d. That in the case of cottonseed oils it will probably be sufficient to determine only 5 or 6 points on the curve.

e. That it is possible to compute from the curve a single value for quality and one for brightness, which together give a simple system of notation for color. Aside from this, other methods of notation using three numbers are also available.

f. That the spectral transmittance curves may be useful in studying the efficiency of the bleaching and refining processes.

KEUFFEL AND ESSER CO.,
HOBOKEN, N. J.

THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF CHROMIUM IN FATS

BY A. O. SNODDY

It frequently happens that it is desirable to know whether a fat has been bleached by means of chromic acid and how much, if any, chromium has been left in the finished product made from such a fat.

Fats which have been bleached by chromic acid, even after refining and treatment with fuller's earth and repeated filtration, almost invariably contain small amounts of chromium, the persistence with which the chromium remains with the fat being due perhaps to its being present as a chromium soap, which is either actually soluble in oil or else so thoroughly protected by an oil coating that it escapes caustic refining and clarification treatments. The amount of chromium left in the fat will depend to some extent upon the care with which the treatments subsequent to the chromic acid bleaching are carried out and varies from a few hundredths to one or two parts of chromium per million of fat.

Advantage may be taken of the fact that dichromates react with symmetrical diphenylcarbazide, to give an intensely colored compound, to determine small amounts of chromium in the ash from such a fat. In the course of his work with phenylhydrazine E. Fischer[1] obtained phenylsemicarbazide and diphenylcarbazide. Skinner and Ruheman[2] obtained diphenylcarbazide by heating one mole of ethyl carbamate with two moles of phenylhydrazine until ammonia was no longer evolved. They also used urea instead of ethyl carbamate, this being considered at present the most efficient way of preparing this compound. They noted that mild oxidizing agents such as $CuSO_4$ and $HgCl_2$ gave colored compounds with diphenylcarbazide, and gave this as one of the differences between carbamide and those substances which contain groups of two atoms of nitrogen directly connected. They proposed this reaction with copper sulfate as a qualitative test for copper and showed that thiocarbazides also gave

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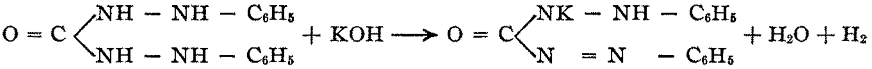
[1] *Ann.*, **190,** 113 (1877); *Ann.*, **263,** 272 (1891); *Ber.*, **22,** 1935 (1889).

[2] *Ber.* **20,** 3372 (1887); *J. Chem. Soc.* (London), **53,** 551 (1888).

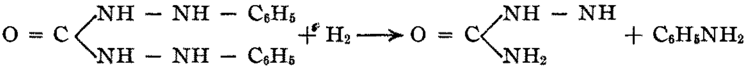
characteristic colors. Aside from $HgCl_2$ no other reactions with salt of metals are mentioned.

In 1900, M. P. Cazeneuve[3] reported the results of his investigation on the reaction between metals and their salts with diphenylcarbazide. His diphenylcarbazide was made by heating together phenylhydrazine and urea and purifying by crystallization from acetic acid or acetone. The reaction of metallic sodium, potassium and mercury and salts of mercury, copper, chromium, iron, lead, manganese, zinc, gold and silver are described.

Cazeneuve is of the opinion that in these reactions the diphenylcarbazide is oxidized to diphenylcarbazone which then reacts with the metal present to form an organo-metallic compound. Alcoholic sodium or potassium hydroxide reacts the same as the metals as indicated by these formulae.



