

	Soluble arsenious oxide.			Cupric oxide. Per cent.	Insoluble in hydrochloric acid.
	Wash on filter.	500 cc. cold water. Per cent.	Water at 50°-60° C.		
Paris green "A".....	Abandoned	4.02	11.10+	30.07	None
Paris green "B".....	"	4.86	8.86+	29.79	None
Scheele green.....	"	17.76	22.87+	38.14	None
Arsenious oxide, C. P.	....	....	....	....	None

A continuation of this paper will appear during the next few months, which will have for its object the creation and improvement of the methods of estimating the various constituents of London purple as well as a study of the improved method of estimating arsenic gravimetrically by Martha Austin,<sup>1</sup> which has only come to my notice since the above work was completed.

## THE DETECTION OF COAL-TAR DYES IN FRUIT PRODUCTS.

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SOON after its discovery fuchsine came into use for coloring wines and replaced to a large extent the vegetable dyes which from very early times had been employed for this purpose. More recently various other coal-tar dyes, particularly the azo-colors, have been extensively used in wines although fuchsine and acid fuchsine are still preferred by some makers.

Within the past few years the use of coal-tar dyes in articles of diet has attracted the attention of food analysts in the United States. In the case of confectionery, pastries, and some other products they serve merely to render the articles more attractive to the eye without deceiving the purchaser, but as a rule they give imitation products the appearance of the genuine or, to use the legal phraseology, "they make the products appear better or of greater value than they really are."

Some of the results obtained by Winton, Ogden, and Mitchell, in the examination of foods at the Connecticut Agricultural Experiment Station, illustrate the fraudulent use of dyes. In 1898, sixty-three samples of jellies purporting to have been made from fruit were examined, and of these, twenty-eight were spurious mixtures colored with coal-tar dyes. Some of the most remarkable samples, labeled "strawberry jelly," "raspberry

<sup>1</sup> *Ztschr. anal. Chem.*, 23, heft 2.

jelly," etc., consisted of starch paste, flavored with artificial "fruit ethers," sweetened with glucose and preserved with salicylic acid, the dye having been used to carry out the deception. Of twenty-eight samples of fruit preserves, eight were also colored with coal-tar dyes. During the following year (1899) ninety-two samples of soda-water sirups, chiefly strawberry, raspberry, and orange, were subjected to analysis. Of these, forty-five were colored with coal-tar dyes. As a rule the sirups which were artificially colored were also artificially flavored and contained no genuine fruit juice whatever. Dyes were also found in bottled carbonated beverages.

The relation of these dyes to public health deserves attention. The experiments carried on with dogs and other animals by Cazeneuve and Lépine, Weyl, and others have proved beyond a doubt the poisonous nature of picric acid, dinitrocresol, and Martius' yellow, among the nitro-colors, and of orange II and metanil yellow among the azo-colors. Fuchsine, sulphonated nitro-colors, and most of the azo-colors did not act as poisons although some of the azo-colors produced vomiting, others diarrhea, and many developed slight albuminuria.<sup>1</sup>

Although there is evidence that the bulk of the coal-tar dyes are not injurious to some of the lower animals, it is not safe to assume that they are entirely harmless to human beings. The dog, the animal used in most of Weyl's experiments, has a proverbially strong stomach and eats, with no apparent discomfort, many things which would disturb the digestion of a man.

The unwholesomeness of certain coal-tar dyes not classed as poisons is indicated by the experience of Weber<sup>2</sup> who tested their effect on the artificial digestion of fibrin with pepsin and with pancreatin. He found that oroline yellow (acid yellow) retarded the action of pepsin and that methyl orange, saffoline (acridine red), and magenta (fuchsine) seriously interfered with the pancreatic digestion. Of these, fuchsine, at least when pure, had been pronounced entirely harmless by earlier investigators who based their conclusions on experiments with lower animals and some few with man.

<sup>1</sup> "The Coal-tar Colors" by Theodore Weyl, translated by Henry Leffmann, pp. 54-148.

<sup>2</sup> This Journal, 18, 1092.

Even if the entire harmlessness of most of the coal-tar dyes is conceded, in view of the injurious properties of some of them and the difficulty of distinguishing these from the harmless dyes when present in food products, the safe course is to exclude all dyes of coal-tar origin from articles of diet. In Austria their use is entirely prohibited and in other countries they are regarded with suspicion.

In carrying out the work of food examination under adulteration laws the analyst is often called upon to determine whether or not a coal-tar dye is present, if not to identify the particular dye.

Numerous methods of testing wines for these dyes are described in the journals and in the works on food analysis but almost nothing has been published on their detection in jellies, preserves, fruit sirups, and other fruit products.

