

nesium carbonate, and find strong support in observations made elsewhere. Where calcium carbonate instead of magnesium carbonate is present in the culture solutions, the process of nitrification is modified, and the presence of unoxidized ammonia does not seem to inhibit the development of the nitric ferments. Under actual soil conditions the formation of nitrites and nitrates may not only occur at the same time, but the nitrites may be oxidized as fast as they are formed, and the activity of the nitrous ferments may thus be concealed. It should be noted here, however, that organisms may exist in the soil, which have the power of converting ammonia directly into nitrate without the intermediate formation of nitrites. Such, at least, is the claim made by Kasser,¹ and there are observations made by others, which would lend support to this claim.

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THE FLUORINE CONTENT OF MALT LIQUORS.

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In a previous paper² the authors outlined a method for the approximate estimation of fluorides when present in minute quantities, such as might occur in food products. At that time the hope was expressed that it might be possible to examine by means of the method, various classes of food products with a view to determining the limiting values for their fluorine content. For obvious reasons, malt liquors seemed excellent material for beginning such an investigation, and it is the purpose of the present paper to summarize the results obtained in the examination of a number of the brands of malt liquor on the market, as well as the materials used in brewing.

Method.—The method used was similar to that already described, except that on account of the large amounts of carbonic acid in the beers, it was found necessary in every case to add a somewhat greater quantity of barium acetate, enough being used to ensure an excess in the filtrate from the barium sulphate and fluoride. For the same reason more sulphuric acid (3-4 cubic centimeters instead of 2-3 as previously directed) is necessary during the etching. An insufficient amount of either of these would occasion negative results, even if an appreciable amount of fluoride were present.

In extracting the fluoride from malts and barleys it was found inadvisable to grind the sample and extract with hot water, as would be done in the brewery operation of mashing, because the large amount of sugary and starchy matters extracted interfere with the subsequent precipitation of the fluoride. Satisfactory results were obtained in the case of malt by

¹ Centr. Bakt., Parasitenk., II, 16, 68r and 769 (1906).

² This Journal, 28, 1437, (1906).

digesting the unground sample with boiling water for three or four minutes, pouring off the water and repeating the operation. In the extract thus obtained fluorides were precipitated in the usual manner. In the case of barley, where reducing sugars were practically absent, the extraction was made on the ground sample but the digestion was carried out for half an hour at 40°-50°, a temperature below the gelatinizing point of starch.

Results.—The results obtained with a number of commercial malt liquors and with the principal raw materials of brewing are shown in the following tables. The results are stated in milligrams of fluorine per liter, or per kilogram in the case of solids. For convenience, the table of amounts of fluorine corresponding to the different "etching temperatures" given in the earlier paper¹ is here stated again in this form.

The values taken are based in each case upon the use of 150 cc. of the sample. With solids, the values will depend upon the weight taken and can be found readily by a simple calculation. Differences due to variations in specific gravity are so slight as to be neglected.

The samples of beers and ales represented about 50 different brands. The samples of malt and barley included both Eastern and Western growths.

TABLE 1.

MILLIGRAMS OF FLUORINE PER LITER (OR PER KILO) CORRESPONDING TO THE "ETCHING TEMPERATURES" WHEN 150 CC. (150 GRAMS) ARE USED.

Temperature	
79°-82°	10 to 40
113°	1 to 10
136°	0.2 to 10
173°-178°	0.04 to 0.2
213°-218°	Less than 0.04

TABLE 2.

FLUORINE IN MALT LIQUORS AND BREWING MATERIALS. MILLIGRAMS PER LITER (PER KILO).

	40	30	10	8	3	1.0	0.5	0.2	0.04	Less than 0.04
Barley.....	15	1	4	1	9
Malt.....	15	2	13
Brewing Sugar.....	9	1	8
Domestic Ale and Beer	.34	4	9	21
Imported Ale and Beer	.15	3	5	2	5

A sample of beer was brewed in the laboratory from materials which had been previously examined and had been found, with the exception of the malt, to be free from fluorides. This was done to determine if, under

¹ Loc. cit.

these conditions the fluoride content of the malt would be sufficient to account for the amount found in the finished product. This was found to be true, since the resulting product gave a test at 143°, corresponding to an amount of fluoride equal to that present in the equivalent amount of malt used.

