

The greater portion of the domestic samples examined did not contain over 1:5,000,000 (0.2 mg. per liter).

Testing a malt liquor by the method described, then, we should think that if 150 cc. contained enough fluoride to give a visible etching at 80°, the sample was open to suspicion as containing added fluoride.

In conclusion, the authors take pleasure in acknowledging their indebtedness to Miss Elizabeth Anison for much painstaking and careful analytical work.

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FACTORS IN BORIC ACID MANUFACTURE.

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One who may be interested in the subject of borax will find the phase relating to its occurrence, production and uses, in the U. S. Mineral Resources for any year from 1900 to 1905; the phase relating to its physiological action in Dr. H. W. Wiley's Report, Bull. 84 or Cir. 15; and the phase relating to its detection and estimation in minute quantity in foods in this Journal, July, 1906. For the analytical phase among the best references are: J. Soc. Chem. Ind., July, 1904; Sutton Vol. Analysis; Zeitsch anal. Chemie., 34, (1900); Chemiker-Zeitung, Jan. 16, 1901. And for the geological phase the best works are those of Kemp, G. W. Miller, The Calif. State Mining Report 1892. The "Saline Deposits of California" by G. E. Bailey (Cal. State Mining Bureau S. F.).

These authorities seem to agree with the practical men in the borax fields that the origin of the borates must have been emanations from volcanic vents and hot springs; and likely in the form of boric acid carried by the steam and other gases; and that subsequently such borates as colemanite (which is borate of lime with water of crystallization), and others must have crystallized from lakes and springs on evaporation, and, of course, were deposited as strata. As a rule these strata are found associated with secondary clays, which clays may also be impregnated with borate. Borate formation appears distinctive.

A number of analyses of these borate clays show them to have the following general composition:

SiO ₂	45-55	per cent.	Na ₂ O and K ₂ O	1/2-2 1/2	per cent.
Al ₂ O ₃	5-15	" "	CO ₂	1/2-3	" "
FeO and Fe ₂ O ₃	4-12	" "	SO ₃	1/2-5	" "
CaO	7-15	" "	B ₂ O ₃	0-30	" "
MgO	1-4	" "	Org. matter	moisture, considerable.	

The borates are mixed with gypsum and carbonates, which makes manufacture much more expensive. The sodium carbonate is mixed

with sodium sulphate and other soluble salts. And that is the case in general.

The affinity holding boric acid to lime at ordinary temperatures appears to be not very great: Acid fumes in moist conditions like sulphur dioxide or nitric fumes, or even dilute acetic acid, decompose calcium borate readily and completely. Also, in Death Valley, and in other places, where sodium carbonate comes in contact with calcium borate, in warm moist condition, in contact with air, the sodium gradually displaces a part of the calcium, forming calcium-sodium borate, known as "cotton-ball," or ulexite. This is always found near the surface. Boiling with sodium carbonate readily transposes it further to borax. This was the way the first borax in Death Valley was made. In some marshes crude borax is actually disseminated through the clays.

The higher grade of calcium borate, say that running 30 per cent. or more in terms of boric acid or 45 per cent. in terms of crystallized borax, is shipped directly from the mine to the factory. A somewhat lower grade is first roasted at a red heat, when the borate loses its water and falls to a powder, and is then separated from the heavier gang, and shipped. At the factory the raw material is ground to a very fine flour and boiled for hours in iron drums with soda ash and bicarbonate of soda. The borax is then crystallized away from the sodium sulphate, which is generally present, (originally as gypsum in the ore), on iron rods. It is refined by recrystallizations. The bulk of it goes in the enamelling works: *e. g.*, a bath-tub is a cast iron trough coated with a borax enamel. (For description of this process see *Trans. Am. Ceram. Soc.*, 8, 172-80, Ohio). The formulas of the mixtures are worked out by experiment and kept secret.

Some of the low grade ore (which by the way is of too low grade to boil directly with soda—profitably—too much bulk) is ground in water to a slurry, and decomposed by dilute sulphuric acid, or by sulphur dioxide fumes forced into it till all the boric acid is set free. In either case it is then diluted with water, agitated and allowed to settle; the cleared leachings evaporated by sun and wind in large solar vats; and during the process of evaporation, the acid is crystallized away as much as possible from the impurities, which are chiefly silicic acid and soluble sulphates.

According to Patent literature the Germans employ carbon dioxide under pressure instead of sulphur dioxide. The carbon dioxide is forced into the slurry till it becomes saturated with acid carbonate of calcium. Then the pressure is released. The calcium carbonate to a large extent precipitates. More CO_2 is then forced in; and process repeated till all of the borate is decomposed or nearly so. Now the calcium carbonate formed does not so readily counter-react with the freed boric acid in the cold, and especially where the slurry is saturated with carbon dioxide.

There are some especial advantages to this procedure :

(1) The reagent, (which is one of the heavy items of expense) does not waste itself on the carbonates, which are generally present and sometimes to a considerable percentage.

