PURIFICATION OF ORGANIC DYES, PARTICULARLY OF THE ANTHRAQUINONE SERIES

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INTRODUCTION

In any scientific investigation it is desirable to start with pure materials in order to ensure reproducibility of results. Unfortunately, many studies involving dyes have been carried out with materials of questionable purity, but although the importance of this point is becoming more appreciated, there are still cases where dyes have been insufficiently purified. A true understanding of the fundamental processes occurring in systems in which dyes are used can only be obtained by a study of the properties of pure dyes.

Many workers have started with samples of commercial dyes and purified them by conventional means. In commercial dyes three types of impurities may be present, *viz.*:

(1) Diluents, such as sodium chloride or soluble starch, which have been added to bring the dye to a standard tinctorial strength for convenience in use. In the case of water-insoluble dyes comparatively large quantities of dispersing agents may also be present.

(2) Substances, other than the required dye, which have been formed during manufacture. These may arise from the use of impure intermediates, side-reactions, incomplete reaction, or may be isomers of the main dye component.

(3) Dyes of different constitution and colour added for shading.

The advantage of chemical synthesis of the dye over the use of the commercial dye is that only type (2) impurities will be present, together with small amounts of electrolytes obtained during neutralisation. However, with water-insoluble dyes the removal of electrolytes is a relatively simple matter, as it is merely necessary to extract the inorganic material with water or to extract the dye with a suitable organic solvent.

The conventional method of removing organic impurities is fractional recrystallisation, utilising differences in the solubilities of the dye and its impurities. Disperse azo and anthraquinone dyes can readily be obtained in a crystalline form from a variety of solvents, while the vat dyes, particularly those of the substituted indigo type, can also be obtained crystalline. The anthraquinone vat dyes present more difficulty owing to their greater insolubility, but many can be crystallised from high-boiling solvents, such as pyridine and nitrobenzene. Some of the disperse,

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indigoid and anthraquinonoid dyes are sufficiently volatile to be sublimed *in vacuo* without decomposition. If the impurities present differ considerably in molecular weight from the main component, they can sometimes be separated by distillation in a simple molecular still, although the efficiency of the method is poor.

In order to decide when the process of purification has been carried far enough, it is necessary to have some method for estimating the purity of the sample, either by estimating the concentration of pure dye in the sample or the concentration of impurities still present. The various methods which are available have been reviewed by TROTMAN AND FREARSON[1], but unfortunately there is no completely satisfactory method of wide application. Tests of purity based on gravimetric and volumetric analysis are rather tedious and the most commonly employed are those based on colorimetric and melting point data. According to many workers[2,3] it is merely necessary to observe the increase in the optical density of a standard solution of the dye, or the melting point of the solid dye, with successive treatments and to continue until these characteristics remain constant on further treatment. Optical methods are purely relative, however, and an absolute estimate of purity can only be obtained by chemical analysis. The purity of a sample of dye of known constitution can be estimated by gravimetric analysis for elements such as sulphur and nitrogen in the usual way. With large dye molecules, the accuracy and reproducibility of this method is not sufficiently high to distinguish between similar molecules and so it is unlikely to reveal small quantities of impurities. Estimation of the purity of water-insoluble dyes has received very little attention, although it is possible to estimate azo disperse dyes by reduction with titanous chloride in the presence of a suitable water-miscible solvent.

In this study of the purification of anthraquinone dyes it has been found that small quantities of impurities may still remain in such substances even though they have been purified to constant melting point and absorption spectrum. Contrary to general belief the removal of the small quantities of these final impurities does not seem to have a significant effect on these physical properties in many cases. Large-scale adsorption chromatography on activated alumina often appears to be the most suitable method for the final purification of anthraquinone compounds, and it seems that impurities can be detected by this procedure which are not apparent using other methods, *e.g.* paper chromatography. The reason for this seems to be that the detection of impurities in a substance by paper chromatography is limited by the small size of the sample employed, and the method is usually incapable of detecting amounts of impurities of less than 2.5 %. The method to be discussed here appears to be capable of detecting impurities in concentrations as low as one part per million, but on the other hand does require a large sample. This is not a disadvantage if the procedure forms part of the purification process of the substance in bulk.

