

nation very slowly at a low temperature, I have detected as little as forty-four hundred thousandths of one per cent. I give below the results of my last determination of benzoic acid in tomato ketchup.

Two samples were taken and to one, 0.12 g. of sodium benzoate (0.1 g. benzoic acid) was added. Original sample, sodium benzoate, found equals 0.0531 per cent. ; benzoic acid equals 0.045 per cent.

Original sample plus added sodium benzoate, sodium benzoate, found = 0.172 per cent. ; benzoic acid = 0.145 per cent.

Subtracting :—

$$0.172 - .12 \text{ (added)} = 0.052 \text{ sodium benzoate.}$$

$$0.145 - .1 \text{ " " } = 0.045 \text{ benzoic acid.}$$

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SOLUBILITIES AND EXTRACTION VALUES OF FOOD COLORS.

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Few data are found in the literature on the solubilities and the extractive values of the vegetable and coal tar colors commonly used in foods. In collaborating with the Association of Official Agriculture Chemists, the following report was submitted to Prof. E. F. Ladd, Associate Referee on Colors. It was recommended by the Referee that special attention be given among other points, to investigations along the following lines :—

a—Solubility of coal tar and vegetable dyes, in various solvents, ether, acetic ether, petroleum ether, methyl and ethyl alcohols, acetones, etc., and mixtures thereof, arranging the compounds according to their solubility as—easily soluble, difficultly soluble and insoluble.

b—Extractive values of the various solvents for dyes in neutral, acid and alkaline solutions.

The terms "easily soluble", and "difficulty soluble" being very indefinite, the actual amounts of color dissolved and extracted were determined.

In determining the solubility of the colors, certain factors must be taken into consideration and considered as constants, *viz* : Amount of color to solvent ; time of bringing into solution, and temperatures.

In determining the extractive values, the constants must be : Amount of color in solution ; amount of solvent to solution extracted ; time of extraction and temperatures.

Working with colored food products, naturally colored or otherwise, the extraction values will be materially affected by the unknown factors, due to the composition of the food products, the presence of oils, fats, saccharine substances, nitrogenous matter, fiber, mineral substances (ash), etc., which may change the extractive properties of many solvents, and which in many cases act as mordants on the colors themselves, so that

the data obtained on the colors themselves will not be conclusive and often of little or no value. In working on food products directly, it has been found advantageous to separate the colors by means of dyeing tests¹ modifying the tests, when necessary, so as to extract without addition of any salts or mordants, and dyeing large pieces of wool (6x24 inches) in hydrochloric acid, ammonia and neutral baths. The extraction value of the color fixed on the wool can then be determined directly on part, and other tests applied to the rest of the cloth. The color is separated from a part of the dyed cloth and a second dyeing test made with this, thereby separating many of the natural colors and enabling the investigator in some cases to identify by chemical and solubility tests, the actual class or kind of color present in the food product.

The results obtained on the solubilities and extractive values as applied to colors in or separated from food products is left for a later report, the investigation not having been concluded.

In determining the solubility—cold—all reagents were at room temperature (18° – 20°). One gram of the color was thoroughly shaken for one minute with 100 cc. of the solvent. The solution was allowed to stand for one hour. If not perfectly clear, it was clarified either by filtration or in a centrifuge. The actual amount of color dissolved was determined by direct comparison, in color tubes, using known standard solution of the same color for comparison. No attempt was made to completely dissolve or extract any colors, by continued treatment.

In determining the solubility—hot—the solutions were immersed in a boiling water bath for 30 minutes, shaken every five minutes, flasks being connected with reflux condensers. The hot solutions were filtered quickly, using a suction pump when necessary. The filtrates were compared with standard solutions of the same color. It was found that an increase in time of heating or varying the amount of the solvent, slightly changed the amount of colors dissolved, in many cases. This was especially noticeable with colors that gave some soluble part differing in shade or color from the original color. Impurities in the colors themselves, due to raw materials used or processes of manufacture, may be extracted by some solvents and thereby give slight color to the solvent, not actually due to the color itself. The extraction of colors by means of solvents, is a method of partial or complete purification of food colors. The tables of solubilities show that only small differences exist between hot and cold solutions, although in some cases the solvent became super-saturated and allowed some of the color to separate or crystallize out on cooling.

All solvents used were redistilled and dried with calcium chloride for

¹ Sostegni and Carpentieri, *Arata*, Bull., 65, Bureau of Chemistry, Dept. of Agr.

solvent tests ; for extraction tests the drying was omitted. When the solubility of the color is less than one to 2000, the results are not conclusive, as this may be due to the moisture contained in the color itself and taken up by the solvent. In some cases, with very low solubility it was found that on drying with calcium chloride, after treatment, the color disappeared from the solvent and colored the calcium chloride. As many of these colors are sensitive to heat, no attempt was made to dry the colors themselves, the amount of moisture present varying from 0.5 to 6.0 per cent., depending on the class of color and kind of package in which it was kept. The absolutely dry color will absorb moisture quickly unless kept in hermetically sealed packages.

