

CREAM OF TARTAR SUBSTITUTES: THEIR CHEMISTRY AND ANALYSIS.

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TO make an intelligent analysis of any complex substance, the chemist must possess not only the requisite skill, but also a certain amount of knowledge of the material he is working with, in order that the bare analytical results may be correctly interpreted, and given their proper meaning in relation to the particular substance yielding them.

Among the substances with which the majority of practicing chemists appear to be little familiar, is the class of products known in trade under the generic name of cream of tartar substitutes.

Under this general name are included a great many acid powders which are used to replace cream of tartar in the manufacture of baking powders, self-raising flours, and also directly in baking, their function being always that of an acid to liberate carbonic acid gas from sodium bicarbonate.

All cream of tartar substitutes have the common feature that their active acid element is primarily monocalcium phosphate, ($\text{CaH}_4\text{P}_2\text{O}_8$), but in other respects they differ so widely in composition and function, that for convenience in considering them it is best to divide them into two primary classes or types.

The first class (hereafter referred to as class I) consists of goods prepared by treating calcium phosphate (in practice usually in the form of boneblack) with sufficient sulphuric acid to produce monocalcium phosphate and calcium sulphate, filtering off the sulphate, evaporating the solution of monocalcium phosphate to crystallization, mixing with starch, drying and grinding. The resulting product is chiefly a mixture of monocalcium phosphate with starch, but invariably contains a small amount of "free" or uncombined phosphoric acid (varying from one per cent. to six per cent. P_2O_5), and also a considerable quantity of insoluble phosphates, chiefly calcium but frequently iron and aluminum phosphates also. Tartar substitutes of this class are frequently known in trade as "Leached goods."

The other primary type (hereafter referred to as class II) differs from the preceding in method of manufacture, in chemical composition and also in its use and behavior.

The raw material is carefully prepared, pure white bone ash which is treated with the requisite amount of concentrated sulphuric acid, and the resulting mixture, monocalcium phosphate and calcium sulphate, is dried and ground without separation. Hence goods of this type contain a large amount of calcium sulphate, equivalent to the amount of sulphuric acid used in their preparation, and are frequently referred to as "sulphate of lime base" goods.

The essential difference between the two principal types is, that one is practically free from calcium sulphate, while the other contains a large amount of this salt.

Like class I the goods of the second class almost always contain a small amount of free phosphoric acid, and generally considerable quantities of insoluble phosphate, chiefly tricalcium. As a rule they contain very little starch, and frequently none at all.

With regard to this content of calcium sulphate in goods of the second class, it is a common mistake of chemists who are not familiar with these materials, to stigmatize it as an "adulteration," or "the result of careless or imperfect manufacture." Such statements are entirely erroneous, as the calcium sulphate is an essential part of the goods and has a very important influence on their action, as explained later.

A point to be noticed, which is a stumbling block to many chemists, is the simultaneous occurrence of free phosphoric acid and insoluble phosphates. It is usually supposed that these two substances in contact will at once react to produce monocalcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_3\text{PO}_4 = 3\text{CaH}_4\text{P}_2\text{O}_8$) and I have seen the statement, over the name of a well-known chemist, that "free phosphoric acid and insoluble phosphates cannot exist together." As a matter of fact the above reaction, like many others, is seldom, and only under exceptional circumstances, complete, and free phosphoric acid and insoluble phosphates not only can, but almost invariably do co-exist in tartar substitutes. This fact has an important bearing on the analysis of these substances.

acid to do more work, and the final product is tricalcium instead of dicalcium phosphate.

This secondary reaction only takes place on heating, and is the more complete the longer the mixture is boiled. The practical effect of this in the use of tartar substitutes is of very great importance.

Goods of class I, whose neutralizing power depends entirely on their contents of monocalcium phosphate and free phosphoric acid, when mixed with sodium bicarbonate and water, liberate the carbonic acid gas at once and completely in the cold; and hence, if this combination is used in baking, it is necessary that the dough should be placed in the oven immediately after mixing, as otherwise the gas escapes and the resulting loaf is "heavy."

