NOTES ON THE ESTIMATION OF SALICYLIC ACID.

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(Read at the Meeting, November 5, 1902.)

THE following notes are a record of some years' laboratory experience, no claim being made for any original matter.

The accurate estimation of salicylic acid in wines and other organic fluids and articles of food is attended with such difficulty and uncertainty that, after testing every published process, I have felt compelled to fall back upon the well-known colorimetric process based upon the characteristic tint struck by persalts of iron in solutions of the acid.

This reaction is so delicate that, quoting Allen's "Commercial Organic Analysis," 1 part in 100,000 of water is easily detected by the tint imparted by a trace of ferric chloride.

I find, however, that in actual practice the use of this iron salt is attended with some difficulties, due probably to ferric chloride in weak solution having a tendency to dissociate, and in so doing affecting the purity of the characteristic violet tint sought, and I have for some time been in the habit of adopting a 1 per cent. solution of iron alum as an improvement.

In my hands I have found the following advantages from an iron-alum solution: The colour struck is purer and deeper. It is much more stable, often retaining its depth of tint for twenty-four hours. It is much more delicate—solutions of salicylic acid in pure water, 1 per 1,000,000, in the ordinary Nessler glasses treated by the iron-alum test giving a very distinct colour which can be imitated, while 1 part in 3,000,000 gives a distinctly visible coloration. Several precautions are, however, necessary. The salicylic acid must be isolated as perfectly as possible, no great amount of saline matter must be present, and the slightest inclination to alkalinity is fatal to success; on the other hand, the slight acidity communicated by the iron-alum solution is an advantage.

Test experiments conducted in pure solutions of salicylic acid have yielded very encouraging results, using ordinary Nessler tubes. The iron-alum solution is preferably 1 per cent. in strength, and with a drop or two of dilute sulphuric acid per 100 c.c. will keep very well. One or two c.c. should be used for each test.

The salicylic acid solutions should be two in number, one to contain 1 milligramme of acid per c.c., and this solution may be diluted to one-tenth for the purpose of making comparative estimations by "Nesslerizing." These solutions are not permanent, and should therefore be freshly made when wanted.

Bearing in mind the fact that the above-named solutions of salicylic acid will not keep well, it will probably be admitted that the amount of "preservative" found in organic liquids does not correctly represent that originally introduced, and this I

have proved to my own satisfaction. Moreover, the heating of solutions of the acid (whether acid or alkaline) tends to loss, and I have therefore arrived at the conclusion that the simpler the process of isolation adopted and the less "cooking" practised the better for success, and two methods suggest themselves, viz., distillation from an acid aqueous solution and extraction by ether.

With regard to the distillation method, after very numerous experiments and much work of apparent promise, I have been compelled to abandon it, the behaviour of salicylic acid mixed with organic liquids being most erratic; the frothing and intumescence is quite unmanageable at times, and even when the device of blowing steam through a hot solution is adopted the amount of steam required is very large, the consequence being that the bulk of this distillate is unwieldy, in addition to which certain volatile matters pass over and interfere.

In all cases the rate of distillation is apparently very irregular. I have never succeeded in exhausting a solution by this means, and the only use I can see in the process is as a means of qualitatively testing, for which when adopting the iron-alum reaction it is valuable.

The ether method in my hands works well in an acid solution. I find two successive shakings out quite sufficient, and the ether has but little colour imparted in the process. The ether in its turn is shaken out with two successive volumes of water containing a known amount of deci- or semi-normal alkali, the mixture obtained is carefully neutralized, and is made up to 250 c.c., or 500 c.c. with water. The liquid is very slightly coloured, if at all.

As salicylic acid in a pure state can be successfully titrated with caustic alkali, I at first hoped that this process could be adopted with the alkaline extract, but the results were wildly wide of the mark, as other volatile and organic acids were found to be present, having been absorbed by the ether, and success was hopeless. The colour process had therefore to be adopted—a measured portion withdrawn, diluted to 100 c.c. if necessary, 1 or 2 c.c. of iron-alum solution added, and the colour matched in the same way, using the weaker solution of salicylic acid mentioned above for the purpose.

The maximum amount of salicylic acid capable of being judged by the iron-alum test is a solution of the strength of 1 milligramme per 100 c.c., less than this being preferable; and as regards the addition of the iron-alum solution, while 1 c.c. may occasionally be sufficient to strike a full tint, 2 c.c. is never too much. Of course, the same procedure must be adopted both in the trial and comparison liquids.

In comparing the tints I have hitherto had no difficulty whatever, but Allen's advice "to add a definite amount of salicylic acid to a liquid of the same kind as that in which the acid is to be determined" should be kept in view. However, the very rich tint struck by iron-alum solution appears to supersede any such precaution. For acidulating the solution previous to extraction with ether I use dilute sulphuric acid. Hydrochloric acid seems to interfere with the colour struck.

Concentration is not to be recommended, and in the case of syrupy and highly alcoholic liquids dilution may be permitted, so delicate is the colour-test described above.

In conclusion, while small amounts of neutral alkaline salts do not appreciably

affect the violet tint, the salts of the alkaline earths are very prejudicial, and hence the use of distilled water in *all* the dilutions is most imperative.

I have pleasure in acknowledging the help rendered in the above work by my assistant, Mr. Ernest M. Hawkins, F.I.C.

DISCUSSION.

Mr. ALLEN said that it had been found by Continental chemists that in the examination of wine for salicylic acid, ethylic ether was apt to extract some other body which more or less simulated salicylic acid in its reaction with ferric chloride; and it had been recommended that petroleum ether, or a mixture of that solvent with ordinary ether, should be substituted for ethylic ether alone, and that not more than 50 c.c. of the wine should be employed for the test.

Mr. CHAPMAN said that in the application of ferric chloride to the colorimetric estimation of very small quantities of salicylic acid he had always found considerable difficulty to be caused by the extraction of traces of tannins, which seriously interfered with the colour produced with ferric chloride. Some years ago he had made a number of experiments to ascertain whether it was possible to determine accurately small quantities of salicylic acid in beer, and the main difficulty had been to obtain colours that were comparable. Of course, in the case of pure solutions the matter was quite simple, but when small quantities of tannin and similar substances were present he, personally, had found it very difficult indeed to get a satisfactory result with any degree of certainty. For large quantities there was probably no better method than the ordinary bromine precipitation process, but that was hardly applicable to the estimation of small quantities in foods or beverages.

To a question put by Mr. Allen, Mr. CHAPMAN replied that in applying the bromine precipitation process it was his custom not to weigh the bromine compound, but to estimate it volumetrically.

Mr. ALLEN said that his reason for asking was that there was some disagreement among investigators as to whether the compound in question was dibromo-salicylic acid or tribromo-phenol.

Mr. HEHNER said that if any large quantity of wine which had not been salicylated were extracted with ether a reaction would be obtained which was identical with that of salicylic acid. It was, indeed, a debateable question whether or not it was actually salicylic acid that was extracted. The German Government had accordingly laid down that a certain bulk—namely, 50 c.c.—and no more should be worked upon in testing wine for salicylic acid.

Mr. HARVEY, in reply, said that the process he had described adapted itself conveniently to very small quantities, so that, even in the case of beer, any error due to the presence of tannin would be reduced almost to nothing. The latter, however, if in quantity, could be eliminated previously.

Mr. CHAPMAN inquired whether the use of iron alum made any difference.

Mr. HARVEY said that the colour was so characteristic that he did not think it would be interfered with even by tannin—at any rate, with the quantities upon which he worked.