Because of the absence of special methods I have adapted some methods originally devised for wines for use in testing other products and publish the following details, with precautions learned by experience, for the benefit of others engaged in similar work.

In applying these tests to jellies and other semisolid products it is necessary to bring into solution by boiling with 1 to 5 parts of water.

#### ARATA'S WOOL TEST.<sup>1</sup>

One hundred cc. of the liquid to be tested, prepared if necessary as described in the preceding paragraph, are boiled for ten minutes with 10 cc. of 10 per cent. solution of potassium bisulphate and a piece of white wool, or woolen cloth, which has been previously heated to boiling in a very dilute solution of sodium hydroxide and thoroughly washed in water. After removal from the solution, the wool is again washed in boiling water and dried between pieces of filter-paper. If the coloring-matters are entirely from fruit, the wool either remains uncolored, or takes on a faint pink or a brown color which is changed to green by ammonia and is not restored by washing in water; but if certain coal-tar dyes, chiefly of the azo-group, are present,

<sup>1</sup> *Ztschr. anal. Chem.* 28, 639. See also Borgman: "Anleitung chem. Anal. d. Weines," Wiesbaden, 1898, p. 91. Koenig: "Untersuchung landw. u. gewerb. wich. Stoffe," Berlin, 1898, 577.

the wool is dyed and the color on the fibers is either not changed by ammonia or, if changed, is restored by washing.

The dye present may often be identified by noting the color of the wool after addition of enough concentrated sulphuric acid to thoroughly moisten the fibers and again after dilution of the acid.<sup>1</sup> As a rule it is not desirable to proceed further with the test although Arata gives instructions for removing the dye from the wool and testing the dye itself. For this purpose the wool is treated with dilute tartaric acid solution to remove vegetable colors, washed in water and dried between sheets of filter-paper. It is then transferred to a test-tube and saturated with concentrated sulphuric acid. After standing five or ten minutes, water sufficient to make 10 cc. is added and the wool is removed. The solution after making alkaline with ammonia and cooling is shaken with 5 to 10 cc. of pure amyl alcohol, to which a few drops of ethyl alcohol are added, to facilitate the separation. The alcoholic extract is separated, evaporated to dryness, and the residue tested according to the scheme of Girard and Dupré, Witt,<sup>2</sup> Weingaertner<sup>3</sup> or Dommergue.<sup>4</sup>

I have applied this test to samples of juices, sirups, jellies, and preserves prepared in the laboratory from the fruits, as well as to numerous commercial fruit products including catsups. The woolen cloth used was "nun's veiling" cut into pieces one inch wide and three inches long.

When strawberry, raspberry, blackberry, currant, grape, and cherry juices, without dilution, were treated as has been described, the wool acquired a dull pink or brownish pink color. With ammonia the color changed to green, and washing with water in no case restored the original color. Treatment with 10 per cent. tartaric acid solution in the cold was without effect, but on boiling for some time the pink color was largely removed. From orange, lemon, pineapple and tomato juice or pulp, the wool absorbed no color at all, or only a faint yellow color.

Jellies, preserves, sirups, and catsups known to be pure gave up to the wool very slight colors, but many of the commercial

<sup>1</sup> See scheme of Girard et Dupré: "Analyse des Matières Alimentaires et Recherche de leurs Falsifications."

<sup>2</sup> *Ztschr. anal. Chem.*, 26, 100.

<sup>3</sup> *Ibid.*, 27, 232.

<sup>4</sup> *Ibid.*, 29, 369.

products imparted to the wool intense red, orange, magenta, and even green shades. Treated with ammonia, these bright colors remained unchanged or, if changed, washing restored the original color.

Boiling with tartaric acid solution also failed to affect the colors. By treatment with concentrated sulphuric acid and dilution of the acid, color reactions for acid fuchsine, tropæolins, ponceaus, Bordeaux red, eosins, and other dyes were obtained.

I have found it more satisfactory to test the dyed wool directly, rather than the color obtained from the wool as directed by Arata, because only a few dyes are extracted by amyl alcohol from alkaline solutions, and, as explained further on, tests of the residues left after evaporating the extracts are indecisive.

Care should be taken to determine whether the wool is dyed, or merely coated with the color. For example, chlorophyl from green coloring preparations of vegetable origin, is deposited on wool, together with fat and resin, but the color, unlike the coal-tar dyes, rubs off on the fingers and is readily washed out with soap and water.

For the purpose of illustrating the amount of artificial color present in each glass of adulterated carbonated beverages, I have employed 250 cc. portions of the beverages (or 40 to 50 cc. of sirups diluted to 250 cc.) and pieces of nun's veiling six inches square. The dyed squares thus obtained furnish striking object lessons. From strawberry, raspberry, cherry, and blood-orange flavors, brilliant red and magenta shades were fixed on the wool (acid magenta, Bordeaux red, ponceaus, etc.); from orange and lemon flavors, orange and yellow shades (tropæolins, etc.); and from mint preparations, bright green and yellow-green colors.