With goods of class II, on first mixing the dough a portion only of the gas is liberated (corresponding to the primary reaction), making the dough spongy, but on putting in the oven, the secondary reaction commences and a steady evolution of gas occurs, which keeps the loaf porous and light.

This two-fold reaction has, in fact, the same practical effect as is obtained by the use of a less readily soluble salt than monocalcium phosphate; *viz.*, the action is slower.

The special suitability of cream of tartar for baking powder purposes rests on its property of being only sparingly soluble in cold water, but quite readily so in hot water, the effect of which is that the carbon dioxide is developed in the right amounts at the right time; exactly the same result is obtained in tartar substitutes by means of the secondary reaction with calcium sulphate.

The calcium sulphate in some tartar substitutes cannot, therefore, be regarded as an adulterant, neither is it the result of carelessness on the part of the manufacturer; but it purposely forms part of the substance, and has an important, and for some uses, quite an essential function.

It is not my purpose at present to treat the matter from a hygienic point of view, but, inasmuch as calcium sulphate seems to be something of a bugbear to many health officers and state chemists, it may be pointed out that a greater part at any rate of this substance is actually converted in the baking process

into sodium sulphate, and further, that in the small amounts used in practical baking the resulting dose of the latter salt would be extremely small.

ANALYSIS OF TARTAR SUBSTITUTES AND STATEMENT OF RESULTS.

It might at first sight seem supererogatory to detail any methods of analysis of a material composed of such familiar substances as lime, phosphoric and sulphuric acids, magnesia, etc., etc., still more so to enter into a matter apparently so simple as the determination of the neutralizing power of an acid substance.

The determination of the working power of tartar substitutes, however, presents peculiar difficulties, so much so that an analyst inexperienced as regards these materials as a rule fails entirely to get results of any value whatever, and as regards the more complete analysis, the determinations of lime, phosphoric acid, etc., etc., indeed present no difficulty. But when the attempt is made to group the acids and bases, it frequently results in surprising misstatements.

A matter of primary importance in the analysis of tartar substitutes is the determination of the "strength," or neutralizing power, always stated in terms of sodium bicarbonate.

To determine this "strength," two obvious methods present themselves; *viz.*, titration with standard alkali, and the determination of the amount of carbon dioxide evolved from sodium bicarbonate by a known weight of the substance. Inasmuch, however, as the indications given by the above two processes are two entirely different things, it must first be decided before adopting one or the other method, exactly what is meant by "strength" in a powder of this kind.

When monocalcium phosphate and sodium bicarbonate are heated together in presence of water, the carbonate is decomposed until the salt Na_2HPO_4 is formed. This salt, although chemically "acid," is already strongly alkaline to phenolphthalein, the salt of the formula $\text{R}_3\text{H}_3\text{P}_2\text{O}_8$, probably being the neutral salt to this indicator. It is obvious, therefore, that "acidity" of tartar substitutes, as indicated by titration, is quite a different matter from their ultimate power of determining the liberation of carbon dioxide from carbonates.

Ordinarily, for reasons above given, the "evolution" method indicates a power of evolving carbonic acid gas very considerably in excess of the "acidity" as indicated by titration. Unfortunately, however, both methods offer ample opportunity for error.

When a mixture of acid phosphate and sodium bicarbonate is heated with water, the amount of carbon dioxide evolved is dependent on the relative proportions of the two substances, on time, temperature, dilution and a host of other factors; and, by varying the conditions, results can be obtained differing from each other and the truth, not slightly, but to an extent to render the test useless.

