gram of bitartrate, with ·5 gram of tartrate, and ·5 gram sulphate of calcium, the product was again excessive, namely 107·83 per cent.

Having now considered the application of the indirect methods to the analysis of lees, and the errors to which they are liable, we turn finally to the direct methods of determining the tartaric acid present.

In seeking for a direct estimation of tartaric acid, I desired, if possible, to obtain the acid in the form of bitartrate of potassium, this form being the most characteristic of tartaric acid. The first plan tried was the decomposition of lees by boiling with carbonate of potassium. By this method the tartrate and sulphate of calcium are decomposed, and all the tartaric acid passes into solution, while all the lime, except a trace, remains with the residue of the lees. The residue was washed on a vacuum filter, the solution neutralised with hydrochloric acid, concentrated on a water-bath to a small bulk, and the tartaric acid precipitated as bitartrate of potassium by the addition of citric acid. This method has the disadvantage that large quantities of colouring and other matters are dissolved out of the lees by digestion with carbonate of potassium, and as soon as the solution is neutralised they are precipitated, and either considerable trouble must be taken to separate them, or the precipitate of bitartrate will be very impure and difficult to filter. I think the carbonate of potassium process is one that may be worked, but the method finally adopted being easier to carry out, I need not enter into further particulars.

The next plan tried was the exhaustion of the lees with hydrochloric acid. By this process solutions far purer were obtained than those yielded by carbonate of potassium. If, however, the lees are rich in bitartrate, strong hydrochloric acid must be employed, if it is wished to dissolve the salt in a small volume of fluid. The difficulty of washing bitartrate completely out of the residue is also much greater than the difficulty of washing out a neutral tartrate. The hydrochloric solution, when obtained, is also not available for the immediate determination of the tartaric acid in the form of bitartrate, but the lime present must be first removed with carbonate or oxalate of potassium. Though, therefore, the bitartrate finally obtained was very white and clean, the method was not satisfactory.

The method finally adopted was the decomposition of the lees with neutral oxalate of potassium. The details of the operation are as follows:—

A preliminary analysis by the alkalimetrical method C, reveals the character of the lees, if not already known, and enables the chemist to calculate approximately the amount of oxalate of potassium required to decompose the calcium salts. In this calculation the neutral tartrates found are reckoned as tartrate of calcium, and if the lees be Spanish, or otherwise from its low proportion of acid to neutral tartrates yields evidence of being plastered, 13 per cent. of gypsum is also assumed to be present.* Over and above the quantity of oxalic acid required by the calcium, a further amount of 1 gram should be added to insure the necessary excess. The oxalate of potassium is conveniently made by dissolving 40 grams of crystallised oxalic acid in hot water, neutralising with carbonate of potassium, and diluting to 280 c.c.; 7 c.c. then equal 1 gram of oxalic acid. The quantity of ground lees taken is such as will contain 2—2·5 grams of tartaric acid. The lees is placed in a small beaker, covered with water, and heated in a water-bath till thoroughly softened. The calculated volume of oxalate of potassium solution is next added, and the heating continued with frequent stirring for a quarter of an hour. The solution, which will, except in rare cases, be strongly acid, is now carefully treated with solution of caustic potash till almost neutral. If the lees or tartar operated on contains crystalline bitartrate it must be finely powdered before analysis, else the neutralisation will be tedious, bitartrate being very little soluble in a solution containing potassium salts. After a short further heating the whole is ready for filtration: the bulk of the liquid at this point should not exceed 40 c.c. The lees residue is collected on a small vacuum-filter. The main filtrate is transferred to a small beaker, marked at 50 c.c.; the residue is washed six times by means of the vacuum, and the washings after concentration on the water-bath are added to the main filtrate, which is then brought to 50 c.c.† Citric acid, about twice the quantity required to precipitate the tartaric acid (2 grams is sufficient in the case here assumed) is now added, either as strong solution or as crystal, and the solution stirred till precipitation is completed. After standing for 12 hours the precipitate of bitartrate is collected on a small filter, and washed twice with a 5 per cent. solution of chloride of potassium, then twice with 50 per cent. spirit, and finally with strong spirit till the washings are no longer acid to tincture of litmus.‡ The washing is

---

* This figure is taken as being the highest percentage of gypsum I have found in Spanish lees.

† If the filtrate and washings were mixed and evaporated together, gelatinous matter, probably silica, would sometimes be deposited, and occasion trouble when filtering the bitartrate.

‡ This method of washing was employed in the test experiments and analyses hereafter given; the use of a 5 per cent. solution of potassium chloride, saturated

best conducted on a vacuum-filter. The filter and precipitate are then removed to a beaker, and the amount of bitartrate present determined with standard alkali. The whole operation as here described occupies one day and a-half.

If a strong solution of neutral oxalate of potassium is treated with excess of acid, a crystalline precipitate of acid oxalate of potassium is thrown down; this precipitation does not occur in dilute solutions, or in the presence of sufficient citrate or acetate of potassium. As the test experiments show, no such precipitation occurs when the method is pursued as here described; the use of a great excess of the oxalate must, however, be avoided.

If good tartar is analysed by this method, it is unnecessary to filter the neutral tartrate of potassium from the residue, but after the digestion with oxalate of potassium and neutralisation, citric acid may at once be added to the cold solution. The precipitated bitartrate contains in this case a little vegetable matter, sand, and oxalate of calcium, but these will not affect the titration with standard alkali.

In all the test experiments made with pure bitartrate, or with tartrate of calcium, the whole of the tartaric acid was never absolutely recovered, owing chiefly to the partial solubility of the bitartrate of potassium finally obtained; it is necessary therefore always to precipitate the bitartrate from the same bulk of liquor, and to wash it always in a uniform manner; the correction derived from test-experiments may then be transferred to the analysis of unknown materials. The correction to be used is best determined by each analyst for himself; the peculiarities of his mode of work are then allowed for. The correction I am in the habit of employing for lees is ·070 gram of tartaric acid; this is added to the quantity of tartaric acid found before calculating the percentage. If the quantity of lees taken is that already mentioned, this correction will represent about 3 per cent. of the tartaric acid found. The following test-experiments were made. The products are the proportions of tartaric acid actually obtained; from their deficiency the correction applied in the case of lees and tartar is derived:—

I. 4 grams of tartrate of calcium decomposed with oxalate of potassium, the solution (20 c.c.) precipitated with acetic acid. Product, 98·21 per cent.

II. 2 grams tartrate of calcium, 1·1 gram of potassium bitartrate, decomposed with oxalate of potassium, the neutralised solution (50 c.c.) precipitated with 2 grams of citric acid. Product, 97·69 per cent.