(2) It does not introduce so many impurities into the liquors.

(3) Carbon dioxide can probably be generated more cheaply than other acid reagents:—*e. g.*, from coal. In burning coal the heat can be utilized for heating large quantities of water, which seems impracticable, so far, in sulphur furnaces.

In this country Blumenberg has devised and covered by patent a muffle in which sulphur dioxide is blown from burning sulphur (or pyrites) into the slurry until all the boric acid is freed. This does not require the high pressure of the carbon dioxide process ; and, as against the sulphuric acid process, it attacks the impurities in the ore to a lesser extent. These impurities are silicates, the lower oxides of iron, aluminium and other bases. On the other hand, more or less, of the gas is carried out with the leachings, and oxidizes, in part, to sulphuric acid. However, the liquors are clear then, but become somewhat harder to evaporate upon concentration ; and the loss of boric acid by volatilization becomes a trifle greater than in neutral solution. Nitric acid is not required ; nor a sulphuric acid plant ; but the boric acid plant has to be larger, since it takes much longer to decompose the slurry with the gas. The gas has to be blown in by an air compressor or other machinery, which may become expensive if not well regulated. This is not necessary in a sulphuric acid plant. The loss in gas is about the same in the slurry as in the acid chamber. Acid sulphites are not formed till after all the borate is decomposed. The sulphites of calcium and of other metals dissolve in the solution of sulphur dioxide. The calcium precipitates, (partly as sulphate) as soon as the gas oxidizes, or is whipped out by the wind.

Sulphur burning under forced draught, however, requires a special set of conditions, or a part of the sulphur will sublime ; a large excess of air seems necessary both for oxidation and the cooling of the furnaces. For that reason the side-doors to the draw-furnaces have improved matters materially.

In the matter of leaching the old process has been to dilute the decomposed slurry with more water and agitate thoroughly, let settle, and allow the clear leachings to reconcentrate and evaporate in the sun and winds. This system is now to be superseded by a scheme of concentrating the pulp or slurry ; then filter-pressing it, and crystallizing the acid from the concentrated solution. The cake, wherever possible, is to be manufactured into brick. This takes the industry away from the climatic elements and yields quicker returns. It is analogous to the case in

cyaniding, where the slurry from the mills was run out of doors, and aerated for months to fully oxidize the ore, before it could be cyanided to advantage, but it is now roasted and cyanided at once.

Analytical Methods.

Qualitative.—A little of the finely powdered material in a butter dish is treated with enough of concentrated sulphuric acid to make a paste. Then a little wood alcohol is added. On igniting and stirring with a lead rod, a green flame indicates borate. The test is quite delicate. Wood alcohol gives a better test than grain alcohol.

For slurry, to determine undecomposed ore: A perforated 4 inch pipe-plug is screwed into a 4-inch coupling; a piece of canvas is laid in this cap and a little of the slurry is poured in. The cap is then screwed onto a 4 x $\frac{1}{2}$ -inch bushing, which bushing is in turn screwed onto a $\frac{1}{2}$ -inch steam line with a valve to regulate the steam. Steam is turned on a few minutes, which carries all of the free boric acid with it through the perforations, leaving the undecomposed borate behind. The above flame test is then applied.

Quantitative; Method I.—This is limited to ores or residues where concentrated sulphuric acid does not liberate acid fumes, except carbonate; that is to say, chlorides, nitrates, sulphites and similar salts must be absent. The method may, however, be altered so as to include at least a part of these. Put 1 g. of the finely flowered material into a 125 cc. flask; (0.5 g. if over 40 per cent. H_2SO_4). Mix thoroughly with about 1.5 cc. of sulphuric acid, sp. gr. 1.84; heat to 70°-80° to expel most of the carbon dioxide; let cool; connect to a condenser, and distill the boric acid over on steam-jet or steam-bath (not flame) with 6-10 cc. portions of wood alcohol, taking care that each portion is well over before adding the next. The alcohol is admitted to the flask through a stopcock. In the receiver should be such a volume of glycerol as to equal $\frac{1}{3}$ the volume after titration. The glycerol should contain a little water, say 5-8 per cent. When the six portions are well over, the residue (should be small) must be tested by the flame test. If any "green" appears the assay must be repeated, using 7-10 cc. portions of alcohol; or a less quantity of ore. When the distillation is completed, add about 1 cc. 0 $\frac{1}{2}$ per cent phenolphthalein to the receiver and mix well; and titrate with about N/5 sodium hydroxide free from carbonate. To standardize the alkali use from 0.2 to 0.4 g. of perfectly c.p. boric acid in place of the ore, and distill in exactly the same way. Then run "a blank," using only the 1 $\frac{1}{2}$ cc. of sulphuric acid and subtract the amount of alkali required from the other readings. This gives good results. An improvement is to use a very concentrated aqueous solution of known strength of pure mannitol in place of the glycerol. A much sharper end point is then obtained. A volume of mannitol containing about 1 g. of mannitol will

be found sufficient. Again, if hydrochloric acid or any other acid distils over, then in place of the glycerol or mannitol solution, put about an equal volume of distilled water into the receiver; and distil the boric acid over into this as before. When completed make neutral with sodium hydroxide free from the carbonate, using about one drop of *p*-nitrophenol (1 g. of *p*-nitrophenol dissolved in 75 cc. ethyl alcohol and 25 cc. of water added). Now add the same amount of mannitol in powdered form, and let dissolve. Titrate as before. The receiver should be a flask and kept cool during the distillation.