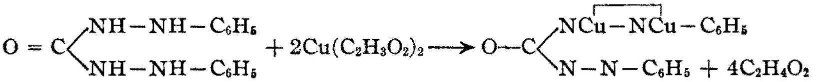
$$\mathrm{O=C}\begin{matrix}\mathrm{NH-NH-C_6H_5}\\ \mathrm{NH-NH-C_6H_5}\end{matrix} + \mathrm{KOH} \longrightarrow \mathrm{O=C}\begin{matrix}\mathrm{NK-NH-C_6H_5}\\ \mathrm{N=N-C_6H_5}\end{matrix} + \mathrm{H_2O} + \mathrm{H_2}$$



$$\mathrm{O=C}\begin{matrix}\mathrm{NH-NH-C_6H_5}\\ \mathrm{NH-NH-C_6H_5}\end{matrix} + \mathrm{H_2} \longrightarrow \mathrm{O=C}\begin{matrix}\mathrm{NH-NH}\\ \mathrm{NH_2}\end{matrix} + \mathrm{C_6H_5NH_2}$$

No hydrogen is liberated as the nascent hydrogen is rapidly taken up by the diphenylcarbazide to form phenylsemicarbazide and aniline. The potassium salt of diphenylcarbazone can react through double decomposition with the salts of many metals.

Diphenylcarbazide may also react with salts of metals directly according to the following equation:



$$\mathrm{O=C}\begin{matrix}\mathrm{NH-NH-C_6H_5}\\ \mathrm{NH-NH-C_6H_5}\end{matrix} + 2\mathrm{Cu(C_2H_3O_2)_2} \longrightarrow \mathrm{O-C}\begin{matrix}\mathrm{NCu-NCu-C_6H_5}\\ \mathrm{N-N-C_6H_5}\end{matrix} + 4\mathrm{C_2H_4O_2}$$

The highly colored organo-metallic compounds formed are in general unstable in the presence of acid, so that the reaction must take place in neutral or only faintly acid solutions. The chromium compound is an exception to this, being stable in concentrations of acid which do not permit the formation of a compound with other metals. This chromium compound gives a violet color to its aqueous solution which possesses such a tinctorial power that one part of chromium per million of solution may be easily recognized.

In 1906, Brandt[4] described a method for the analysis of iron based on the oxidation of ferrous to ferric iron by means of dichromate, using diphenylcarbazide as an inside indicator. Later, in 1913, Barnebey & Wilson[5] examined Brandt's method and were not able to obtain concordant results through its use in the analysis of iron. This they found to be due to

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[3] *Bull. Soc. Chem., 3rd Ser.*, pp. 592, 701, 769 (1900).

[4] *Z. Anal. Chem.*, **45**, 95 (100).

[5] *Jour. Am. Chem. Soc.*, **35**, 156 (1913).

the fact that Brandt seems to have overlooked the fact that diphenylcarbazide consumes dichromate so that the amount of indicator used must be taken into account and a correction made for it. They found that each mole of potassium dichromate was equivalent to 1.5 moles of diphenylcarbazide and advanced the following equation "for the lack of a better one at the present time."

$3C_{13}H_{14}N_4O + 2KCr_2O_7 + 16HCl — 4CrCl_3 + 4KCl + 14H_2O + 4C_{13}H_{10}N_4O$

They believe that side reactions occur, and think the correction for the indicator should be made on a blank rather than through the use of a factor taken from the equation. When correction is made for the dichromate consumed by the indicator they find this a good method for the analysis of ores and other materials for their iron content.

Scott[6] describes a method for detecting and estimating small amounts of chromium by means of diphenylcarbazide.

Procedure.—200 grams of the fat to be analyzed for chromium are burned in a platinum dish. It is not necessary that the dish be large enough to hold the entire charge at once, a dish capable of holdng 40 to 50 cc. will suffice. The portion of the charge placed in the dish is heated over a gas burner until the oil takes fire, when the burner is removed and the oil allowed to burn quietly. As the oil is consumed, fresh portions may be added from time to time until it is all burned. A residue of coke is always left after the fat has burned, which is best reduced to ash by placing the dish in a muffle furnace, as small losses almost invariably take place when the coke is ashed over a free flame, due to draughts blowing some of the ash out of the dish. If a muffle furnace is not available the coke may be ashed over a flame, taking precautions not to lose any of the ash. Losses as great as 10% of the ash may easily occur if great care is not used.

