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PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS. NOTE ON THE DETECTION OF HOP SUBSTITUTES IN BEER.

BY A. H. ALLEN AND W. CHATTAWAY.

Read at Meeting, June 1890.

THE method described by one of us in the ANALYST for June, 1887, satisfactorily distinguishes between hops and hop-substitutes in the majority of cases.

It fails sometimes to remove the whole of the natural bitter of the hop, especially in cases where the hops are old. In such cases a better result can be obtained if the excess of lead be removed by boiling with sulphuric acid, instead of by sulphuretted hydrogen, in accordance with the suggestion of Mr. Adams. Concentration in presence of the sulphuric acid appears to be preferable to mere boiling of the dilute acid solution before neutralising with chalk. If the concentrated liquid be agitated with chloroform, most of the bitter principles are extracted (with the exception of chiretin). On evaporating the chloroform solution to dryness, taking up the residue in a few drops of alcohol, adding water, and *tasting* the solution, traces of bitter principles can be detected which wholly escape recognition when the taste of the treated and concentrated beer is observed. Traces of hop-bitter are often detectable when this delicate means of observation is used. According to Dr. James Bell, the extractive matters of the beer interfere with the complete precipitation of the hop-bitter by lead acetate, though that reagent precipitates the bitter principles perfectly from a simple aqueous infusion of hops. Dr. Bell finds that the solvent power of ether on quassia bitter is very limited, while the hop-bitters are readily extracted. Hence on concentrating beer and shaking the acidulated liquid three or four times with ether the whole of the hop-bitter is extracted,

while a large portion of the quassia bitter remains in the aqueous liquid and can be extracted with chloroform. If the ethereal solution be evaporated and the residue dissolved and treated with lead acetate, Dr. Bell finds the hop-bitter to be entirely precipitated, while the quassia bitter remains in solution.

We are able confirm Dr. Bell's experience to some extent. That is, we find that if a beer bittered with old hops be clarified by lead acetate, the filtrate extracted by chloroform or ether, and the aqueous solution of the more or less bitter chloroform or ether residue again treated with lead acetate, the remaining hop-bitter is in most cases entirely precipitated; though in the case of one obstinate sample of old hops sent us by Mr. Adams the bitter was not wholly removed even by this supplementary treatment. Our experience is not in accordance with Dr. Bell's so far as the behaviour of quassia with ether is concerned, the bitter being far too easily extracted by ether to render that solvent available as a means of separating quassia and hop-bitters.

With regard to the modified method (Process II.), submitted by the President at the May meeting of the Society, a few experiments made by us have given very satisfactory results. Thus an obstinate sample of old hops, the bitter of which could not be removed by more simple treatment, gave a perfectly satisfactory result when previously treated with baryta-water as recommended by Mr. Adams.

But the advantage gained by a more perfect precipitation of the hop-bitter will be more than counterbalanced if the treatment pursued resulted in the destruction of any of the bitters of the hop-substitutes; and fearing that this might be the case, in our recent experiments we have rather adopted the opposite plan. By so doing, lead precipitation is still relied on as a sorting test, but in the event of a bitter being present which resists the treatment, we prefer to ascertain its nature more fully. This can be done by using the sorting action of chloroform and ether as solvents, and treating the extracts obtained by the evaporation of these with ammoniacal basic lead acetate. This reagent precipitates the bitter principles of old hops and gentian, while leaving those of quassia, calumba, and chiretta in solution. The bitter principles of these substitutes can be recognised to some extent by special tests, which we hope further to amplify and improve; but already we have achieved such a degree of success as to justify us in laying certain of the results before the Society.

Our experiments were first made on decoctions of hops, quassia, chiretta, gentian, and other hop substitutes, and as these proved successful, we proceeded to try the process on mild beer, to which sufficient of the different bittering substances was added to convert it into a fairly palatable bitter beer. Our experiments are not, therefore, open to the objection raised against those of Dr. Bell and Mr. Bannister, described before the Hop Industry Committee. These chemists obtained beer and added quassia and other hop-substitutes in proportions largely in excess of those which would be used in practice, and thus operated under conditions unfairly favourable to their detection.

The following table exhibits the method we have so far found most successful for effecting the separation and detection of bitter principles in beer. By the use of other reagents, especially ferric acetate, a further differentiation can be effected, but we prefer to postpone a description of these experiments till we have verified the reactions at leisure.

OUTLINE PROCESS FOR THE DETECTION OF BITTER PRINCIPLES IN BEER.

A. H. ALLEN AND W. CHATTAWAY.

1 litre of beer is evaporated to $\frac{1}{2}$ and precipitated boiling with neutral lead acetate; the liquid boiled for fifteen minutes and filtered hot. If any precipitate occur on cooling, the liquid is again filtered.

<p>PRECIPITATE contains <i>hop</i> bitter, <i>caramel</i> bitter, <i>ophelic acid</i> (from <i>chiretta</i>) phosphates, albuminous matters, etc., etc.</p>		<p>FILTRATE. The excess of lead is removed by passing sulphuretted hydrogen, and the filtered liquid concentrated to about 150 c.c. and tasted. It is then slightly acidulated with dilute sulphuric acid, and shaken repeatedly with chloroform.</p>	
<p>composed by sulphuretted hydrogen, and the solution agitated with chloroform.</p>		<p>CHLOROFORM SOLUTION on evaporation leaves a bitter extract in the case of <i>gentian</i>, <i>calumba</i>, <i>quassia</i>, and <i>old hops</i> (only slightly or doubtfully bitter in the case of <i>chiretta</i>). The residue is dissolved in a little alcohol, hot water added, and the hot solution treated with ammoniacal basic lead acetate and filtered.</p>	<p>AQUEOUS LIQUID is shaken with ether.</p>
		<p>PRECIPITATE contains <i>old hops</i>, <i>gentian</i>, and traces of <i>caramel</i> products. It is suspended in water, decomposed by sulphuretted hydrogen, and the solution agitated with chloroform.</p>	<p>FILTRATE is boiled to get rid of ammonia, and treated with a slight excess of sulphuric acid, filtered and tasted. If bitter, it is agitated with chloroform, and the residue examined for <i>calumba</i> and <i>quassia</i>.</p>
<p>CHLOROFORM SOLUTION is examined by special tests for <i>gentian</i> and <i>old hop</i> bitter.</p>	<p>AQUEOUS SOLUTION contains traces of <i>caramel</i> bitter.</p>	<p>PRECIPITATE is treated with water and decomposed by sulphuretted hydrogen. The filtered liquid is <i>bitter</i> in presence of <i>gentian</i>.</p>	<p>FILTRATE is treated with a slight excess of dilute sulphuric acid, filtered and tasted. A bitter taste indicates <i>calumba</i> or <i>chiretta</i>, which may be re-extracted with ether and further examined.</p>
		<p>AQUEOUS LIQUID, if still bitter, is rendered alkaline and shaken with ether-chloroform. A bitter extract may be due to <i>Berberine</i> (<i>calumba</i>) or <i>Strychnine</i>.</p> <p>The aqueous liquid, separated from the ether-chloroform may contain <i>Caramel</i> bitter or <i>Choline</i> (somewhat bitter.)</p>	

In conclusion, we may say that the best way to taste bitter principles is to place some of the solution on the back of the tongue with the aid of a small pipette. When there is sufficient material, some of the solution may be swallowed with advantage. But the anterior parts of the tongue are far less sensitive to bitter principles than the parts towards the uvula.

(Conclusion of the Society's Proceedings.)