In an article on the "Commercial Valuation of Cream of Tartar Substitutes," *J. Anal. Chem.*, 4, 4, Prof. Chas. A. Catlin sums up the foregoing in the words "there is found to be no definite ratio between the neutralizing capacity of these preparations and their gas-evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process," and advocates the use of a modified form of the evolution method on the ground that inasmuch as the use of these powders is to evolve carbonic acid gas from alkaline bicarbonate, their power of doing this under the conditions of the baking process is the sole criterion of value.

There is, however, another factor that must be considered; *viz.*, the reaction of the residue. It is no less necessary that a baking powder shall have a neutral residue, than that it shall evolve carbonic acid gas, and there is this much in favor of the titration method, that if properly conducted it indicates exactly the amount of sodium bicarbonate that can be used with a given sample of tartar substitutes to give a neutral residue.

I can quite endorse Prof. Catlin's statement, that the ordinary method of titration with alkali, either direct or indirect, fails to give the proper data, but if the titration is conducted with special precautions, adapting it to the case, it is in my opinion the most satisfactory method of determining the "strength" of tartar substitutes.

The method of valuation proposed by Prof. Catlin is a combination of the titration and evolution methods; *viz.*, first find-

ing by titration with alkali and phenolphthalein the neutralizing power of the sample, and then weighing up exactly the amount of chemically pure bicarbonate, introducing into the evolution apparatus together with its equivalent of tartar substitutes, and weighing the carbon dioxide evolved under certain specified conditions.

It would seem that the evolution part of this method is entirely dependent on the titration, for certainly, if, in the evolution experiment only the exact equivalent of sodium bicarbonate as found by titration is used, the carbon dioxide corresponding to this and no more can possibly be evolved, and inasmuch as under the conditions laid down by Prof. Catlin for the evolution experiment, nearly all tartar substitutes will evolve carbon dioxide from more bicarbonate than is indicated by a properly conducted titration, the evolution experiment can at best only confirm the titration, and had better be altogether dispensed with as a troublesome and useless adjunct.

Prof. Catlin's paper contains many extremely valuable data as to the actual conditions to which the leavening agents are exposed in the practical baking process, and as emphasizing the necessity of making analytical tests as nearly as possibly under these conditions, is well worthy of attention.

The method of conducting the titration test differs with the character of the sample to be tested.

In the case of tartar substitutes of class I (*i. e.*, practically free from calcium sulphate) the amount of alkali neutralized is practically the same whether the titration be conducted hot or cold.

With class II, or intermediate grades containing any considerable amount of calcium sulphate, this is not the case, for when titrated in the cold, the solution reacts alkaline to phenolphthalein as soon as the primary reaction between soluble phosphoric acid and soda is complete. If now this solution be heated, the secondary reaction, previously explained, commences; the red color of the phenolphthalein gradually disappears, till on full boiling it will be found that a very considerable amount of alkali must be added before neutrality is restored. Hence, tartar substitute containing calcium sulphate shows one strength cold and a much greater strength hot; or, as it is expressed in trade, "sulphate of lime base goods show a *cold* test."

As before stated, in the case of goods free from calcium sulphate, the "hot" and "cold" tests are identical, or they "have no cold test."

It will be understood that the difference between the hot and cold test is purely a function of the secondary reaction with calcium sulphate, and from the relation between the two tests an expert can form a tolerably close estimate of the amount of this substance present.

To return to the titration, the test is best made on one gram of the substance suspended in about thirty cc. water in a porcelain basin, and titrating with caustic alkali (carefully freed from carbon dioxide), using phenolphthalein as indicator. The one essential of the method is to use a very large amount of the indicator. If the titration is made using only one or two drops of phenolphthalein, as would ordinarily suffice for an acidimetric titration, a far larger amount of alkali can be added, before the faintest pink color is obtained, than is really required. This may be readily shown by adding a further considerable amount of phenolphthalein when the faint pink darkens to deep red, and on titrating back with acid a considerable amount must be used before the color disappears. For this reason an inexperienced operator always obtains results far too high.