III. 2 grams tartrate of calcium, 1·1 gram of bitartrate, ·5 gram potash alum, ·05 gram phosphoric anhydride, treated as in II. Product, 97·40 per cent.

with bitartrate, may prove more convenient, but in this case the correction for the losses in the method should be re-determined.

IV. 3 grams of bitartrate, 1 gram of gypsum, treated as II. Product, 97·61 per cent.

V. 3 grams of bitartrate, 1 gram of gypsum, 1 gram of Spanish earth, treated as II. Product, 97·44 per cent.

We will now see how the results of the analysis of lees and tartar by this method compare with the results of the indirect alkalimetric and carbonic acid methods; for this purpose we will repeat with one addition the list of analyses already given. The figures in the following table represent the percentage of total tartaric acid found by each method:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Red Italian Lees	Red Italian Lees.	Red Spanish Lees.	Yellow Spanish Lees.	Yellow Spanish Lees.	Argol.	Tartar.	Tartar.
Indirect alkalimetric method	33·4	26·3	23·4	26·0	27·3	49·3	71·6	76·0
Indirect carbonic acid method	27·1	19·7	19·9	22·8	23·2	46·1	—	75·1
Direct oxalate method	28·9	22·6	20·6	23·5	25·6	47·5	71·3	75·8

We have seen reasons for supposing that the alkalimetric method gives results which are too high, and the carbonic acid method results which are too low, the results yielded by the direct method are now seen to lie in every case between these two. In the case of the high quality tartar VIII, there is no very important difference between the results of the three methods; with argol the difference becomes more considerable, and with lees the divergency is in most cases very great. The alkalimetrical results are farthest from the truth, as they involve a double source of error. The alkalimetrical results are nevertheless frequently lower than the results obtained by highly respectable commercial analysts employing method A. Thus lees IV was reported as 27·0 per cent., and argol VI as 51·97 per cent. by one chemist, and tartar VII as 72·25 per cent. by another chemist. I trust that one result of the publication of these investigations will be the reconsideration of the methods now employed by commercial analysts for the analysis of lees and tartar, and the adoption, if possible, of a direct method of estimation in the case of lees and low tartar.

Before leaving the direct method, I may add that the results obtained in the factory are far more uniform and consistent when referred to the analyses of materials made by this method, than when compared with the quantities of tartaric acid assumed to be present by the indirect methods of examination.

I have taken only one step to ascertain if acids other than tartaric exist in lees; the endeavour made was to determine if acids yielding soluble calcium salts were present; the lees operated on were the five already mentioned. Six or seven grams of the lees were boiled with a little hydrochloric acid to destroy carbonates, then exactly neutralised with soda, and excess of chloride of calcium added. After standing 12 hours the precipitate was collected on a vacuum-filter, washed two or three times, then dried, ignited, and the neutralising power of the ash determined with standard hydrochloric acid and alkali. The results were corrected for the loss of tartrate of calcium in the filtrate and washings, which loss was ascertained by performing similar experiments with pure bitartrate of potassium, and the corrected figures were then compared with the results obtained by the use of method D, with which they should agree if organic acids yielding soluble lime-salts were absent. In the case of the three Spanish lees there was no evidence of the presence of acids forming soluble lime-salts, but with the two Italian lees the results obtained were 1·9 and 1·4 per cent. below those given by method D, and pointed consequently to the existence of the class of acids sought for.

Analysis of Tartaric Acid Liquors.—The tartaric acid liquors of a factory which has been long in operation will contain far more impurity than the corresponding citric acid liquors. The mother-liquors of the tartaric acid will in the case supposed contain a considerable amount of organic acid which is not tartaric, and they will hold in solution large quantities of alumina, potash, and phosphoric acid, with some oxide of iron, and of course a good deal of free sulphuric acid.* The different behaviour of tartaric and citric acid towards ferric oxide and alumina, which determines their accumulation in the one case and not in the other, will be discussed in the last section of this paper, we will consider here some methods for analysing tartaric acid liquors. As all the incombustible constituents can be readily determined in the ash by the usual methods, we shall treat only of the determination of tartaric acid, of free sulphuric acid, and of total organic acids.

The direct determination of free tartaric acid may be effected by precipitation in the form of bitartrate of potassium; this is best done by the addition of a strong solution of acetate or citrate of potassium. We have already seen that bitartrate of potassium is much less soluble in a solution of the chloride, sulphate, or nitrate of potassium,

---

* I have known a bad old liquor to contain in 100 gallons as much as 54·61 lbs. of alumina, 58·21 lbs. of phosphoric acid, 9·85 lbs. of oxide of iron reckoned as ferric oxide, and 99 lbs. of sulphate of potassium.

than in the acetate or citrate, and at first sight the former salts would seem the more suitable as precipitants; but the greater insolubility of the bitartrate in these salts is more than counterbalanced by its easy solubility in their respective acids, which are set free immediately their potassium is precipitated as bitartrate. We select therefore a potassium salt the acid of which will exert but little solvent action on the precipitate. Acetate of potassium is probably the best reagent, but its use is limited to pure liquors, for when added to liquors containing phosphate of aluminium or iron, these are precipitated in a gelatinous form along with the bitartrate, and no accurate results can be obtained. Citrate of potassium is without this objection, the citric acid set free in the reaction holding the above-mentioned impurities in solution. The method which has been adopted is the following :—

A quantity of liquor containing 2—4 grams of tartaric acid, and of 30—40 c.c. in volume, is treated with a saturated solution of tripotassic citrate, added drop by drop with constant stirring. If free sulphuric acid is present, no precipitate is at first produced, but as soon as the sulphuric acid is satisfied, the bitartrate begins to appear in streaks on the sides of the vessel. When this is seen the remainder of the citrate is measured in to avoid an undue excess: 4 c.c. of a saturate solution of tripotassic citrate will be found sufficient to precipitate the maximum of 4 grams of tartaric acid supposed to be present. If the liquor contains a great deal of sulphuric acid, a fine precipitate of sulphate of potassium will precede the formation of bitartrate, but is pretty easily distinguished from it. With liquors rich in sulphuric acid, it is advisable to stir the mixture occasionally for several hours after precipitation, to prevent the formation of large crystals.

In the reaction between free tartaric acid and neutral citrate of potassium, only 1 equivalent of citric acid is set free for 2 equivalents* of tartaric acid precipitated. It may happen therefore that the free citric acid produced is insufficient to hold all the impurities in solution; if this is the case a gelatinous precipitate forms on the surface of the precipitated bitartrate. Should this occur, the experiment must be repeated with the previous addition of free citric acid. This case, however, seldom happens, as the free sulphuric acid in the tartaric liquor is generally sufficient to produce an abundance of free citric acid.

