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IDENTIFICATION OF ORGANIC DYESTUFFS  
BY X-RAY POWDER DIFFRACTION

*June 1949*

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By

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### FOREWORD

Dyers and dyestuff chemists are considerably interested in improved methods for the identification of organic dyes because of difficulties and inadequacies of the conventional tests. One of the most modern identification techniques makes use of X-ray diffraction patterns. This method has been practiced quite extensively in Germany since 1933, but until this time no information on it has been available outside the I. G. organization where it was used, except for brief summaries of its development in BIOS Report No. 987<sup>(1)</sup> and FIAT Final Report No. 1313.<sup>(2)</sup> The investigations described herein were carried out at the former I. G. Farbenindustrie plant at Ludwigshafen, Rh., where the X-ray technique was used with great effectiveness for the identification of competitive dyes and also for controlling the dyestuff products made there.

1 June 1949

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# IDENTIFICATION OF ORGANIC DYESTUFFS

## BY X-RAY POWDER DIFFRACTION

### I. INTRODUCTION

Though almost all commercial dyestuffs are crystalline in nature, the crystals are often not visible, even through a microscope. It is known that crystalline materials in powder form give characteristic X-ray diffraction patterns made up of lines in certain positions and of varying intensities. From these lines, the spacing values for different planes of the crystal lattice can be calculated by means of the wave lengths of the radiation. Thus the powder pattern or the spacing values of the crystal lattice are a definite characteristic of any dyestuff.

In this country, J. D. Hanawalt, as early as 1936, suggested the general use of powder patterns for the identification of crystalline materials. He and his coworkers<sup>(3,4)</sup> published the first set of diffraction data for 1,000 common chemical substances. They have also presented much valuable information on the procedure to be followed for the classification of the diffraction patterns and the possibilities of the X-ray technique as it is applied mainly for inorganic materials. The wider use of the X-ray diffraction method depends upon the availability of a large collection of such data. When these are known, powder patterns may be employed as an effective method for "fingerprinting" crystalline substances, since each gives its own characteristic diagram. The work involved in collecting X-ray data in a standard form is considerable. Up to the present time a joint American and British committee has published X-ray data on about ~~2500~~<sup>4100</sup> substances in the form of a card index, but very few organic compounds are among them. This collection, which is continually being extended, is published by the American Society for Testing Materials, Philadelphia, Penna.

Several organic dyestuffs have been investigated by the X-ray method for scientific purposes, but nothing has been published on their identification by this means, although some industrial laboratories make use of the technique. In the following pages is described the identification of dyes by the X-ray pattern as it has been practiced in Germany since 1933. Since these methods differed in some respects from those outlined by Hanawalt, the most useful features of both procedures in terms of current demands will also be indicated.

## II. DESCRIPTION OF THE X-RAY METHODS USED FOR ORGANIC DYE STUFFS

Technique. Most of the powder patterns were made with filtered Cu K alpha radiation, while a few organic dyestuffs required the use of Fe K alpha radiation. In place of the normally employed cylindrical camera, special flat cameras were used with which ten to twelve different patterns could be made on the same 9-by-12-cm (3.5 by 4.7 in.) film. However, only the equatorial part of the powder diagram appeared. These cameras were constructed to speed the work and to facilitate comparison of the samples with the standards as no classification system such as that suggested by Hanawalt was used. Copper radiation and flat cameras are more suitable than molybdenum radiation and cylindrical cameras for organic dyes. Time of exposure varied from 10 to 20 minutes. Short exposure is generally preferable to obtain quick results and to increase the efficiency of normal equipment. It is often necessary to rotate the samples during exposure to avoid misinterpretation as a result of preferred orientation.