Five grams of a mixture of sodium and potassium carbonates (equimolecular mixture) are placed on the ash in the dish and the mixture heated to fusion, the fusion being prolonged until any Cr_2O_3 which will be present in the ash of a fat containing chromium is converted to chromate. When this conversion is complete, the mixture is allowed to cool, the melt taken up in distilled water, made faintly acid with hydrochloric acid, and the solution made up to known volume in a calibrated flask. For amounts of chromium equivalent to about one part per million of fat a 50 or 100 cc. flask may be used, while for larger amounts 250 or 500 cc. flasks are convenient.

In the meantime a standard solution of dichromate is prepared; one which contains the equivalent of 0.000001 g. of chromium per cc. is a convenient concentration. This solution is made by weighing accurately

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[6] Scott, "Standard Methods of Chemical Analysis," 3rd Edition, Vol. I, p. 163.

any convenient amount of C. P. potassium dichromate, dissolving it and making it up to volume, with water, in a calibrated flask, from which an aliquot part is further diluted with water in a second flask. This process is repeated until a final aliquot has been removed, which, when made up to its proper dilution with water, will be of the required chromium content. Before the final dilution is made, 5 or 10 g. of the mixed sodium and potassium carbonates—depending upon whether the dilution is to be 250 or 500 cc.—dissolved in part of the water to be used, are added to the flask. Enough HCl to make the solution slightly acid to litmus paper is added and the mixture made up to the proper dilution with distilled water.

This solution will contain sodium and potassium chlorides in about the same concentration as those resulting from the solution of the product of the ash fusion. The concentration of the chlorides, however, seems to have no important bearing on the reaction between the dichromate and the diphenylcarbazide or upon the color of the solution obtained from the reaction. For this reason nothing is gained by weighing the carbonates for the fusion or the standard solution more accurately than to the first decimal place.

A solution of diphenylcarbazide is made by dissolving 0.1 or 0.2 g. diphenylcarbazide in 10 cc. of glacial acetic acid and diluting this solution to 100 cc. with 95% alcohol. For this purpose No. 30 denatured alcohol is satisfactory.

Diphenylcarbazide can be made by heating 50 g. of phenylhydrazine and 15 g. of urea in a flask over a flame for 4 hours up to 155°C. or until ammonia is no longer given off and by crystallization from alcohol until the crystals are no darker than straw color. As a very good grade of diphenylcarbazide may be obtained at a reasonable cost from the Organic Chemical Department of the Eastman Kodak Company, nothing is gained by making the diphenylcarbazide.

Known amounts, *e. g.*, 1, 2 and 3 cc. of the standard solution are pipetted into Nessler tubes—graduated pipets are a great convenience in this work—to which are added 5 cc. of 20% HCl and water sufficient to make the total volume of liquid in the tube up to a definite volume. The Nessler tubes used in this work made 40 cc. a convenient volume. One cc. of the diphenylcarbazide solution is now added and the mixture shaken. The liquid in the tube at once takes on a violet color, which, even when the equivalent of only 0.000001 g. of chromium is present in the 41 cc., reaches its maximum intensity in less than 10 minutes. The color varies directly as the amount of dichromate used, a variation of as litttle as 0.5 cc. of the standard solution being easily detected.

It is a simple matter to compare the color of known amounts of the solution obtained from the ash of the fat with known amounts of the standard dichromate solution when they have reacted with diphenylcarbazide.

Experimental.—The method has been tested as follows: A definite amount of a standard potassium dichromate solution was placed in a platinum dish to which alcohol and sulfuric acid sufficient to reduce the dichromate to chromous sulfate were added and the mixture evaporated until fumes of SO_3 were obtained.