Many of the colors are very sensitive to acids and alkalis, reacting so quickly that they can be used as indicators, and many of them are used for that purpose. The shade of the color is often changed due to the solvent being either acid or alkaline in character.

The extractive values were determined by dissolving one g. of color in 1000 cc. of distilled water for the neutral solutions, in 1000 cc. of hydrochloric acid, containing one per cent. by weight of the acid for the acid solutions and in 1000 cc. of dilute ammonia water, containing one per cent. of ammonia by weight for the alkaline solutions.

100 cc. of the different solutions, containing 0.1 g. of color, were thoroughly shaken with 50 cc. of the solvent, allowed to stand until a clear distinct separation had taken place. The amount of color extracted was determined by comparison with the standard color solutions of same character, acid, alkaline or neutral. If the solvent was not clear, it was filtered and with colors forming emulsions, the separation was made in a centrifuge. No attempt was made to obtain complete extraction. Very low extractive values are also not conclusive, as the small amount of color going into the solvent may be due to water extracted by the solvent, it also was found, that drying the solvent with calcium chloride would take out the color in the same manner as with the solubility tests. All extractions were made cold, at room temperature. The following colors were partially or completely examined :

Coal tar colors :

Amberine Yellow, Amethine Violet, Saffoline Red, Ruby Red, Amaranth Red, Rasberine Red, Turquine Blue, Turmeric Yellow, Myrtiline Green, Marsiline Orange, Oroline Yellow, Carminoline, Hoffman Violet, Ponceau 2 R, Fuchsine S.B., Indigo Carmine A, Naphthol Yellow, Orange R, and Bismark Brown.

Vegetable colors :

Primoline Yellow, Citronole Yellow, Cochineal, Cochineal Rose, Samoline Orange, Celoline Blue, Chestnut Brown, Koncentrona L, Pansoline

Violet, Veroline Green, Aecoline Yellow, Lazuline Blue, Mintoline Green, Cladonal Red, Turmeric, Annatto and Chlorophyll.

The most commonly used colors in the confectionery industry are the

TABLE I
SOLUBILITIES OF DRY COLORS.

Color = 1.0000 g.
Solvent = 100 cc.

Name of Colors Kind of Color	Grams of Color Dissolved per 100 cc. Solvent.											
	Oroline Yellow Coal Tar Cold	Oroline Yellow Hot	Amaranth Red Coal Tar Cold	Amaranth Red Hot	Turquoise Blue Coal Tar Cold	Turquoise Blue Hot	Aecoline Yellow Vegetable Cold	Aecoline Yellow Hot	Cladonal Red Vegetable Cold	Cladonal Red Hot	Lazuline Blue Vegetable Cold	Lazuline Blue Hot
Water	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Hydrochloric Acid 1% ..	1.0000 ¹	1.0000 ¹	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Ammonia 1%	1.0000	1.0000	1.0000	1.0000	Color Destroyed	1.9000	0.9000	1.0000 ²	1.0000 ²	1.0000 ²	1.0000	1.0000
Ethyl Alcohol	0.1500	0.8000	0.0300	0.0300	0.0700	0.1000	0.0100	0.0100	0.0100	0.0100	0.0400	0.0800
Methyl Alcohol	0.2500	1.0000	0.0500	0.0500	0.1000	0.2000	0.0150	0.0150	0.0220	0.0050	0.0020	0.0020
Amyl Alcohol	0.0400	0.0400	0.0200	0.0200	0.0010	0.0010	0.0100	0.0100	0.0000	0.0000	0.0000	0.0000
Petroleum Ether	0.0030	0.0030	Yellow	Yellow	0.0000	0.0000	0.0020	0.0000	0.0000	0.0000	0.0000	0.0000
Ether	0.0080	0.0080	Yellow	Yellow	0.0000	0.0000	0.0050	0.0050	0.0000	0.0000	0.0000	0.0000
Acetone	0.0080	0.0150	0.0050	0.0050	0.0000	0.0000	0.0050	0.0050	0.0000	0.0000	0.0010	0.0010
Ethyl Acetate	0.0100	0.0250	0.0005	0.0005	0.0010	0.0010	0.0020	0.0020	0.0050	0.0050	0.0005	0.0005
Amyl Acetate	0.0100	0.0100	Yellow	Yellow	0.0000	0.0000	0.0050	0.0050	0.0005	0.0005	0.0005	0.0005
Carbonyl Disulphide	0.0030	0.0030	0.0010	0.0010	0.0000	0.0000	0.0010	0.0010	0.0002	0.0002	0.0010	0.0010
Carbon Tetrachloride ..	0.0020	0.0020	0.0010	0.0010	0.0000	0.0000	0.0005	0.0005	0.0002	0.0002	0.0005	0.0020
Chloroform	0.0020	0.0020	0.0020	0.0030	0.0000	0.0000	0.0015	0.0015	0.0001	0.0002	0.0005	0.0020

¹ Color changed to red.