After standing for 12 hours, the precipitated bitartrate is collected on a small filter, washed two or three times with a 5 per cent. solution of potassium chloride, then with single washings of 50 per cent. and

---

* "Equivalent" is used in the sense of having the same neutralising power, $2\overline{\text{Ci}}''' = 3\overline{\text{T}}''$; or by weight, 70 of crystallised citric acid equal 75 of crystallised tartaric acid.

70 per cent. alcohol, and finally with 80—90 per cent. alcohol till the washings are no longer acid to tincture of litmus. The gradual employment of the alcohol is to prevent the choking of the filter by the sudden precipitation of salts insoluble in that fluid. The filter with its washed precipitate is lastly transferred to a beaker, and the amount of bitartrate determined with standard alkali.

The perfect washing of the precipitate, and the sharpness of the final determination with alkali, depend on the absence of gelatinous phosphate of aluminium and iron. With tolerably pure liquors, two or three small washings with the chloride of potassium solution will suffice, but with impure liquors this washing must be continued a little longer, else the alcohol will precipitate gelatinous matter among the bitartrate. Any great use of the chloride of potassium solution should of course be avoided, as the precipitate is not entirely insoluble in this solution. The employment of a vacuum filter enables the precipitate to be thoroughly washed with a minimum of fluid.

Clean precipitates are more readily obtained when the washing is performed throughout with a cold saturate solution of bitartrate of potassium; the washing is in this case continued till the acidity of the drain-water is no greater than the acidity of the wash-water. If perfect accuracy is desired in this method, the washed filter must be weighed, and then dried and weighed again, to determine the amount of wash-water which it retains; the correction is, however, a very small one, and when ascertained once or twice, may safely be assumed in similar determinations. The use of solution of bitartrate of potassium as a wash-water, answers well if the precipitate contains no crystallised sulphate of potassium, but if sulphate of potassium be present the bitartrate in the wash-water is precipitated on the filter, and the results come out too high. With liquors containing much free sulphuric acid the precipitate is sure to contain a considerable amount of potassium sulphate.

A wash-water consisting of a 5 per cent. solution of chloride of potassium saturated with bitartrate, possesses great advantages, and can be used when the precipitate contains sulphate of potassium. According to an experiment by Mr. Grosjean, even alum may be successfully removed from precipitated bitartrate by its means.

The following test-experiments illustrate the above statements, and show that the method now described gives results of considerable accuracy even in the presence of large quantities of impurities.

I. 3 grams of tartaric acid in 30 c.c. of water, 4 c.c. of a saturate solution of citrate of potassium added, the precipitate washed with alcohol.* Product, 100·54 per cent.

---

* In all cases where alcohol was used there were one or two small preliminary washings with cold water. Chloride of potassium was at this time not employed.

II. Materials as above: the precipitate washed with a saturated solution of bitartrate of potassium, and the result corrected for retained wash-water. Product, 100·06 per cent.

III. 3 grams of tartaric acid, and 20 drops of a saturated solution of citric acid, in 30 c.c. of water, 4 c.c. of citrate of potassium added, the precipitate washed with alcohol. Product, 100·53 per cent.

IV. Materials as preceding: the precipitate washed with bitartrate solution. Corrected product, 100·91 per cent.

V. 3 grams of tartaric acid, and 3·4 grams of brown oil of vitriol (sp. gr. 1·71), in 30 c.c. of water, 15 c.c. of saturated solution of acetate of potassium added; much sulphate of potassium crystallised out; the precipitate was washed with alcohol. Product, 101·3 per cent.

VI. Materials as preceding: 15 c.c. of saturate solution of citrate of potassium added; much sulphate of potassium formed; precipitate washed with bitartrate solution. Corrected product, 104·98 per cent.

VII. Materials and reagents as in VI, but the tartaric acid solution diluted to 60 c.c.; no crystallisation of sulphate of potassium; precipitate washed with bitartrate solution. Corrected product, 101·3 per cent.

VIII. 3 grams of tartaric acid, 3·4 grams of brown oil of vitriol, 3 grams of potash alum, ·4 gram of phosphoric anhydride, and a little ferric chloride, in 30 c.c. of water; 17 c.c. of saturate solution of citrate of potassium added; no apparent crystallisation of sulphate of potassium; precipitate washed with alcohol. Product, 100·67 per cent.

IX. Materials and reagents as preceding; precipitate washed with bitartrate solution. Corrected product, 100·22 per cent.

The materials used in the last two experiments represent pretty fairly the inorganic impurities which may be present in a bad sample of old liquor.

The method of precipitation by citrate of potassium may give results considerably in excess of the truth if the liquor contains alum, but no phosphoric acid; under these circumstances alum crystallises out with the bitartrate, and if imperfectly removed during washing, it finally increases the acidity of the precipitate. This error may be avoided by adding phosphoric acid before the addition of the citrate. The following test-experiments illustrate the facts in question.

X. 3 grams tartaric acid and 5 grams of concentrated oil of vitriol, in 40 c.c. of water, precipitated with 15 c.c. of saturate citrate of potassium. The precipitate contained much sulphate of potassium; it was washed with chloride of potassium solution and alcohol, on a vacuum filter. Product, 99·7 per cent.

XI. Materials as above, with 3 grams of potash alum. A considerable amount of octohedral alum crystallised out. Treated as in X, the product was 121·4 per cent.

XII. Materials as in XI, with ·8 gram of phosphoric anhydride (8 c.c. of Pharmaceutical dilute acid). No alum crystals observed. Product, 99·5 per cent.

The presence of alumina in a bitartrate precipitate is easily detected after titration, by boiling the solution with excess of phosphate of sodium and a little acetic acid; alumina if present is then thrown down as phosphate, tartrates having scarcely any power of keeping alumina in solution at a boiling heat, if excess of phosphoric acid is present. If a distinct quantity of alumina is found, a second determination of tartaric acid might be made, with the previous addition of phosphoric acid. Phosphoric acid cannot, however, be added to very bad liquors without giving rise to a gelatinous precipitate of phosphate of aluminium; in such cases the precipitate containing alum must be washed with the 5 per cent. chloride of potassium solution saturated with bitartrate, which has been already mentioned.

A rather considerable excess of citrate of potassium does not injure the result if free sulphuric acid were originally present; a very large excess will however diminish the precipitate, by increasing the solubility of the bitartrate. The acid citrate of potassium, thrown down by alcohol, noticed by Mr. Allen (*Chem. News*, xxxi, 278), is readily soluble in chloride of potassium solution.