ADSORPTION PROPERTIES OF AMINOANTHRAQUINONE COMPOUNDS

Little has been published on the chromatography of aminoanthraquinone compounds. Many authors have simple stated that the aminoanthraquinone dyes used in their work were found to be chromatographically homogeneous without giving details of the adsorbent/solvent/eluent system. Where the system has been described, in most cases paper chromatography has been used. A basic study of the chromato-

graphy of aminoanthraquinone compounds bringing out the relation between chemical constitution and adsorption affinity has been made by RAO *et al.*[4]. The strength of adsorption depends on the nature and number of substituents and their position. CROPPER[5] attempted to separate a mixture of commercial 1- and 2-aminoanthraquinones by dissolving in a toluene–pyridine mixture and passing down a column of alkaline alumina to which 5 % of water had been added. On development with the same solvent, the 1-isomer washed through completely, while the 2-isomer was retained. At the top of the column he observed two violet zones which he suggested were due to the presence of 1,2- and 1,4-diaminoanthraquinones in technical 1-aminoanthraquinone. An interesting paper on this subject is that by BANSHO and his coworkers[6], who subjected a number of aminoanthraquinone compounds to both adsorption and paper chromatography. Using various adsorbent/solvent/eluent systems according to which system best suited each particular compound, they found up to five components in their samples, the impurities being identified by paper chromatography. These Japanese workers found that even samples recrystallised several times from an appropriate solvent showed considerable heterogeneity. In many cases they observed an increase in melting point after chromatographic treatment, but seem to have neglected to test the purity of their products by re-chromatography.

GENERAL PURIFICATION OF AMINOANTHRAQUINONE COMPOUNDS

The initial purification of these compounds was executed by the conventional technique of recrystallisation from one or more appropriate solvents. In several cases, even after the sample had been repeatedly recrystallised from ethanol, extraction with carbon tetrachloride in a Soxhlet extraction apparatus left an impurity in the thimble. The progress of the purification was monitored at each stage by measurements of melting point and of ultraviolet and visible absorption spectra.

Recrystallisations were carried out in a 2 l Soxhlet extraction apparatus containing 1.5 l of solvent. The compounds were extracted for 7 h during the day, then filtered hot, and allowed to crystallise out overnight. Depending on the solubility of the compound in the solvent being used, the total extraction time was anything up to 130 h.

Further purification of the aminoanthraquinone compounds was effected by adsorption chromatography from non-polar solvents on alkaline activated alumina (type H, 100/200 s mesh, Peter Spence & Sons Ltd.). This adsorbent was found to be the most effective for the bulk purification of those compounds. The substance was extracted in a 2 l Soxhlet apparatus with a non-polar solvent (*e.g.* carbon tetrachloride) and the cold solution filtered and passed down an adsorption column (4 cm diameter), using an all-glass apparatus. The column was then developed with the pure solvent, and the mobile band collected by eluting with a suitable eluent. Development was sometimes improved by adding a quantity of the eluent to the pure solvent. The solution containing the main band was then concentrated and allowed to crystallise, or in cases where crystallisation was difficult, evaporated to dryness under reduced pressure on a water bath. After chromatography each compound was recrystallised at least twice from spectroscopic grade ethanol, and the final crystals re-tested for homogeneity on small test columns of various adsorbents from non-polar solvents.

The procedure can be illustrated by the preparation and purification of 1,5-

dianilinoanthraquinone. This substance was prepared by heating a large excess of aniline (15 moles) with 1,5-dichloroanthraquinone (1 mole), using copper acetate as catalyst. The large excess of amine was used because this intermediate is much easier to remove from the product than unreacted dichloroanthraquinone or amino-hydroxy side products. After removal of copper and excess amine, a crude product was obtained with a melting point of 240°, and on recrystallisation from ethanol the melting point rose to 245.5°. The latter sample was then extracted with carbon tetrachloride and the cold filtered solution passed down an adsorption column of alkaline alumina. The column was developed with a mixture of equal volumes of acetone and carbon tetrachloride with the production of the bands (reading from the top of the column) shown in Table I.

TABLE I

CHROMATOGRAPHIC BANDS OF A SAMPLE OF 1,5-DIANILINOANTHRAQUINONE

Band	*Depth*	*Mobility*
Red	3 mm	Immobile
Purple	3 mm	Immobile
Purple	1 cm	Immobile
Dark red	1.5 cm	Immobile
Red	10 cm	Mobile

The mobile red band is the pure 1,5-dianilinoanthraquinone, while the dark red band is due to a product of low melting point, which is probably 1-anilino-5-hydroxyanthraquinone.

After elution of the main red band, the solution was concentrated and allowed to crystallise, giving a product with melting point 246.5°. The chromatographed product was recrystallised twice from ethanol giving a product with a final melting point of 247°. Measurements of the absorption spectra of (a) the crude product (m.p. 240°) and (b) the chromatographed product after two recrystallisations (m.p. 247°), showed that there were no significant changes in the absorption spectrum as a result of the purification. The final crystals were satisfactorily re-tested for homogeneity on small test columns of various adsorbents from nonpolar solvents.