Specimens. Commercial dyes in the form of a powder can be used as specimens for the X-ray examination in the state in which they are received. Pastes should be dried at room temperature in a desiccator after removal of water-soluble ingredients, and then powdered. Special purification is not necessary as the diffraction patterns are not so sensitive as to be affected by small amounts of impurities. Of course, the elimination of known foreign materials from commercial dyes is preferable prior to X-ray examination. The diffraction lines of crystalline materials, such as inorganic salts, would add to the pattern of the dyestuff, thus complicating its identification. Amorphous materials would obscure the pattern with one or more broad diffraction bands (or halos). A special crystallization is seldom necessary as most dyes are in a well crystallized state. If a characteristic pattern is not obtained due to poor crystallinity there is no objection to transforming the dye into a more easily recognizable form by crystallization, heating, melting and quenching, or sublimation. Only 10 to 20 milligrams of the sample are required. A glass or plastic capillary can be filled with this material or the powder can be transformed into a flat or cylindrical tablet by pressing.

Polymorphism. Attention must be given to the polymorphism of organic dyes in considering their X-ray diffraction patterns. The phenomenon whereby a substance may exist in different solid states which are characterized by different space lattices and physical properties is known as polymorphism. The differences such as density, melting point, crystal lattice, color, hardness, etc., disappear, of course, by dissolving, melting or vaporizing the substance. The polymorphic modification or physical isomers must be regarded as distinctive individual forms in the solid state, although possessing the same chemical structure. The various

modifications can be observed best by powder patterns because the crystal lattice is changed by polymorphism. It was not known that organic dyes existed in different polymorphic forms until they were examined extensively by X-ray. Polymorphism of organic pigments has also been observed recently by electron diffraction and electron microscopy. The results of this work have been published by F. A. Hamm and E. Van Norman.<sup>(5)</sup>

The X-ray patterns of three polymorphic modifications (alpha, beta, and gamma forms) of metal-free phthalocyanine are shown in Figure 1. This blue dyestuff, whose chemical composition is  $C_{32}H_{18}N_8H_2$ , is the only organic dyestuff "fingerprinted" to date in the A.S.T.M. card index. The three strongest lines for the beta form are given as 3.83, 3.45, and 9.64 A.U. The alpha and gamma forms of the dye are used commercially as excellent pigments, the former well known as Heliogen Blue G or as Monastrol Fast Blue G (I.C.I.). Phthalocyanines were investigated by J. M. Robertson<sup>(6)</sup> using single crystals of the beta form. This splendid study completely revealed the structure of phthalocyanines. Single crystals of the beta form are easily obtainable by sublimation or crystallization in various high-boiling organic liquids, such as quinoline, nitrobenzene, or trichlorobenzene. In contrast to the alpha and gamma forms, the beta modification exhibits a high tendency to crystallize. It is mainly for this reason that the beta modification possesses unsatisfactory tinctorial properties and is not used as a commercial pigment.

It is known that the color of various polymorphic forms is sometimes quite different, e.g., the color of carbon as diamond and graphite, or the scarlet tetragonal and the yellow rhombic forms of mercuric iodide. On the other hand, sometimes the color of different forms is the same or very similar, e.g., rhombic and monoclinic sulfur are both yellow; trigonal and rhombic calcium carbonate (calcite and aragonite) are both white.

Among the substances which may change in color as they assume different polymorphic forms are organic dyestuffs. Only those dyes can be used commercially as pigments which remain in the same modification under normal conditions or at least are not seriously affected in color by polymorphic change. If this does occur, the fastness of the dyeing would be affected easily. Polymorphism in organic dyestuffs was first observed in 1933 when it was found that aniline-azo-beta-naphthol, known as Sudan Orange R, existed in four different modifications. These polymorphic forms have no practical significance since this dyestuff is used for the coloring of fats and waxes in the state of a solid solution. Polymorphic forms are more important, however, for pigments, dyes applied in the solid state for coloration of lacquers, plastics, gum, paper, etc. Here the different physical properties of the various forms result in differences in tinctorial qualities.