#### AMYL ALCOHOL TEST, ALKALINE SOLUTION.<sup>1</sup>

Twenty-five cc. of the liquid to be tested, made alkaline with ammonia, are shaken cautiously for some minutes in a separatory funnel, with pure amyl alcohol. If the clear alcoholic layer, when separated from the aqueous solution, is colored, or if addition of acetic acid develops a magenta color (fuchsine), a portion of it, together with an equal bulk of water and a thread of

<sup>1</sup> "Analyse des Matières Alimentaires et Recherche de leur Falsifications", Par Girard et Dupré, pp. 167, 582.

wool, is heated on a water-bath, the water lost by evaporation being replaced from time to time.

The presence of a coal-tar dye should not be affirmed until the color has been fixed on wool and the wool has been washed in boiling water, dried, and tested with sulphuric acid. When fuchsine is present, the color which appears on adding acetic acid to the alcohol extract is changed to yellow by hydrochloric acid. Ether or ethyl acetate may be used in place of amyl alcohol for extracting fuchsine.

#### AMYL ALCOHOL TEST, ACID SOLUTION.<sup>1</sup>

Twenty-five cc. of the liquid, to which have been added a few drops of hydrochloric acid, are shaken with amyl alcohol, and dyeing tests are made as described in the preceding section.

A colored amyl alcohol does not prove the presence of a coal-tar color, as I have found that red coloring-matters are extracted by this solvent from acid solutions of pure fruit juices. These solutions, however, do not dye wool, when treated as above described.

Some authors recommend that the sulphuric acid test be applied to the residue left after evaporating the amyl alcohol extract. This may be satisfactory in wine analysis but with fruit jellies, etc., this residue is liable to contain other organic matters which obscure the color reactions of coal-tar dyes.

If amyl alcohol extracts from the liquid, after acidifying, an orange color which has not been found to be of coal-tar origin, test may be made for cochineal.

The alcohol is washed several times with water and divided into two portions. To one portion is added a solution of uranium acetate, drop by drop, with shaking. In the presence of cochineal the aqueous solution acquires an emerald-green color.<sup>2</sup> As a confirmatory test the other portion is made alkaline with ammonia which changes the orange color of cochineal to purple.

#### GIRARD'S TEST FOR ACID FUCHSINE (ACID MAGENTA).<sup>3</sup>

If a bright magenta color is fixed on wool by Arata's test and

<sup>1</sup> "Analyse des Matières Alimentaires et Recherche de leur Falsifications," Par Girard et Dupré, p. 582.

<sup>2</sup> *Ibid.*, p. 580.

<sup>3</sup> *Ibid.*, p. 169.

if ordinary fuchsine has been proved to be absent, test should be made for acid fuchsine.

To 10 cc. of the liquid are added 2 cc. or more of 5 per cent. solution of potassium hydroxide. The strongly alkaline liquid is mixed with 4 cc. of 10 per cent. solution of mercuric acetate and filtered. The filtrate should be alkaline and colorless. If addition of a slight excess of dilute sulphuric acid produces a violet-red coloration and other dyes have not been found by the amyl alcohol test, the presence of acid fuchsine may be affirmed.

I have found this test useful in the examination of fruit juices and sirups but unsatisfactory in the case of jellies owing to difficulties in filtration and undecisive reactions.

#### CAZENEUVE'S METHOD.

Cazeneuve's mercuric oxide method<sup>1</sup> for detection of coal-tar dyes which has been extensively employed in wine analysis did not prove satisfactory in the examination of jellies. This method, however, deserves trial with fruit juices and sirups, which are more easily handled than the gelatinous products.

In testing a suspected sample I apply first of all Arata's test. The other tests described are employed either to confirm the results obtained by Arata's test or to supply evidence in cases where that test fails.

The analyst should be extremely cautious in naming the particular dye present in a sample. It should be remembered that the number of coal-tar dyes on the market is exceedingly large and that new dyes are continually being introduced. A reaction which a few years ago may have been characteristic of a particular dye may to-day be common to several dyes. As a rule it is only necessary to learn whether or not a color is of coal-tar origin. In fact such terms as "red coal-tar dye" and "orange coal-tar dye" are often to be preferred in an official report to the cumbersome scientific names or the equally unintelligible commercial names.

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<sup>1</sup> "Analyse des Matières Alimentaires et Recherche de leur Falsifications." Par Girard et Dupré, p. 174; *Compt. rend.*, 102, 52.