II. General Method:—When method I fails, the ore is decomposed as before with a very small excess of concentrated sulphuric acid, in a graduated flask, of about 80 or 100 cc. capacity. About 20 cc. of water are added; and, if necessary, a crystal or so of potassium chlorate, and the solution brought to a boil to oxidize the iron. When oxidized a slight excess of sodium carbonate is added and the solution is brought to a boil again. It is then cooled and diluted to the mark; an exact aliquot part of the clear liquor is taken (not over 25 cc.) and made just acid with drops of concentrated sulphuric acid, to one drop of very dilute methyl orange. It is then brought to a boil for a quarter of a minute (not longer); cooled, neutralized exactly by sodium hydroxide free from carbonate, adding (if necessary) another drop of the dilute methyl orange. About 1 g. of powdered mannitol is then added and dissolved; and the solution titrated with about $N/5$ sodium hydroxide and phenolphthalein. ($\frac{1}{2}$ cc.). If mannitol is not at hand, use neutral glycerol. (A volume equal to $\frac{1}{3}$ vol. after titration, deducting the amount required to bring the color.) If glycerol is not at hand, a little sugar may be boiled a few minutes in a little dilute sulphuric acid, making a very concentrated solution of sugar, and neutralized to phenolphthalein by sodium hydroxide free from carbonate. This mixture may be used instead of glycerol, but the end point is not very distinct. The fructose appears to be the active ingredient in this case.

When aluminum or chromium salts are present, instead of using sodium carbonate as the precipitant, nearly neutralize with sodium carbonate and boil with a slight excess of c.p. solid barium carbonate, making sure that the potassium chlorate has previously oxidized the iron.

The $N/5$ sodium hydroxide is standardized with c.p. boric acid in exactly parallel conditions.

*III. The Iodate Method by Jones*¹ is very highly recommended wherever there are no interfering ingredients, as iron, aluminum or chromium.

IV. Mill Liquors:—By way of general precaution, boiling of liquors concentrates them and silicic acid, the heavy metals, ammonium salts, organic material, carbon dioxide and other gases must first be removed, if present. Boric acid is volatile, especially in presence of mineral acids; hence boric acid concentrates cannot be dried over steam, but only in a desiccator.

In evaporating boric acid solution to dryness in order to char organic material, etc., do not use sodium carbonate or bicarbonate (since that forms a clinker) but use c.p. barium hydroxide in slight excess. Boric acid is readily soluble in warm wood alcohol, but the borates are insoluble: a means of separating boric acid from borax, etc. C.p. boric acid should always be tested for impurities before using for standardization, viz., sulphates, carbonates, chlorides, etc., and purified by recrystallization from boiling water. Of the oxidizing agents, barium peroxide, potassium bichromate, nitric acid or ammonium nitrate will not answer. Potassium chlorate and a drop of concentrated sulphuric acid, if necessary, is the best oxidizing agent so far, although bromine may be used with slightly higher results; but bromine in a hot climate fumes too much.

Take about 80 cc. of the mill liquor or solution in a flask; add a drop of concentrated sulphuric acid, if necessary, and a crystal or so of potassium chlorate, and just bring to a boil; let stand a few minutes. When oxidized or nearly so, add a slight excess of anhydrous pure sodium carbonate and bring just to a boil again. Draw off 25 cc. (not more) of the supernatant liquor, make slightly acid with drops of concentrated sulphuric acid, boil for a quarter of a minute, but not longer (this removes about all of the carbon dioxide) and titrate as in the previous methods.

If organic acids are present, the solution must first be made alkaline with barium hydroxide and evaporated to dryness in a small evaporating dish, and the residue very carefully charred with as low as possible heating. The solution is then redissolved with a little sulphuric acid and made up to the former volume. Also the other precautions relating to aluminum, chromium, etc., must be followed as in the previous methods. Further, if much potassium chlorate has to be used, an expansion factor must be determined, and the final result multiplied thereby.

In analyzing borate mixtures for other elements, a good way to begin is to set free the boric acid with a little concentrated hydrochloric acid in an evaporating dish, and on the steam bath, evaporate the boric acid away with pure wood alcohol (which leaves no residue of its own), until the flame burns perfectly blue. A little ferric chloride may thus be lost, but this can be avoided by using concentrated *sulphuric* acid instead of hydrochloric.