Comparison by Standard Samples. In Germany, the diffraction pattern of an unknown sample was identified by comparison with standards. A large collection of X-ray patterns of dyestuffs was available there and these were classified on the basis of their chemical characteristics and tinctorial behavior. Finding the correct standards for comparison presented little difficulty, since enough information as to the structural and functional characteristics of the dye was ascertainable. However, many years are required for the collection of a large set of standard samples, and such is available in only a few places. Wider use of the X-ray method is dependent upon the extensive availability of diffraction data of standard dyestuffs and the adoption of a general classification system.

Hanawalt has suggested a classification procedure by determining the spacing values and intensities of the three strongest diffraction lines of the powder pattern. These data make it possible to select easily from a reference book or card index several substances whose three strongest lines have the same spacing values as those of the unknown. The sample can then be completely identified by comparing its entire diffraction pattern with these few standards.

Use of this method for dyes requires that the A.S.T.M. card index file be extended to include organic dyestuffs as a special group. The powder patterns of the frequently used commercial dyes listed in the color index should be catalogued first, after which less common and new dyestuffs should be added. Many of these data are undoubtedly known in different places, but are not available to all who are interested in them. It is beyond question that such a collection would be of benefit not only to X-ray workers, physicists, crystallographers and organic chemists in scientific laboratories, but also to dyestuff manufacturers and dyers (dyestuff users). If international cooperation were obtained, the considerable amount of work required in securing a collection of this kind could be greatly minimized. Since excellent equipment is available at present, which make use of monochromatic X-ray radiation and Geiger counters for registering the intensities of diffraction lines with high accuracy, it should be possible to secure the required data in a relatively short time.

Limitation of the X-ray Technique. In some cases the crystallites of the substance may be too small or the crystal lattice may be distorted resulting in a powder pattern whose lines are either diffused or too few in number to give an exact characteristic. The X-ray method cannot be used under such circumstances. Nor is it applicable for the few amorphous dyestuffs, such as some sulfur dyes, some complex dyes with chromiura, and some mixtures. The crystallinity of commercial dyes in the form in which they are received is sometimes poor, but can be considerably improved by the methods mentioned above.

It is well known that X-ray diffraction is not sensitive for the determination of impurities or of the minor components in a mixture. Quantitative methods for accomplishing the latter have been proposed, and may be successful in special cases for minerals or other inorganic materials.<sup>(7)</sup> However, when the photographic method is used this technique has not much practical value for dyestuffs. Therefore it is necessary, when dealing with mixtures of dyestuffs, to isolate the compounds first and identify them separately by the X-ray pattern in a nearly pure condition.

To evaluate the effectiveness of the X-ray technique for mixtures, two well crystallized dyestuffs of widely different X-ray diagrams were mixed, with known percentages of each component present. It was found that the photographic method was incapable of revealing the presence of the minor component of a mixture unless it represented more than two per cent of the whole, and even in these cases, determinations can be made only in a semiquantitative way. Use of the photometer and other improved techniques may increase considerably both the sensitivity and accuracy of this method, but in most cases will not be of practical value for dyestuff mixtures. The components of a mixture are often formed together, and in this process their crystallinity is altered. Comparison of a poorly crystallized specimen with standard samples made from perfectly crystallized components could also yield entirely false values. Fortunately, effective methods are known for the separation of the various dyestuffs in a mixture even when they have similar properties. Insoluble materials may be isolated by fractionated sublimation in high vacuum, and soluble substances by chromatography. For example, even though only one gram of Camacyl Seal Brown G (Campbell and Co.) was available for test, it became evident after a short study using chromatography and the X-ray technique, that this dyestuff is composed of the following four substances:

- 4 - Nitro aniline-azo-p-xylylidine
- 5 - Nitro-2-anisidine-azo-dimethylaniline
- Tetramino-anthraquinone and a small amount of
- Triamino-anthraquinone.

### III. EXAMPLES OF IDENTIFICATION

Sensitivity of Technique. In Figure 2 are shown the powder patterns of seven azo dyes, some of which are used commercially under the name of Sudan Orange and Ceres Orange. One of the components (beta naphthol) is the same in all samples of the series, while the other component is changed only slightly. The fact that small variations in the structure of the molecule can be easily identified by these patterns demonstrates the sensitivity of the X-ray technique in this respect. It will be noted in samples b, c, and d that the different positions of the CH<sub>3</sub> group produce entirely different powder patterns.



