DETECTION OF FOREIGN COLORING-MATTER IN SPIRITS.

[SECOND METHOD.]

BY C. A. CRAMPTON AND F. D. SIMONS.

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A method for the detection of caramel in spirits and vinegar, based upon the selective absorption of caramel coloring-matter by fullers' earth, was published by us in this Journal.[1] Since that time the method has given very satisfactory results in this laboratory in the examination of samples suspected of being artificially colored, the chief difficulty encountered in its application being the variable quality and color-absorbing power of fullers' earth as found in the market. This difficulty was partially overcome by obtaining a supply of the material, of uniform color-absorbing capacity to the degree best suited to the purpose in hand, and in quantity sufficient for a very great number of tests, so that it will not be necessary to change the standards for a long time to come.

We have lately perfected, however, a much more satisfactory and convenient test, which is based simply and solely upon the insolubility in ether of the coloring-matter of caramel and prune juice, the only foreign coloring materials known by us to be used for the artificial coloring of spirits. The coloring-matter of oak wood, on the other hand (principally flavescin), is soluble in ether, which readily removes it from its solution in water or alcohol when shaken with it.

It was found that one treatment with ether was sufficient to completely remove all coloring-matter soluble therein, a second treatment with a fresh portion of ether giving no color whatever. The test is made by shaking the sample with ether, separating the ethereal from the watery layer, and comparing the color of the latter with the color of the original spirits by means of the tintometer. It is necessary, however, to bring the sample to a standard alcoholic strength, as the ether layer takes up most of the alcohol, and consequently the watery layer containing the ether-insoluble coloring-matter would be more concentrated in the case of a high proof than a low proof spirits, giving variable results. In order to insure uniformity in this respect the sample

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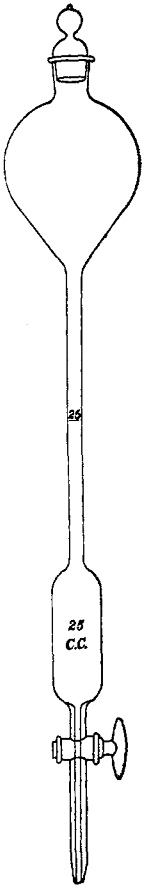
[1] This Journal, **21**, 355 (1899).

is evaporated on the water-bath until all the alcohol has been driven off; a known quantity of water-white absolute alcohol is then added, which redissolves the coloring-matter precipitated by the removal of the alcohol, making a bright solution, which is then made up to the original volume, and its color taken by means of the tintometer. A definite portion of this solution is then treated with a definite volume of ether, the watery layer separated, and its color taken by the tintometer. A comparison of the two readings will show the character of the sample, genuine spirits giving up about 40 to 50 per cent. of its color, while spirits colored by caramel alone are entirely unaffected, the ethereal layer remaining water-white.



For making the ether extraction we have found it very convenient to use a separatory funnel, which is a slight modification or rather simplification, of Bromwell's modification of Röse's apparatus for the estimation of fusel oil in spirits.[1] Our apparatus is shown in the accompanying figure, and is simply an ordinary globe-shaped separatory funnel or flask with its stem above the stop-cock expanded into a bulb holding 25 cc., the graduation coming up in the stem. The upper bulb should have a capacity of about 100 cc.

Following is the detailed method of procedure: Fifty cc. of the sample under examination are measured out at a standard (room) temperature, and evaporated on the water-bath nearly to dryness; the residue is washed into a 50 cc. glass stoppered flask, 25 cc. absolute alcohol added, and the solution, after cooling to the standard temperature, is made up to the mark with water. After mixing, 25 cc. of the solution are transferred to the separatory apparatus and treated with 50 cc. ether for half an hour, being shaken at intervals; at the end of this period, the layers having separated well, the lower layer is made up with water to the original volume, 25 cc. This is conveniently accomplished by connecting

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[1] Bull. No. 49, Chem. Div., Dept. of Agriculture, p. 115.

the lower end of the apparatus with a rubber siphoning tube which carries water from an elevated flask, the inflow of water being regulated by the stop-cock of the apparatus. The contents of the flask are again shaken, and again allowed to separate (whereby the volume of the lower layer is slightly increased), and the watery layer is drawn off through the stopcock for a reading of its color in the tintometer. At the same time a reading is taken of the 25 cc. of the solution which was not subjected to the treatment with ether; from these two readings the amount of color extracted by ether is calculated in percentages.

The accuracy of the test is much promoted by adhering carefully to the same conditions throughout, especially with regard to temperature.

Applied to a series of 34 samples of spirits known to be naturally colored, the test gave the following results·

	Color removed. Per cent.
Maximum	51.1
Minimum	36.4
Average	41.7

A series of 17 samples known to be artificially colored gave the following figures :

	Color removed. Per cent.
Maximum	23.2
Minimum	0.0
Average	14.8

The results do not show quite so wide a variation between the two sets of samples as the results obtained from the same samples by the fullers' earth test, but the ether extraction method is more satisfactory in a general way. The results obtained by the two methods were confirmatory in every case, and the former will be valuable as a supplementary test. In comparing the figures it must be kept in mind that the results by the two methods are in opposite directions; that is, fullers' earth removes the color from an artificial spirit, while ether removes the color from a natural spirit.

Since the work on this test was completed our attention was drawn to an article by Leach,[1] wherein he recommends the

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[1] This Journal, **22**, 207 (1900).

detection of caramel coloring in milk by means of its insolubility in ether, or rather its separation in this way from other coloring-matters (annatto and aniline orange), its identification by "any of the usual tests" to follow.

We have found the method inapplicable to vinegars colored with caramel, genuine apple vinegar giving no color when shaken with ether.

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[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

A RAPID METHOD FOR THE DETECTION OF "ANILINE ORANGE" IN MILK.

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DURING the year ending September 30, 1900, there have been examined by the Department of Food and Drug Inspection of the Massachusetts State Board of Health 6137 samples of milk, of which number 45, or 0.7 per cent., contained foreign coloring-matter. Of these colored samples, 20 contained annatto, 3 contained caramel and 22, or 48 per cent., contained "aniline orange" which generic term is used to describe those azo colors used for this purpose. The statistics of the previous five years show that 0.6 per cent. of the total samples of milk were artificially colored, of which 10 per cent. contained aniline orange. The statistics of 1900 show a decided increase in the use of aniline orange as a milk "improver."

In view of the facts that if a sample is carefully colored with a view of not getting in too much, that many samples containing color are above the legal standard and that it is very difficult to tell at a casual glance whether or not a sample is colored, a rapid method for the detection of foreign coloring-matter in milk would be invaluble to the milk analyst.

In testing a sample of milk for formic aldehyde by the well-known method of boiling with an equal volume of strong hydrochloric acid containing ferric chloride,[1] the writer found upon

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[1] See Twenty-ninth Annual Report of the Massachusetts State Board of Health, 1897, p. 558.