The most convenient method of procedure when working with unknown samples is, first to make a cold titration, adding a large amount of phenolphthalein and titrating to a faint pink. The alkali should be added drop by drop with constant and vigorous stirring to break up the little clots of precipitated phosphates formed by each drop.

In the case of sulphated goods the first pink tinge indicates the "cold test" and the burette reading should be recorded. The solution is then rapidly brought to a boil under the burette, and if the pink disappears more alkali is added till the very faintest color reappears.

This first test serves as a guide for a more exact titration in which it is best to add nearly the full amount of alkali required, drop by drop as before, then bring to a brisk boil, add the phenolphthalein and finish the titration rapidly while still actively boiling. The ending should be the first faint pink permanent

for one minute at a boiling temperature. The end reaction is not sharp and is very difficult to determine exactly.

With heavily sulphated goods prolonged boiling will cause the pink to disappear owing to the greater completeness of the secondary reaction; but as Prof. Catlin has pointed out, in the baking process the chemicals are exposed to a temperature of 100° for a period not exceeding one minute at the most, and therefore in the test this time of boiling should not be exceeded.

Any process of indirect titration, by adding alkali in excess and titrating back with acid is entirely inadmissible, as is also any separation of the insoluble portions of the powder by filtration before titrating.

The more complete analysis of a tartar substitute involves the determination of the phosphoric acid, and *the forms in which it exists*, the lime, magnesia, starch, sulphuric acid, and occasionally iron and alumina.

The determination of these substances requires no special notice, except as regards the forms in which the phosphoric acid exists, which is a matter of the highest importance in determining the relative merits of tartar substitutes.

Disregarding the small amounts combined with magnesia, iron, and alumina, the phosphoric acid in tartar substitutes is present in three different states:

“Free,” or uncombined.

Combined with one molecule of lime, as $\text{CaH}_4\text{P}_2\text{O}_8$.

Combined with more than one molecule of lime as insoluble phosphates; and in order to make an analysis of any value whatever, it is absolutely necessary to determine the amount present in each of these forms.

The “free” acid may be determined by titration with standard alkali and methyl orange, which indicator reacts neutral with salts of the formula $\text{R}'\text{H}_2\text{PO}_4$, and consequently indicates the “free” phosphoric acid only.

The titration is best effected on the filtered aqueous solution, adding standard alkali to pink-yellow color. Inasmuch as a slight precipitate forms before the point is reached the indications are a trifle too high, but sufficiently accurate for all technical purposes.

For the determination of the phosphoric acid existing as mono-calcium phosphate and insoluble phosphates two analyses are necessary.

First, the *total* phosphoric acid on the solution of the powder in acid, and secondly, the "water soluble" phosphoric acid, best extracted by shaking a weighed quantity with water in a graduated flask, filtering clear and determining the dissolved phosphoric acid in an aliquot of the filtrate.

The phosphoric acid can of course be determined by any orthodox method, but for convenience and rapidity the volumetric method of Pemberton, (this JOURNAL, July, 1893) far surpasses any other.

The total phosphoric acid minus the "water soluble" gives the "insoluble" phosphoric acid, which may exist as $\text{Ca}_3\text{P}_2\text{O}_8$, $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$, or frequently as a mixture of the two. The determination of the insoluble phosphoric acid by difference is far more satisfactory than a direct determination.

The "water soluble" minus the "free" equals phosphoric acid existing as $\text{CaH}_4\text{P}_2\text{O}_8$.

It is necessary here to call attention to a very vicious practice followed by some chemists. Instead of determining the three forms of phosphoric acid as above, they determine only the *total* phosphoric acid and the total CaO. The CaO they then calculate into $\text{Ca}_3\text{P}_2\text{O}_8$, an excess of phosphoric acid of course remaining uncombined—which excess they then combine with the $\text{Ca}_3\text{P}_2\text{O}_8$, according to the reaction $\text{Ca}_3\text{P}_2\text{O}_8 + 4\text{H}_3\text{PO}_4 = 3\text{CaH}_4\text{P}_2\text{O}_8$, leaving an excess of either $\text{Ca}_3\text{P}_2\text{O}_8$ or H_3PO_4 as the case may be, but necessarily showing only one or the other.