The powder pattern of Setacyl Direct Orange SRR Supra (Geigy) is illustrated in Figure 3 as an example of the use of the X-ray technique for dyestuff identification. The certain determination of this commercial dye as either p-nitroaniline-azo-o-toluidine (b) or p-nitroaniline-azo-m-toluidine (c) by the melting point is difficult, since both substances melt at approximately the same temperature. The X-ray patterns show unquestionably that the commercial dye (a) is p-nitroaniline-azo-m-toluidine.

Figure 4 illustrates the identification of Maroon 331 by X-ray diffraction. It had been suspected that this dye probably was made from one of the following compounds: (a) 3-Nitro-4 toluidine-azo-2.3 hydroxynaphthoic acid-m-nitroanilide or (b) 3-Nitro-4 toluidine-azo-2.3 hydroxynaphthoic acid-4-nitrotoluidide. The second compound is the same as the first except for the presence of a CH<sub>3</sub> group. Differentiation between the two products was impossible either by elementary analysis or by dye tests, since their tinctorial properties are very similar. When heated, both compounds decompose without showing a definite melting point, thus eliminating the use of this method. However, when the diffraction pattern of the commercial sample (c) is compared with those of the other two compounds as shown in Figure 4, it becomes immediately evident that Maroon 331 is identical with the first (a) and different from the second (b).

In Figure 5 are shown the powder patterns of seven samples of Indanthrene Brilliant Blue R (a very pure commercial brand of Indanthrone) obtained between 1933 and 1937 at I. G. plant at Ludwigshafen, Rh. Some of the samples were taken from the industrial production of the plant. In spite of the standardization practiced by every dye manufacturing company to avoid any variation, these seven diffraction patterns are considerably different. Only samples a and f are in the beta form, (8) while samples b, c, d, and g contain more or less of the alpha form, and sample e is in the delta form. It may be mentioned that the delta modification has no tinctorial value and that none of the more than 35 standard commercial brands of indanthrone manufactured by I. G. in 1938 was in this form.

Detection of Polymorphism. Various samples of the same organic dye are often not entirely identical because they may exist in different polymorphic forms and give different powder patterns. For X-ray identification it is necessary that both the commercial dye and the standard samples be compared in the same polymorphic form. This may be illustrated by the examination of Caledon Jade Green 3BS (I.C.I.). As shown in Figure 6, the powder pattern of this dye as received does not correspond either with 12, 12' - dimethoxy-dibenzanthrone, 12, 12' - diethoxy-dibenzanthrone, or 12, 12' - dibutoxy-dibenzanthrone. However, after sublimation in high vacuum the four samples are transformed into a comparable state and it

becomes clear from their powder patterns that Caledon Jade Green 3BS is identical with diethoxy-dibenzanthrone.

Since samples must be in the same polymorphic form to permit X-ray comparison, it is recommended that all substances be converted to the same form before beginning the X-ray examination. This conversion may be accomplished by sublimation, melting and quenching of the fused substance, or by redissolving. For dyes soluble in organic liquids the latter is the most convenient and reliable method and is carried out as follows: First, all samples in question should be dissolved to a cold saturated solution in the same liquid. Then a part of this solution should be allowed to evaporate at room temperature. To ensure that the substances thus obtained will be in the same polymorphic form, seed crystals are mutually introduced into the solutions. This method effects no purification of the substance, but it is more reliable than crystallizing from hot saturated solutions (as is normally practiced in organic laboratories) because the samples are thus always obtained in the same modification.