It was deemed advisable to follow, if possible, the brewing process as carried out on a commercial scale, noting the proportion of fluoride present at each stage of the brewing process.

Through the kindness of Dr. W. H. Walker it was possible to follow in this way one of the brews of a large brewing company, making examinations of the raw materials used, of the water, and of the wort at frequent intervals during the process of concentration and fermentation. The results are shown graphically in the accompanying tabular scheme.

They are calculated in each case to the amount of raw material that would be actually represented by 150 cc. of the finished product.

TABLE 3.
CHANGE IN FLUORIDE CONTENT DURING BREWING. MILLIGRAMS PER LITER (PER KILO).

Malt (1.0)	Water (None)	Rice (None)
----- ----- -----		
Wort Before Hopping and Boiling		
	(0.2)	Hops (None)
----- ----- -----		
Wort After Hopping and Boiling		
	(0.2)	Yeast (0.4)
----- ----- -----		
Wort After Addition of Yeast.		
	(1.0)	
Wort 3 days after adding yeast.....		(1.0)
“ 6 “ “ “ “		(1.0)
“ 9 “ “ “ “		(1.0)
“ 12 “ “ “ “		(1.0)
Wort after 5 days in storage		(10.0)

In examining this table it should be borne in mind that the great difference shown in the beer before and after the period of five days storage is more apparent than actual. Owing to the limitations of the method it is impossible to follow closely gradual changes in the fluoride content until the amount present approaches one of the limits fixed by the etching temperature.

It is no doubt true that the content of fluoride was steadily increasing during the fermentation and that not until the final test was enough pre-

sent to show at the 10 milligram point, although it had passed the 1 milligram point some time before.

It is also true that the presence of sugary matter prevents to some extent the precipitation of the fluoride, even when the latter is present. It is highly probable that the apparent increase in fluoride content is due rather to the decrease in sugar as the fermentation proceeded, and the consequent availability of the fluoride for precipitation.

Through the cooperation of a large malting establishment we were enabled to go one step further back and follow the malting process in its effect on the fluoride content of the grain. Samples were sent us of the barley, the water used for steeping, and dried samples of the malt at various stages from the steeping tank to the finished product. On these samples the following results were obtained:

	Milligrams per kilo
Hard steep water.....	10.0
Soft " "	None
Barley before steeping.....	3.0
Steeped barley.....	3.0
Malt 2 days old.....	3.0
" 4 " "	3.0
" as put on kiln.....	3.0
" from kiln.....	8.0

Summary.

From the results obtained two things are strikingly apparent. First, that the presence of a slight amount of fluoride in malt liquors is the rule rather than the exception, and second, that the principal source of this fluoride is the malt itself. In the majority of cases it is undoubtedly true that the proportion of fluoride in the beer is entirely accounted for by the malt.

This amount may be slightly increased in some cases by smaller quantities introduced through the use of brewing sugars, from the water, especially if artificially hardened by the use of gypsum containing fluoride, or from the yeast.

It is of course possible that fluorine was present in all the samples of barley and that the simple method used for the extraction failed to remove it, especially that present as insoluble calcium fluoride. A more probable explanation, however, is to be sought in natural geographical variations in the soil, the use of commercial fertilizers, such for instance as phosphate rock, notoriously rich in fluoride, and other primary agricultural factors. Judging from the results obtained on a considerable variety of samples, it would seem that one part of fluoride in 100,000 (10 mgs. per liter) was not too severe a standard to set for the maximum limit of permissible fluoride in malt liquors.

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 Amison for much painstaking and careful analytical work.

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FACTORS IN BORIC ACID MANUFACTURE.

By JOHN WINKLER.
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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