Racemic acid, if present, will in this method be determined as tartaric acid. Inactive and metatartaric acid will only be partially precipitated, as their acid potassium salts are more soluble than normal bitartrate. A test experiment was made with the same mixture used in VIII, to which ·5 gram of metatartaric acid (prepared by gently fusing ·5 gram of tartaric acid) was added; the precipitate washed with alcohol gave a product of 104·1 per cent. of the tartaric acid taken. It is evident that here only a portion of the metatartaric acid had been precipitated; had the whole been thrown down, the product would have been 116·7. The acid metatartrate of potassium being so much more soluble than the acid tartrate, I expected that by washing the precipitate with a cold saturated solution of normal bitartrate, I should be able to remove the whole of the metatartrate without touching the true bitartrate; experiment showed, however, that the presence of the metatartrate greatly increased the solubility of the tartrate, so that this mode of washing resulted in a great loss. Materials the same as used in VIII were taken, and 1 gram of fused tartaric acid added; the precipitate was washed with a cold saturate solution of bitartrate. The washings instead of regularly diminishing in acidity soon reached a constant point, nearly double that of the wash-water, and though half a litre of washing was applied, the acidity of the drain-water was maintained at this high figure. The experiment being stopped, the precipitate was found so much diminished as to contain only 61·5 per cent. of the tartaric acid taken. Another experiment in which the wash-water was a 5 per cent. solution of sulphate of potassium, saturated with bitartrate, gave a similar result. Only half a gram of fused tartaric acid was present, yet 600 c.c. of the washing fluid failed to bring the acidity of the drain-water down to that of the wash-water: the product was 93·6 per cent. It appears, therefore, that no complete separation of tartaric and metatartaric acid was effected by any of the washings employed.

Oxalic acid does not apparently interfere with the results yielded by this method. To a mixture similar to that used in VIII, 1 gram of oxalic acid was added; the precipitate was washed with chloride of potassium and alcohol on a vacuum filter; the product was 101·5 per cent. of the tartaric acid taken.

The determination of free sulphuric acid in tartaric acid liquors is not so simple as in the case of citric acid, owing to the tendency of tartaric acid to form insoluble potassium and calcium salts in presence of alcohol, and also from the occurrence of alum in some liquors. If a solution of sulphate of potassium in tartaric acid is poured into alcohol, bitartrate of potassium is at once precipitated, and the quantity of sulphuric acid in the filtrate is of course in excess of the free sulphuric acid originally present. If potash-alum is dissolved in tartaric acid and poured into alcohol, the precipitate is a mixture of bitartrate of potassium and alum, and the filtrate contains much sulphuric acid which was not originally free. If sulphate of calcium also is dissolved in tartaric acid, the addition of alcohol precipitates some tartrate of calcium along with the sulphate, occasioning the same error as above. These errors are removed as soon as the quantity of free sulphuric acid in the tartaric liquor reaches a certain point. Thus a solution of gypsum in tartaric acid, with a little free sulphuric acid, gave with alcohol a precipitate of pure sulphate of calcium. With sulphate of potassium, experiments were made with rising quantities of sulphuric acid, till the alcohol precipitate contained no bitartrate. Taking in every case 20 c.c. of liquor, containing 2 grams of tartaric acid and ·5 gram of sulphate of potassium, and dropping the solution, with constant stirring, into 100 c.c. of 90 per cent. alcohol, it was found that with ·64 gram of oil of vitriol, 46 per cent. of the potash was precipitated as bitartrate, but that when 1 gram of oil of vitriol was present, the amount of bitartrate in the precipitate was reduced to a trace, and with 1·25 gram, the precipitate after washing with alcohol was found to be perfectly neutral, and to consist entirely of sulphate of potassium.* Experiments with potash-alum gave a like result. With a small quantity of free sulphuric acid, the alcohol precipitate consisted of alum free from bitartrate, and the filtrate contained only a trace of alumina.

It appears from these facts that the treatment of tartaric liquors with alcohol for the purpose of separating sulphates from free sulphuric acid, will lead to accurate results only when the free sulphuric acid reaches a certain amount, and that when this is not the case, the determination of free sulphuric acid will be too high. Practically, however, the error here described will be confined to the case of new liquors of bad quality.

The determination of free sulphuric acid is conducted as follows:—5—20 c.c. of the liquor is slowly dropped into 100 c.c. of 90 per cent. alcohol, stirring the whole time. If the liquor is concentrated, and of bad quality, it should be diluted with its own volume of water before being poured into the alcohol. The alcohol precipitate contains, besides sulphates, phosphate of aluminium, and other substances. After standing for 24 hours the solution is filtered, the precipitate washed with alcohol, and the filtrate and washings precipitated with an alcoholic solution of calcium chloride. If only a small excess of calcium chloride has been used, it is possible to determine the quantity of sulphate of calcium as directed in the case of citric acid liquors, but since tartaric acid is precipitated by calcium chloride in the presence of alcohol, it is safer not to do so. The sulphate of calcium-precipitate is therefore separated from the liquor by decantation or filtration, and without washing dissolved in dilute hydrochloric acid; the sulphuric acid is then precipitated from a hot, very dilute solution, with chloride of barium.

The total organic acids in tartaric acid liquors may sometimes be determined as in citric liquors, by subtracting the acidity of the free sulphuric acid from the total acidity of the liquor, but this method would generally lead to excessive results from the presence of acid phosphates, and of alum, which determine a part of the total acidity. The amount of total organic acid is better ascertained by exactly neutralising the liquor with soda, evaporating to dryness, igniting the residue, and finally determining its neutralising power with standard sulphuric acid and alkali. Both by this method, and by the preceding, the true weight of the organic acids present is undetermined, only their equivalence is ascertained; it is most convenient to express the result in terms of tartaric acid.

---

* Only neutral sulphate of potassium is precipitated when a solution of neutral sulphate and free sulphuric acid is dropped into alcohol.

In the method last mentioned, the presence of aluminium, iron, and phosphoric acid may affect the result.

If tartaric acid is exactly neutralised with soda, and the resulting salt ignited, the amount of tartaric acid present may of course be accurately ascertained, either by the neutralising power of the ash, or from the amount of carbonic acid it contains. If the tartaric acid contains alumina* in solution, a smaller quantity of soda will be required for its neutralisation than if the tartaric acid was pure; the whole of the tartaric acid will thus not be converted into disodic tartrate, and the carbonate of sodium resulting on ignition will be less than equivalent to the tartaric acid employed. If the tartaric acid contained phosphoric acid as well as alumina, the amount of soda necessary for neutralisation will again be less (except, perhaps, when the phosphoric acid is in great excess) than that required by the tartaric acid and by the phosphate of aluminium if neutralised separately. In both cases the tartaric acid is either partially satisfied by the aluminium, or the latter exists as a more acid salt than it would have done in the absence of tartaric acid. The deficient conversion of the tartaric acid into disodic tartrate, coupled with the decomposition of sodium carbonate during ignition with basic aluminium salts, is fatal to the determination of organic acids from the amount of carbonic acid present in the ignited sodium salt. The results of test-experiments by this method were always greatly below the truth. These facts are not however fatal to the alkalimetric method, if certain considerations are borne in mind.