For example, the powder pattern of a competitive sample of Zapon Fast Yellow C2G as received (a) differed from that of the standard sample (b) as shown in Figure 7. A careful chemical investigation showed them to be identical, suggesting that the two specimens existed in different modifications. After redissolving in methylene chloride they changed into a third form [(c) and (d) respectively] which was the same for both. Thus the X-ray technique proved that the competitive sample was indeed identical with Zapon Fast Yellow C2G and also that this dyestuff was capable of assuming three polymorphic forms.

Solution of Special Problems by the X-ray Method. The X-ray method is also very valuable in the field of dyestuff chemistry for the solution of difficult research problems. The investigation of the compounds formed by the action of sodium hydroxide solutions on alizarine illustrates this. It is known that different sodium alizarates are formed by this reaction which have an intense violet or blue color. With one exception, monosodium alizarate, they are not clearly identified by chemical means as they decompose upon washing or purifying and are destroyed even by the moisture or carbon dioxide of the air. They exist only in the presence of sodium hydroxide of a special concentration. As the diffraction pattern is not sufficiently sensitive to reveal foreign substances, it can be used for the investigation of materials that are not entirely free of impurities. The examination of the different nearly pure reaction products obtained by increasing NaOH concentrations revealed that beside monosodium alizarate, three disodium alizarates are formed and also two other complex sodium compounds which produce four sodium hydroxide molecules and one alizarate molecule after hydrolysis. (Figure 8) This information made it possible to determine the conditions of their formation, stability, and solubility in diluted sodium hydroxide.

The X-ray technique has also been used in investigating the dyestuffs on dyed cotton and rayon fibers. The amount of the dye in normal dyeing is too small to be visible in the diffraction pattern of the sample. However, Valko's method<sup>(9)</sup> of strong dyeing makes it possible to obtain viscose and cuprammonium filaments or films which contain 10 to 50 per cent dyestuff and which are suitable for X-ray identification. As a result of his work in this field, Valko divided vat dyes into three different groups with relation to their crystallinity on the dyed cellulose. The crystallization of the dyestuff, which can be readily recognized by the aid of X-ray diffraction patterns, is responsible for the peculiar behavior of many vat dyes. Textile materials dyed with Indanthrene Brilliant Scarlet RK, for example, change from orange to scarlet by soaping or even by rinsing. In Figure 9 is shown a series of diffraction patterns of cuprophane film which was colored by this vat dye. In the diffraction pattern of the dyed material (b) no lines are visible except those of the hydrate cellulose as in the undyed film (a), indicating that the dyestuff is present in an amorphous state. After rinsing (c) and even more so after soaping (d) the strongest diffraction lines of the dyestuff (e) appear as a proof of crystallization, explaining the reason for the color change from orange to scarlet. Similarly, it has been found that Caledon Ming Blue BX (I.C.I.) crystallizes on rayon and not on cotton, thus explaining why it dyes rayon fabrics violet and cotton fabrics blue. This process is analogous to the well known recrystallization of metals by heating and was first observed on dyed fibers by the microscopic studies of the famous Swiss colorist, R. Haller, who called it "physical condensation."<sup>(10,11)</sup>

#### IV. OTHER METHODS OF IDENTIFICATION

Dye Tests and Chemical Investigations. The identification of organic dyes is usually attempted by colorimetric tests and by determination of the chemical composition. Use of physical methods of investigation such as spectrophotometry is increasing, but not at a rate commensurate with their value. The dyeing methods are empirical in nature and are necessary to determine the tinctorial properties and the technical value of the dyestuffs. Such tests can be conducted conveniently and they reveal the character of the dye in a short time. Chemical examination is more time consuming. First, the commercial sample must be purified, its solubility must be examined and its melting point determined, and then an elementary analysis of the dyestuff must be made. The reaction of the dye to heat and its behavior in the presence of acids, bases, oxidative and reductive agents, etc., must be examined. An experienced dyestuff chemist can find out in a relatively short time what compound is in question, provided it is a common dyestuff. In most cases it is advisable to include an X-ray examination for confirmation of the result by an entirely different technique. Identification by chemical means is much more difficult when dealing with uncommon dyes, new substances of complicated structure, or mixtures