Two hundred grams of fat, known to be free from chromium, were then burned in the dish and the coke ashed. The chromium added will now be in the form of Cr_2O_3, as it is in the ash from a fat which contains chromium as a result of being treated with chromic acid, and, due to the temperature to which it has been heated, not very soluble in acids. The ash was then fused with mixed carbonates, put into solution and matched against a standard dichromate solution as above.

The very finest grades of edible fats, even when they have been filtered several times through the purest filter paper, invariably give a trace of ash which contains iron, aluminum and silica, and if the fat has been hydrogenated with a nickel catalyzer, it will, regardless of any method of purification, contain traces of nickel.

To test the effects of nickel in small amounts, the fat used contained about two parts of nickel per million, and to increase the amount of iron, silica, etc., present, in some cases, a few tenths of a milligram of fuller's earth were added with the fat.

The following table gives the results of these tests:

Comparison of the Amount of Chromium Found by Analysis to That Actually Added to Fats

Grams of Chromium Added to Fat	Grams of Chromium Found by Analysis	Parts of Chromium per Million	
		Added	Found
0.0002825	0.000275	1.41	1.38
.00013	.000112	0.56	0.51
.000565	.00055	2.83	2.75
.00036	.00041	2.00	1.80
.00028	.00025	1.40	1.25
.00006	.000058	0.30	0.29

Discussion of Results.—Although the salts of many metals, some of which are sure to be present in the ash of any fat, react with diphenylcarbazide, the chromates appear to be the only ones which give a colored reaction product in an acid solution. If care is taken to have a sufficient excess of free acid present, they either do not react or else give colorless products and even when the salts themselves are colored, for instance iron chloride, the dilution of the solutions used prevents their interfering in matching the colors.

Summary

Fats which have been treated with chromic acid usually contain traces of chromium.

Small amounts of chromium may be detected and estimated by means of diphenylcarbazide.

Small amounts of other metals, especially iron, aluminium, copper and silica which are apt to be found in the ash of fats, do not interfere in this reaction.

THE PROCTER & GAMBLE CO.,
IVORYDALE, OHIO

ACTION OF FATTY ACIDS AND OILS ON A PHOTOGRAPHIC PLATE[1]

BY WALTER F. BAUGHMAN AND GEORGE S. JAMIESON

Photographers know that a developable impression can occur on a photographic plate which never has been exposed to the light. Old plates frequently show black borders after development and markings are sometimes observed on "daylight" films. The printed identification marks on the black paper of these films have been known to register themselves on the negative.

Russell[2] has demonstrated that many substances produce on a photographic plate results very similar to those produced by light. Some of the substances mentioned by Russell are magnesium, cadmium, zinc, nickel, aluminium, lead, bismuth, tin, cobalt, antimony, wood, leaves, seeds, roots, bulbs, petals of flowers, linseed oil, olive oil, terpenes and resins. He found starch, cellulose, gum, sugar, pith, pollen and paraffin oils to be inactive.

These active substances differ widely in character but their action on the plate is apparently the same except for intensity. With some substances a developable impression can be obtained in an hour; with others 18 or 20 hours are necessary. No visible change is produced on the plate before it is developed and the development is the same as for an ordinary photograph. It is not necessary to have the substance in contact with the plate. Russell found that with some substances the action would travel through a distance of 200 mm., although in most of his experiments the plate was within several millimeters of the substance.

The object of the present investigation was to examine the photographic action of fatty oils. The photographic plate was exposed to the oil in a desiccator jar so as to preclude any possible action from fumes that might be in the atmosphere. The jar was placed in a box, which was painted black inside and provided with a tightly fitting lid, so that the dark room in which the box was placed could be entered and left without affecting the experiments. Uncovered petri dishes holding about 35 g.

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[1] Presented before Am. Chem. Soc., Washington Meeting, April, 1924.

[2] Proc. Royal Inst. of Great Britain, **16,** 140 (1899–1901); Proc. Royal Soc. of London, *Biol. Sci.,* **78,** 385 (1906) and **80,** 376 (1908).