If the ash of a neutralised solution of tartaric acid, containing alum, is entirely dissolved in sulphuric acid, the sulphate of aluminium will consume more alkali for its neutralisation than it did when originally neutralised in the presence of tartaric acid, the alumina being now precipitated as a highly basic salt, while previously it was held in solution in combination with a greater quantity of acid; the tartaric acid calculated from such an analysis will consequently be below the truth. If, however, after dissolving the ash in standard sulphuric acid, we add a sufficient amount of neutral Rochelle salt to keep the alumina in solution during neutralisation, we establish the same conditions as occurred in the original neutralisation of the tartaric liquor; the alumina in each case consumes the same amount of alkali, and all that has been done is to replace an unknown quantity of organic acid by a known quantity of standard sulphuric acid; the equivalence of the organic acid is thus arrived at with perfect exactness.

When, as in ordinary tartaric liquors, phosphoric acid is present as well as alumina, the result by the alkalimetric method will also be too

---

* The test-experiments have been made with alumina only, but ferric oxide may be considered from analogy to behave in a similar manner.

low if Rochelle salt is not employed.* When, however, much phosphate of aluminium is present, it becomes impossible to neutralise the original liquor with soda without precipitating a part of the phosphate, and this is especially the case if excess of phosphoric acid be present (see the concluding section of this paper). Under these circumstances the addition of Rochelle salt to the solution of the ash equally fails to produce a permanent solution. Perfectly accurate results are obtainable only when the original liquor can be neutralised with soda without precipitation, and when, by addition of Rochelle salt, the final neutralisation is also made without a precipitate. When circumstances do not admit of these conditions, the process is less accurate, though still the best I am aware of. It is essential that the whole of the ash be dissolved in the standard acid; the ash must, therefore, be burnt nearly white that the fact of its solution may be ascertained. The standard sulphuric acid should be allowed to concentrate on the ash, it will then effect its solution in a few hours. When much phosphate is present, it is well to pour off the first solution in acid, and act on the residue with a fresh portion. The Rochelle salt should be added to a cold, concentrated solution, heat and dilution diminish its solvent power.

Before quoting the test-experiments another condition must be mentioned which affects the amount of soda required for neutralising a tartaric liquor; this is the presence of lime. It is probably well known that phosphoric acid is neutralised (to litmus) by very different quantities of lime and soda, the neutral sodium phosphate containing less soda than is sufficient to form disodic phosphate, while the neutral calcium phosphate approaches tricalcic phosphate in composition. In an experiment in which the same quantity of phosphoric acid was neutralised in the cold by lime-water and by standard soda, it was found that for 1 equivalent of soda 1·59 equivalent of lime was required to produce perfect neutralisation. This difference between lime and soda is also observed in neutralising tartaric liquors containing alumina. A dilute solution of tartaric acid and potash-alum, exactly neutralised with soda, becomes strongly acid if neutral chloride of calcium is poured in.† This new acidity may be neutralised with soda without producing any precipitate. In an experiment in which a solution of 1 part of potash alum and 5 parts of Rochelle salt was neutralised in the cold by lime-water and soda respectively, it was found that for 1 equivalent of soda 1·21 equivalent of lime was

---

* In the presence of phosphate of aluminium there is an error of excess if the ash is not wholly redissolved in the standard acid; the two errors may balance each other.

† This action of calcium salts is possibly one cause of the acidification of neutralised lees when boiled.

required. The solutions in both cases were perfectly clear after neutralisation. The amount of lime demanded for neutralisation, or the amount of soda required in the presence of calcium chloride, was exactly equal to the sulphuric acid of the sulphate of aluminium present; alumina thus exerts no neutralising power in a solution containing Rochelle salt and lime. The compounds formed under these conditions deserve further study.

These curious facts have no influence on the method of analysis just described, if the ash is perfectly dissolved in the standard acid, as there must then be the same amount of lime present in the final titration as in the first.

The following are some of the test-experiments made :—

I. 1 gram of potash-alum dissolved in cold water took 41·4 c.c. of standard soda for neutralisation (47·8 c.c. would be required for the sulphuric acid of the sulphate of aluminium). Boiled with a small excess of soda, and neutralised with acid, it took in all 47·6 c.c. of alkali.

II. 1 gram of potash-alum and 5 grams of Rochelle salt, neutralised in the cold with 38 c.c. of alkali. Excess of chloride of calcium added, it took 47·5 c.c. of alkali.

III. 1 c.c. of dilute phosphoric acid (B.P.) took 17·5 c.c. of alkali.

IV. 1 gram of potash-alum and 1 c.c. of phosphoric acid took 52 c.c. of alkali. Boiled with small excess of soda, and neutralised with acid, it took 56 c.c. of alkali.

V. 1 gram of potash-alum, 1 c.c. of phosphoric acid, and 5 grams of Rochelle salt, took 48·5 c.c. of alkali; solution quite clear. Excess of chloride of calcium added, it took 54 c.c. of alkali.

VI. 1 gram of potash-alum and 2 c.c. of phosphoric acid took 63 c.c. of alkali. Excess of chloride of calcium added, it took 68·5 c.c. of alkali.

VII. 1 gram of potash-alum, 2 c.c. of phosphoric acid, and 5 grams of Rochelle salt, took 62 c.c. of alkali (a precipitate from the first). Excess of chloride of calcium added, it took 68 c.c. of alkali.

VIII. 1 gram of potash-alum, 1 gram of tartaric acid, neutralised with soda, evaporated, ignited, ash dissolved in standard sulphuric acid and titrated with alkali. Product 92·3 per cent.

IX. Materials as VIII; solution of ash treated with Rochelle salt before titration. Product 100 per cent.

X. 1 gram of potash-alum, ·2 gram of ferrous sulphate, 1 c.c. of phosphoric acid, 1 gram of tartaric acid; solution of ash treated with Rochelle salt. Product 100·47 per cent.

XI. 1 gram of potash-alum, 2 c.c. of phosphoric acid, 2 grams of tartaric acid; the addition of Rochelle salt to solution of ash produced a large precipitate. Product 100 per cent.

When from the total organic acids ascertained by this method we deduct the tartaric acid found by direct experiment with citrate of potassium, we arrive at the amount of organic acid other than tartaric present. Thus a bad old liquor treated by this method gave 2·77 lbs. per gallon of total organic acids; the tartaric acid directly determined was 1·62 lbs., the organic acids not tartaric were therefore 1·15 lbs. Another old liquor gave 5·18 lbs. of total organic acids, 3·36 lbs. of tartaric, and consequently 1·82 lbs. of other acids. The total weight of other organic acids thus ascertained is of course not their actual weight, but only their equivalence in tartaric acid.