of several dyestuffs. In such cases a long investigation is required, including finally a synthesis of the dyestuff in question. Even then it may not be successful, especially when only a small sample of the unknown dye is available. Under such circumstances the X-ray technique is of outstanding value in facilitating examination of the dyestuff. The various substances obtained during the detailed chemical examination (provided they are crystallized) can be identified by X-ray pattern very easily, thus saving considerable time by eliminating the necessity for their individual chemical investigation. This is possible because the X-ray technique is applicable for organic compounds regardless of their color, such as basic materials of dyestuffs, intermediates, or products of decomposition. Sometimes it is preferable as the first step in the identification procedure to compare the X-ray pattern of the unknown dye with those of several others of known chemical composition which are suspected to be identical with the sample in question. However, it is only in rare cases that colorimetric and chemical tests can be omitted entirely.

Heated Specimen Microscopy. In addition to the X-ray technique, mention should also be made of another method of identification of organic materials, namely, microscopic examination of heated specimens. This latter technique, practiced in recent years by Drs. A. and L. Kofler,<sup>(12)</sup> makes it possible to observe at the same time the melting point, sublimation, crystalline form, color, optical properties, polymorphism, formation of mixed crystals and other characteristics of organic substances. This examination can be done quickly and with a very small amount of the material. Obviously the results obtained characterize a substance very well. This technique is capable of revealing any structural change and small percentages of minor components, and if corresponding data on known dyestuffs were available, would provide an excellent "fingerprinting" method. In spite of its usefulness, this method has not been applied to dyestuffs. The method is mentioned here from the standpoint of the development of reliable and sensitive methods for identifying complicated organic compounds in a short time using small specimens. Like the X-ray technique, heated specimen microscopy may have its limitations and disadvantages as a method of solving this problem, but both are beyond any question of outstanding value. Their extensive use is dependent, however, upon the availability of a large collection of comparative data.

## V. SUMMARY

The X-ray technique for the identification of organic dyes has been used effectively in Germany since 1933 in conjunction with conventional chemical investigations and dye tests. It is a very simple method of identification and is capable of a high degree of sensitivity. The extensive application of this technique is dependent upon the collection, classification, and publication of diffraction data on organic dyestuffs for use as standards of comparison. Identification by X-ray is particularly valu-

able when only small samples are available for examination, when dealing with products which do not show a definite melting point, when the unknown substance melts at approximately the same temperature as other dyestuffs with which it may be identical, and when the determination of the mixed melting point fails to give a conclusive result.

#### ACKNOWLEDGMENTS

The development of the identification of dyestuffs by X-ray diffraction patterns is partly due to the interest shown in this technique by Drs. A. Kirsch and H. Krzikalla. Dr. Kirsch was charged with the responsibility of identifying complicated competitive dyes of commercial value and frequently had difficulties in doing so by the conventional methods. The author is indebted to him for many helpful discussions on the subject. The outstanding interest in this work of the late Dr. Arthur Lüttringhaus and Dr. M. A. Kunz, former chiefs of the main laboratory of the I. G. plant at Ludwigshafen, Rh., must also be gratefully acknowledged. The help of Mr. Norman E. Roberts, Information and Editorial Specialist, Textile and Leather Products Section, Office of The Quartermaster General, in the writing of this paper is appreciated greatly by the author.

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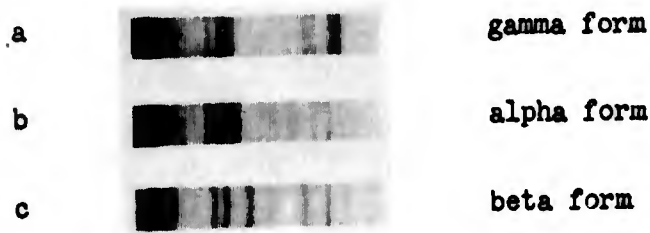