Such a calculation cannot by any chance give correctly the composition of the substance for the reason before gone into, that tartar substitutes always contain both free acid and insoluble phosphates.

One word as to the form of stating results may not be out of place as this is a frequent source of *apparent* disagreement between two analyses that are really identical—a matter that it is often difficult to satisfactorily explain to the lay mind.

Having found, correctly or otherwise, the amount of mono-calcium phosphate present in a sample, the analyst generally

states this in his report in the anhydrous form, $\text{CaH}_4\text{P}_2\text{O}_8$, calling it variously "monocalcium phosphate," "acid phosphate of lime," and occasionally "superphosphate," or some other name.

Equally in the case of calcium sulphate, it is a usual practice to report in the anhydrous form CaSO_4 , and to call it variously "sulphate of lime," "gypsum," "terra alba," "plaster of Paris," etc., etc., according to the state of mind of the analyst. Even the starch present in tartar substitute is capable of being reported under the misleading term of "organic matter."

Having reported the salts as present in their anhydrous state, the difference between the sum of results and 100 is put down as "combined water," etc., etc.

While such a method of reporting is very convenient, as saving trouble of calculation and giving a pretty analysis adding up exactly to 100.00, it is doubtful if it is the best way.

In my opinion the results of an analysis should always be reported in a form as nearly approaching the truth as may be, and at any rate the statement should always show on the face of it exactly what is meant.

In the case in point, monocalcium phosphate always exists (and indeed can only exist) in a crystallized state, and in consequence it would seem to better represent the truth if stated in this form and called "crystallized monocalcium" or "acid phosphate."

With regard to the calcium sulphate in highly sulphated goods, it appears to exist partly in the anhydrous state and partly crystallized, and as it is impossible to determine the amount of water of crystallization, the exact statement of this cannot be made. It is, however, easy to convey exactly what is meant by stating either as "anhydrous" or "crystallized" calcium sulphate.

The practice of calling calcium sulphate found by analysis "terra alba," "gypsum," etc., etc., is to be unqualifiedly condemned, as it suggests, and is intended to suggest by implication, a fraudulent addition of a foreign substance,—a suggestion that is justified neither by the analytical data nor the real facts of the case.

The neutralizing strength should always be stated in terms of

sodium bicarbonate neutralized by 100 parts of the sample, and where there is a considerable difference between the hot and cold tests, this should be stated, as it is an important factor in deciding as to the suitability of a tartar substitute for any particular use.

The best grades in the market have a neutralizing strength of 100 parts equivalent to forty-four to forty-five sodium bicarbonate, *i. e.*, about the working strength of cream of tartar.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE, No. 3.]

THE ANALYSIS OF VARNISHES.

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AT present varnishes are seldom analyzed because no means are known of determining with any approach to accuracy, the amounts of the substances composing them. The tests used are practical ones and usually consist in varnishing a suitable surface with the sample to be tested and subjecting the varnished object to treatment as nearly as possible like that which it will receive in practice. If it is desired to ascertain the proportions of the different constituents, practical varnish-makers claim to be able to make up samples which will match in properties one to be tested, and in this way to arrive at the proper result. However this may be, it is out of the question for the chemist who is not a varnish-maker to use such a process. If methods can be devised whereby a chemist can make an actual analysis with a fair degree of accuracy, buyers can be certain of what they purchase and manufacturers can work more intelligently.

The different kinds of varnish may be classified as follows:

1. Spirit varnishes.
2. Volatile oil varnishes.
3. Fixed oil varnishes.
4. Miscellaneous; collodion varnishes, etc.

Spirit varnishes are composed of a resin dissolved in alcohol. Shellac spirits,* made by dissolving shellac in wood or grain alcohol, is the most common.