Nature of the Organic Acids in Tartaric Liquors.—It has just been mentioned that the mother-liquors in a tartaric acid factory contain a considerable quantity of organic acid which is not tartaric. Concerning the nature of this acid some experiments have been made.

Attention was directed in the first place to those acids which are known to be formed when tartaric acid is subjected to heat: metatartaric and ditartaric acid were therefore sought for. In examining liquors for ditartaric acid, use was made of the property of its salts of becoming acid when boiled. Old tartaric liquors neutralised with soda and boiled do not become acid as far as my experience goes. If chloride of calcium is added to the neutralised liquor, it becomes indeed strongly acid, but this acidification takes place in the cold as well as in the hot, and is therefore not due to the splitting up of a ditartrate. The acidification caused by the addition of chloride of calcium to neutralised tartaric liquors containing alumina has been already noticed; the same reaction probably takes place when calcium chloride is added to neutralised old liquor.

While old liquor yields only negative results as to the presence of ditartaric acid, the evidence furnished by the waste liquor of the factory, obtained by precipitating old liquor with excess of chalk, is more ambiguous. If this waste liquor, which must contain all the ditartaric acid present, is neutralised with soda and boiled, it becomes distinctly acid, and in some rare instances the amount of acidification is very considerable. As, however, neutralised solutions containing phosphates of iron, aluminium, or calcium, become acid on boiling from the splitting up of the phosphates into basic and acid salts, I hesitate to conclude from this reaction the presence of ditartaric acid. The large acidification on boiling sometimes observed in waste liquors is, however, much greater than I have succeeded in obtaining from artificial waste liquors containing phosphates unprecipitated by chalk.*

Some further evidence as to the presence of altered tartaric acid was furnished during the examination of an old liquor. The free sulphuric acid had been removed with carbonate of barium, and the tar-

---

* For the action of chalk on the inorganic ingredients of old liquor, see the last section of this paper.

taric acid with acetate of potassium; the solution was then heated with a small excess of lime and filtered. The resulting liquid would now contain the metatartaric and ditartaric acid present, as both the potassium and calcium salts of these acids are far more soluble than the corresponding tartrates. The solution was acidified with acetic acid, and fractionally precipitated with nitrate of lead. The second fraction, a nearly white precipitate, was decomposed with sulphuric acid, the excess of sulphuric acid removed with nitrate of lead, the solution made hot, and acetate of lead added as far as possible without occasioning a permanent precipitate. On cooling, a lead salt was deposited on the sides of the beaker in the form of clear globular masses. A further crop of the same salt was obtained by a second addition of acetate of lead. The mother-liquor again heated with lead acetate yielded a precipitate which was distinctly plastic while hot. It will be recollected that in an earlier section of this paper it was shown that a hot solution of fused tartaric acid treated fractionally with acetate of lead yields both the plastic and globular lead salts here described. The small quantity of globular lead salt obtained was decomposed with sulphuretted hydrogen, the resulting solution concentrated, and placed over oil of vitriol. It crystallised like ordinary tartaric acid, and when tested qualitatively gave all the ordinary reactions of that acid. The altered acid had thus apparently reverted into tartaric acid. I have since examined two or three old liquors in a manner similar to the above, but in these cases have failed to obtain the characteristic lead salts just described.

As a third method of ascertaining the presence of altered tartaric acid in old liquors, experiments were made to determine whether the amount of normal tartaric acid present was increased by dilution and long boiling. Test-experiments were first performed as to the applicability of this mode of investigation.

I. 2 grams of powdered tartaric acid were brought to fusion, then dissolved in 100 c.c of water, and boiled for three hours. The solution was then concentrated to 40 c.c., 1 c.c. of oil of vitriol added, and 10 c.c. of a nearly saturate solution of citrate of potassium; the precipitation was immediate. The precipitate was washed first with chloride of potassium solution, and finally with alcohol. It required 100·5 c.c. of alkali for neutralisation, corresponding to 100 per cent. of the tartaric acid taken.

II. 2 grams of tartaric acid, fused, and treated as above, except that the oil of vitriol was added before boiling. The precipitate required 101·5 c.c. of alkali, corresponding to 101 per cent. of the tartaric acid taken.

III. 2 grams of tartaric acid, fused, dissolved in 40 c.c. of water, 1 c.c. of oil of vitriol added, and 10 c.c. of citrate of potassium. No precipitation occurred for some minutes; the precipitate then gradually increased, and became at last the most bulky of the three. Collected and washed as above, it required only 39·5 c.c. of alkali for neutralisation, equal to 39·3 per cent. of the tartaric acid taken.

It appears from these results that the amount of dilution and boiling here employed was quite sufficient to reconvert all the metatartaric and ditartaric acid into normal tartaric acid, and that the presence of much free sulphuric acid had no practical influence on the result. Similar experiments were now made with old liquors.

I. 5 c.c. of old tartaric liquor diluted to 40 c.c., 1 c.c. of citric acid added, and 12½ c.c. of citrate of potassium. The precipitate washed with chloride of potassium and alcohol, required 59·5 c.c. of alkali for neutralisation.

II. 5 c.c. of the same liquor, diluted to 100 c.c., l [illegible] 3 hours, then concentrated to 40 c.c., and treated exactly as [illegible] precipitate required 61·5 c.c. of alkali, showing an increase by boiling of 3·36 per cent.

III. 5 c.c. of another old liquor, unboiled, diluted to 40 c.c. and treated in a similar manner, gave a precipitate requiring 89·5 c.c. of alkali.

IV. 5 c.c. of the liquor used in III, diluted to 100 c.c. and boiled for 3 hours, then concentrated to 40 c.c. and treated exactly as in III, gave a precipitate requiring 92·8 c.c. of alkali, showing an increase by boiling of 3·68 per cent.

These results show in both cases the presence of a small quantity of altered tartaric acid, which dilution and long boiling was capable of reconverting into tartaric acid. I am disposed therefore to conclude that small quantities of metatartaric acid, and possibly also of ditartaric acid, may be present in concentrated liquors which have been long heated in the factory. In *Gmelin's Chemistry* it is stated that both these acids are formed when tartaric acid is heated with a small quantity of water, as well as when it is heated in the dry state.

Jungfleisch has recently called attention to other products of the action of heat on tartaric acid. He has shown that when tartaric acid and water are heated in a sealed tube to 175° for many hours, the acid is entirely converted into racemic and inactive tartaric acid. Racemic acid has long been a bugbear to tartaric acid manufacturers; to its supposed presence in some tartars they have been ready to attribute the irregular losses of their factories. I have not met with any indications of the presence of racemic acid in the liquors of Mr. Lawes' factory; the results of Jungfleisch, however, appeared to make its occurrence probable, I have consequently made a few experiments on the subject.