Figure 1

Polymorphic forms of metal-free phthalocyanine

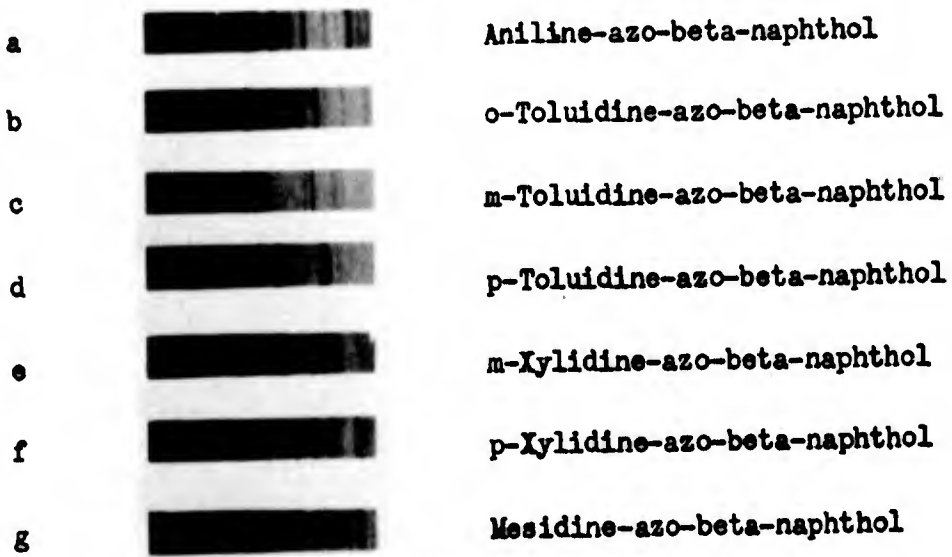


Figure 2

A series of azo dyes



Figure 3

Identification of Setacyl Direct Orange SRR Supra (Geigy)

- a. Setacyl Direct Orange SRR Supra (Geigy) melting point 135 C.
- b. p-Nitraniline-azo-o-toluidide melting point 136 C.
- c. p-Nitraniline-azo-m-toluidide melting point 135 C.



Figure 4

Identification of Maroon 331

- a. 3-Nitro-4 toluidine-azo-2,3 hydroxy-naphthoic acid-m-nitranilide
- b. 3-Nitro-4 toluidine-azo-2,3 hydroxy-naphthoic acid-4-nitro-toluidide
- c. Maroon 331



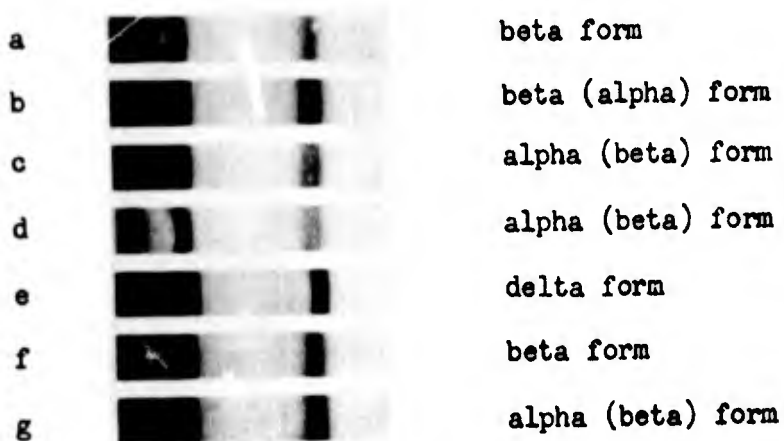


Figure 5

Samples of Indanthrene Brilliant Blue R (I.G.)