² Color changed to blue.

TABLE 2.
EXTRACTION VALUES OF COLORS.
Solutions == 1,000 g. Color to 1000 cc.
Solvents == 500 cc. per Extraction
Grams of Color Extracted by 500 cc. Solvent.

Name of Color Kind of Color Solution	Oroline Yellow Coal Tar			Amaranth Red Coal Tar			Turquoise Blue Coal Tar			Acoline Yellow Vegetable			Cladonal Red Vegetable			Lazuline Blue Vegetable			
	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	Neutral	Acid 1 %	Alkali 1 %	
Solvents Used																			
Water	Slightly Cloudy
Hydrochloric Acid 1%..	Changes to Red			Clear, lighter shade
Ammonia 1%	Changed to Orange			Color Destroyed	Changed to blue		
Ethyl Alcohol.	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible			
Methyl Alcohol	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible			
Amyl Alcohol	.010	.5000	.0000	¹	.600	1	.0010	.5000	.0 ²	.0500	.3500	.0000	.0050	.7000	.0005	.0010	.3000	.0100	
Petroleum																			
Ether.....	.001	.0010	.0020	0.	.000	1	.0000	.0000	.0 ²	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	
Ether005	.0080	.0040	0.	.000	1	.0000	.0000	.0 ²	.0080	.0500	.0000	Yellow	Yellow	.0000	.0000	.0000	.0000	
Acetone	Miscible			Miscible			Miscible			Miscible			Miscible			Miscible			
Ethyl Acetate	.015	.0150	.0005	1	1	1	.0005	.0005	.0005 ³	.0500	.6500	.0500	.0020	.0050	.0010 ⁴	.0000	.0000	.0005	
Amyl Acetate	.002	.0050	.0150	0.	1	.0000	.0000	.0000	.0 ²	.0050	.0200	.0000	.0010	.0050	.0005	.0000	.0000	.0000	
Carbon Disulphide000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0 ²	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	
Carbon Tetra- chloride ..	.000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0 ²	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	
Chloroform .	.000	.0000	.0000	0.	.0000	.0000	.0000	.0000	.0 ²	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	

¹ Color extracted yellow.

² Color destroyed by alkali, reproduced by acid.

³ Color extracted is blue.

⁴ Color extracted is blue.

reds, blues and yellows. Most other colors are mixtures and combinations of these three colors. The foregoing tables give the results obtained on three vegetable colors and three coal tar colors, having similar shades and having exceptional great color intensities for the classes of colors they represent.

Examination of these tables shows that the use of miscible solvents like methyl and ethyl alcohols and acetone are of no value for extraction purposes. Solvents of an acid like character (ethyl acetate) are not suitable as the results obtained are misleading, due to the effect of the solvent on the color.

The solubilities of many colors in petroleum ether, ether, carbon disulphide, carbon tetrachloride and chloroform is so slight, that these solvents are very suitable for preliminary extraction of food products thereby extracting oils and fats, before making dyeing tests to separate the colors. Care must be exercised, as many colors are soluble in fats or oils and are liable to be extracted in such preliminary treatment. Examination of the fats or oils will show whether any color has been extracted with these.

Conclusions drawn from a very large number of solubility and extraction tests, extending over a long period of time, are that the colors extracted or dissolved by many solvents under varying conditions from neutral, acid or alkaline solutions, give no conclusive data for deciding upon the character or class of the colors themselves. The differences in solubility and in extractive values of vegetable colors compared with coal tar colors, are no greater, nor less, than the differences found between the various colors themselves, belonging to the same class of colors.

Comparative color intensities were also determined and it was found that only a very limited number of vegetable colors, had a color intensity equal to one-fourth that of a corresponding shade of coal tar color and that the largest number of vegetable colors had one-tenth or less color intensity, than the corresponding coal tar color of similar shade.

The colors used were supplied to me by Messrs. H. Kolnustamm & Co., to whom I wish to express my thanks for assistance rendered.

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ON THE DIGESTION OF URINE IN THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

BY P. B. HAWK.

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Having made use, in several metabolism experiments, of various modi-