Two samples of old liquor of different origin were diluted, the greater part of the sulphuric acid removed with acetate of barium, the solutions concentrated, divided into two equal parts, one half neutralised with potash, and the other half then stirred in, a little acetate of potassium being also added; the precipitates were finally collected and slightly washed. The attempt was now made to separate the various acid potassium tartrates by fractional crystallisation, this being the method employed by Jungfleisch. Of the three salts the biracemate is the most insoluble, and the salt of the inactive acid the most soluble, while ordinary bitartrate lies between the two. The fractions which should contain the more insoluble salts were tested for racemic acid by adding solution of sulphate of calcium to a cold saturate solution of the salt. An aqueous solution of biracemate of potassium is precipitated immediately by a solution of gypsum, racemate of calcium falling as a fine white precipitate. A solution of ordinary bitartrate, treated in the same way, yields large transparent crystals of tartrate of calcium after some hours standing. It was found on trial that a cold saturated solution of biracemate of potassium might be diluted with three times its volume of solution of ordinary bitartrate, and would still afford a distinct precipitate two or three minutes after the addition of sulphate of calcium. No indication of racemic acid was obtained from any part of the acid potassium salts crystallised from old liquor.

The mother-liquors from the fractional crystallisations should of course contain the salt of the inactive acid. From this liquor some unusually large crystals separated, which I hoped might prove to contain the acid sought, since its acid potassium salt is stated by Jungfleisch to yield crystals of remarkable size and beauty. Two small crops of these crystals were collected and weighed. On neutralising with soda they required the same amount of alkali as normal bitartrate. The neutralised solutions were kindly examined by Dr. Gladstone in the polariscope, each solution being compared with a solution containing the same weight of ordinary Rochelle salt. Dr. Gladstone found that the rotations in the comparative experiments were in each case of the same amount and in the same direction; the crystals examined were therefore only ordinary bitartrate.

As far therefore as these few experiments go, racemic acid and inactive tartaric acid are not produced during the heating which tartaric acid liquors undergo in a factory.

I have ascertained the presence of one acid, which I think has not been previously recognised in tartaric acid liquors, this is oxalic acid. It was first observed crystallised in long needles in old liquor which had been diluted and exposed to cold. These needles melted at a low heat, and volatilised entirely with all the characters of oxalic acid. Dissolved in water they gave an immediate precipitate with sulphate of calcium. The acid was converted into a calcium salt, which was purified by solution in hydrochloric acid and reprecipitation by acetate of ammonium from a hot very dilute solution. The purified salt, dried at 100°, yielded 38·17 per cent. of lime; theory ($C_2CaO_4.H_2O$) requires 38·35 per cent.

In another case a precipitate of calcium salts from an old liquor, previously deprived of sulphuric and tartaric acid, was suspected of containing oxalic acid. The precipitate was treated with very dilute cold nitric acid, which dissolved the associated salts and left the oxalate of calcium, which was then purified as above described. Dried at 100°, the salt, which was very small in quantity, yielded 38·09 per cent. of lime.

Oxalic acid is of frequent occurrence in old liquors; it is usually recognised by its appearance in the form of crystals. It is not easy to detect oxalic acid in the liquor by any qualitative test, even when it is known to be present; of the difficulties involved anyone may convince himself by dissolving oxalic acid in a solution of tartaric acid containing alum, and then trying to detect the oxalic acid added.

The subject of the organic acids present in old tartaric liquors is a very promising one for chemical investigation. I am sorry that I have no further light to throw on the matter.

Behaviour of Tartaric and Citric Acid towards Iron, Aluminium, and Phosphoric Acid.—The marked difference between tartaric and citric acid, shown in the gradual accumulation of alumina and phosphoric acid in tartaric liquors, and the absence of such accumulation in the case of citric liquors, led me to investigate the subject.

If ferric oxide is dissolved in citric acid, or ferric chloride added to the acid, the acid being in excess, the solution may be boiled with excess of chalk without precipitating the iron. The precipitated citrate of calcium is white, the solution is of a lemon-yellow colour, and quite neutral to litmus. With alumina the results appear to be similar; the solution becomes neutral on boiling with chalk, and a great part of the alumina, probably the whole, remains in solution. If instead of the citric acid being in excess at starting, an excess of ferric chloride is present, then on boiling with excess of chalk the whole of the iron is precipitated, and the solution becomes colourless. The complete precipitation of the iron in this case is doubtless due to the fact that the citric acid is carried down as a basic ferric salt.

With tartaric acid the reactions are different. The addition of chalk to a hot solution containing ferric oxide or alumina precipitates these bases even when the tartaric acid is in great excess. The tartrate of calcium thrown down by the first small addition of chalk is yellow in colour, even when but little iron is present, and at the conclusion of the operation the solution is found to be colourless, neutral, and containing only a trace of iron.

In the cold, the reactions of citric acid with ferric salts are similar to those in hot solutions. When moderate quantities of iron are present the whole of the iron remains in solution; with excess of iron the whole is precipitated: the solution is neutralised by the chalk. Tartaric solutions of iron are also neutralised by chalk in the cold. When only a small quantity of iron is present a little falls with the tartrate of calcium, and the greater part remains in solution; with an excess of iron the whole is precipitated. The excess of iron required for this purpose is much smaller than in the case of citric acid. The affinity of tartrate of calcium for iron is remarkable; tartrate of calcium crystallising from a ferric solution is sure to be yellow, even when little iron is present, and the solution strongly acid with tartaric acid.

Ferrous salts, it is well known, are not precipitated by chalk in the cold; nor is ferrous sulphate perfectly precipitated by chalk on long boiling, if air be excluded; the solution in this case remains somewhat acid. In the presence of tartaric acid ferrous sulphate is also not precipitated by chalk in the cold, but at a boiling heat chalk occasions a bluish precipitate clearly containing iron; a considerable quantity of the iron remains however dissolved, forming an acid, olive-coloured liquid, which further boiling with chalk does not seem to affect if air be excluded. With citric acid and ferrous salts, the addition of chalk fails to precipitate iron, either in the cold or on boiling.

It appears from the above, that citric acid liquors containing ferric or ferrous salts, may be treated with excess of chalk even at a boiling heat without precipitating the iron, but that in the case of tartaric liquors there is at a boiling heat a complete precipitation of ferric, and a partial precipitation of ferrous salts. Alumina appears to behave with these acids in much the same manner as ferric oxide.