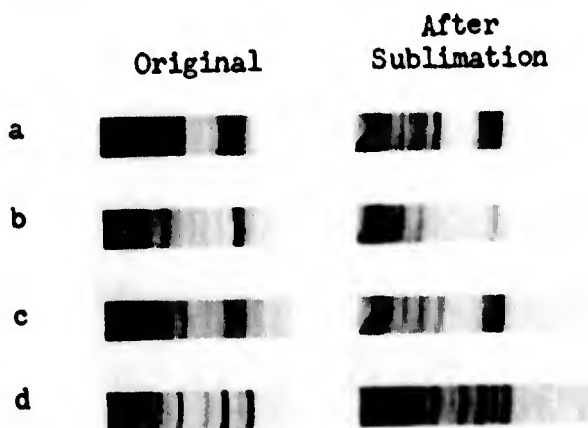


Figure 6

Identification of Caledon Jade Green 3 BS (I.C.I.)

- a. Caledon Jade Green 3 BS (I.C.I.)
- b. 12,12'-Dimethoxy-dibenzanthrone
- c. 12,12'-Diethoxy-dibenzanthrone
- d. 12,12'-Dibutoxy-dibenzanthrone

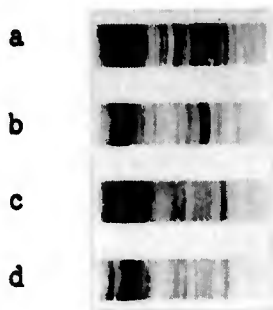


Figure 7

Identification of a competitive sample of Zapon Fast Yellow C2G (I.G.)

- a. Original competitive sample
- b. Original standard sample
- c. Competitive sample redissolved in methylene chloride
- d. Standard sample redissolved in methylene chloride

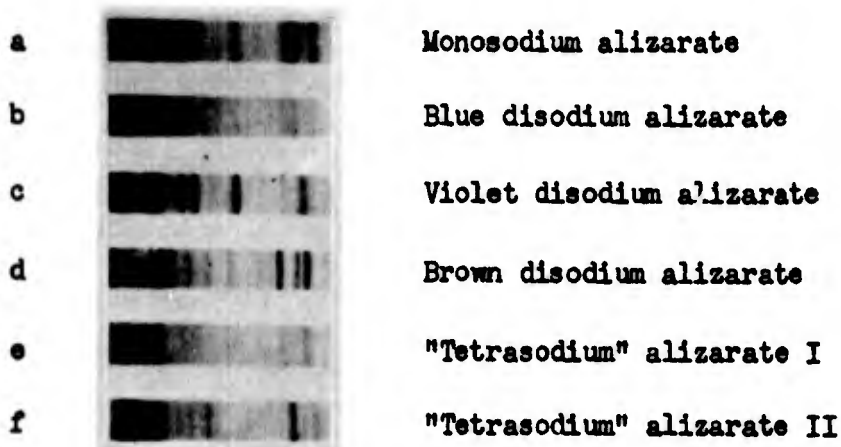


Figure 8

Sodium alizarates obtained by the action of increasing concentrations of NaOH on alizarine

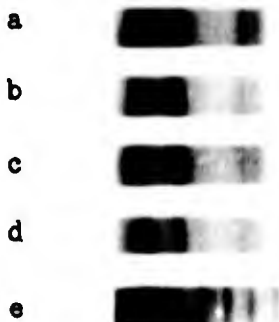


Figure 9

Recrystallization of Indanthrene Brilliant Scarlet RK (I.G.)  
dyed on cuprophane film

a. Cuprophane film undyed.

The equatorial diffraction lines  $A_0$  (101),  $A_3$  (101), and  $A_4$  (002) of hydrate cellulose are visible.

b. Cuprophane film dyed with 14.4 per cent Indanthrene Scarlet RK after oxidation.

Only the diffraction lines of the hydrate cellulose are visible. Dyestuff is in amorphous state. Color: orange.

c. Same as (b) after 24 hours' rinsing.

Besides diffraction lines of the hydrate cellulose, the strongest lines of the dye begin to be visible. Color: scarlet.

d. Same as (b) after soaping one hour at 100 C.

Same pattern as (c), but more clearly visible. Color: scarlet.

e. Commercial sample of Indanthrene Brilliant Scarlet RK in powder form.