The behaviour of phosphoric acid in tartaric and citric liquors must next be considered, as this acid occurs with iron and aluminium in old liquor. Tartaric, citric, and phosphoric acids are singly easily neutralised by chalk at boiling heat, but if phosphoric acid is mixed with tartaric or citric acid the solution may be boiled with chalk a long time without neutralisation being accomplished. The solution in this case contains an acid calcium phosphate. When the solution is separated, and neutralised with soda, it again becomes acid on boiling, especially if chloride of calcium be added. This acidifying is probably due to the splitting up of the phosphates into acid and basic compounds. See *Journal of Chemical Society*, 1873, 983.

Tartaric acid mixed with ferric chloride and phosphoric acid is not perfectly neutralised by chalk, even when boiling is long continued, the acidity may, however, become very faint. The solution contains a small quantity of acid phosphate, but no iron. Tartaric acid with ferrous sulphate and phosphoric acid, is not neutralised by long boiling with chalk in a covered beaker; the solution is in this case very acid, and contains a notable amount of iron, and some phosphoric acid. Tartaric acid mixed with potash alum or sulphate of aluminium, and phosphoric acid, behaves as in the experiments with ferric salts if the phosphoric acid is in excess to the alumina, but if the alumina is in excess, neutralisation takes place after a short digestion with chalk near a boiling heat. In the case of ferric salts I have not succeeded in obtaining the same speedy neutralisation by increasing the proportion of iron to phosphoric acid.

These reactions of tartaric solutions containing iron and aluminium with phosphoric acid, explain the facts observed when old tartaric liquors are treated with chalk, which is the ordinary mode of purification employed in tartaric acid factories. This treatment with chalk, however long continued, always leaves a very acid liquor, containing ferrous salts in considerable quantity, but very little of ferric salts, alumina, or phosphoric acid. In one quantitative experiment on a large scale, it was found that the waste liquor, containing all the matters unprecipitated by chalk, held in solution 30·1 per cent. of the iron, 1·02 per cent. of the alumina, and 3·58 per cent. of the phosphoric acid originally present in the old liquor. The treatment with chalk thus effects a tolerable purification from iron, but scarcely any from alumina or phosphoric acid; the two latter, therefore, as already mentioned, continually accumulate in the tartaric liquors. The considerable acidity of the waste liquor resulting from precipitation with chalk, is probably mainly due to the ferrous salts and phosphates which it contains. The ferrous salts in tartaric liquors are probably formed by the reducing action of tartaric acid at a high temperature.

In the case of citric acid, the admixture of a ferric salt and phosphoric acid yields a solution from which iron is not precipitated by boiling with excess of chalk, and which remains more strongly and more permanently acid when boiled with chalk than the corresponding tartaric solution. If an aluminium salt is substituted for iron, the solution also remains acid after long heating with excess of chalk, even when the alumina is in such excess as would cause an early neutralisation in the case of tartaric acid. The solution after boiling with chalk contains much alumina and phosphoric acid.

It appears from the above that citric acid liquors can be far more effectually cleansed by precipitation with chalk than tartaric acid liquors. With citric acid the whole of the iron, whether ferric or ferrous, will be removed by such treatment, and at least a considerable proportion of the alumina and phosphoric acid. This agrees with experience acquired on the large scale, which proves that there is no such accumulation of impurities in citric liquors, even after many years' working, as that which takes place in the case of tartaric acid. The easy removal of the impurities in citric acid is, however, at the expense of that acid. Iron is not precipitated from citric acid by chalk simply because it forms a soluble stable compound with the citric acid. In short, the larger the amount of impurity, the greater will be the loss of citric acid when the liquors are treated with chalk.

The following reactions of tartaric and citric acid towards ferric and aluminic salts in presence of phosphoric acid have also been observed:—

When phosphoric acid is added to a dilute freshly-prepared solution of ferric chloride till the liquid becomes colourless, no precipitate is produced, but on heating opalescence commences at 40°—50°, and at a boiling heat a considerable precipitate of ferric phosphate is produced; on cooling, this precipitate slowly redissolves, forming an opalescent liquid. If the solution contains an excess of ferric chloride, no turbidity is produced on boiling; a tolerable excess of phosphoric acid does not, however, hinder the precipitation.

If tartaric acid is added in some quantity to a solution of ferric chloride containing just sufficient phosphoric acid to be colourless, the tartaric acid will actually produce a precipitate in the cold, which will be greatly increased on boiling. If, however, the solution contained an excess either of ferric chloride or phosphoric acid, tartaric acid produces no precipitate in the cold, but on heating considerable precipitation takes place. The precipitates have the appearance of ferric phosphate, they redissolve very slowly on standing in the cold. If citric acid is substituted for tartaric acid, no precipitation takes place in any case, either in the cold or on boiling.

If ferric chloride is mixed with a considerable amount of tartaric acid, and excess of phosphate of sodium added, no precipitate is formed if the solutions are very concentrated and cold, but on dilution, or heating, precipitation of ferric phosphate takes place. If the phosphate of sodium is in excess to the iron, very large quantities of tartaric acid may be added without preventing precipitation on dilution or boiling, but with a smaller proportion of the phosphate permanent solutions are obtained. Under any of the above conditions, the substitution of a small quantity of citric acid for the tartaric acid suffices to prevent precipitation.

A mixture of sulphate of aluminium and phosphoric acid is precipitated on boiling only when the solution is very dilute, the precipitate speedily redissolves on cooling if the boiling has not continued too long. Precipitation is prevented both by tartaric and citric acid, a smaller quantity of the latter sufficing.*

---

* A mixture of phosphoric acid and sulphate of aluminium is not precipitated by

If sulphate of aluminium is mixed with a small quantity of tartaric acid, and excess of phosphate of sodium added, no precipitate is produced if the solution is strong; but if largely diluted and boiled, or if acetate of sodium is added, precipitation takes place. When much tartaric acid is added, the solution is permanent under the conditions named, but it requires about seven times as much tartaric acid as of citric to produce a permanent solution.

A mixture of potash-alum with excess of phosphoric acid is precipitated on the addition of Rochelle salt, but is not precipitated by citrate of potassium.

It appears from the latter experiments, that the capacity of tartaric acid or tartrates for holding phosphate of iron or aluminium in solution is very small, and far inferior to that possessed by citric acid and citrates.

In concluding this account of the notes made in the Millwall Laboratory, I would express my own sense of their imperfection, and of the incompleteness in which many of the subjects are still left. I have no doubt that many of the questions raised will be carried by others to a successful issue. I venture to hope that the publication of these notes may lead to many similar communications. A large amount of information is acquired in the laboratories of our great manufacturing concerns; most of this might be published without any injury to the individual manufacturer. Especially is this true of analytical methods, and the publication and discussion of these would do much to remove the disgrace to which science is often subjected from the wide discrepancies of commercial analyses.

---

acetate of sodium in the cold when the aluminium is in excess ; this reaction is well known in the case of ferric salts.