The results obtained in the purification of a number of aminoanthraquinone derivatives are summarised in Table II. In general the later stages of chromatographic purification did not lead to changes in either the melting point of the solid or the absorption spectrum of a solution in a suitable solvent which were significant in relation to experimental error. It would appear that the concept of purification to constant melting point and constant absorption spectrum is not valid during the removal of the last traces of impurities in these organic compounds.

Sometimes, the procedure may be complicated by a form of permanent adsorption on the column by the main component. Thus, in the case of 1-benzamidoanthraquinone a sample recrystallised twice from ethanol with melting point 256.5° was dissolved in xylene and the solution adsorbed on alkaline alumina, acetone being used to elute the main band. A small (3 mm) red immobile band at the top of the column and a wide (7.5 cm) deep yellow immobile band were left behind after a pale

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TABLE II

PURIFICATION OF AMINOANTHRAQUINONE COMPOUNDS

Solvent/eluent system was carbon tetrachloride/acetone, except for (a) ethanol/ethanol; (b) carbon tetrachloride/mixture of equal volumes of acetone and carbon tetrachloride; (c) xylene/acetone; (d) benzene/acetone; (e) toluene/acetone.

Anthraquinone derivative	*Melting point (°C)*				*Number of immobile bands on column*	*Description of crystals*
	Original recrystallised product	*After chromatographic purification*	*Sample recrystallised twice after chromatographic purification*	*Literature*		
1-Anilino-	142	143.5	146.5	147.5[7,8]	1	Short red needles
1,4-Dianilino-	218.5	221	221	218[8,9]; 217[7]	2	Blue plates with metallic cast
1,5-Dianilino-	245.5	246.5	247	239[8]	4	Short red needles with green reflex
1,8-Dianilino-	236.5	241	240.5		2	Long red needles with green reflex
1-Piperidino-[a]	120	120	121	118[10]	1	Red plates with reflex
2-Piperidino-[b]	164	164.5	165.5		3	Long dark red crystals
1,5-Dipiperidino-	204	204	205		1	Red diamond plates with reflex
1,8-Dipiperidino-	184	184.5	187		1	Large dark red plates
1-Methylamino-	167	169.5	169.5	170[7,8]	4	Small red crystals
1,4-Bis-(methylamino)-	205	222	224	224[11]	2	Fine violet needles
1-Benzamido-[c]	256.5	257.5	256.5	246[12]; 255[8]	1*	Long yellow needles
1-Amino-[d]	253	253.5	253.5	253.5[8]	4**	Long red needles
1,4-Diamino-[e]	269	268.5	270	268[7,8]	1	Small purple crystals

* In addition, there was a permanently adsorbed band containing material identical with the pure compound.

** Two of these bands were artifacts.

yellow mobile band (4 cm) had been eluted. However, the two yellow bands were found to be of identical composition. The alumina containing the permanently adsorbed yellow band was removed and the compound extracted from it with hot acetone in a Soxhlet apparatus. This method of chromatographic purification increased the melting point of the product to 257.5° but had no effect on its absorption spectrum in ethanol. On recrystallisation twice from ethanol the final crystals had a melting point of 256.5°. Here again, insignificant changes in melting point and absorption spectrum of the substance were observed in the final stages of purification. It is probable that this problem of permanent adsorption can be avoided by deactivation of the alumina using controlled amounts of water[13], since it was absent on less active adsorbents, such as magnesium carbonate.

Artifacts, caused by the decomposition or change of state of the solute, on adsorption columns have been reported from most fields in which adsorption chromatography has been used[14–18]. In order to obtain a true picture from a chromatographic separation, decomposition of the solute and other artifacts of this type must always be kept in mind. To ascertain whether a zone is an artifact or not, the product should be chromatographed free from the impurity or apparent impurity, the solute extracted from the eluent, re-dissolved in the solvent and re-chromatographed on the same adsorbent. If any of the zones, apart from the main zone, reappear to the same order of intensity as before, then this must be regarded as an indication of decomposition, isomerisation, change of ionic state, etc. In the purification of anthraquinone dyes by adsorption chromatography described here it has been observed that primary aminoanthraquinone compounds are more susceptible to this type of decomposition than N-substituted derivatives. This decomposition was not observed by BANSHO *et al.*[6].

NATURE OF IMPURITIES IN ANTHRAQUINONE COMPOUNDS

In the preparation of 1,8-dianilinoanthraquinone impure products are obtained from the reaction of 1,8-dichloroanthraquinone and aniline. The copper catalyst required to give a reasonable rate of amination also increases the rate of deamination, although this can be counteracted by increasing the relative proportion of aniline to chloro derivative. When the chromatographic technique was applied to the separation of the deaminated product from 1,8-dianilinoanthraquinone it was found that a third band was present at the top of the column in addition to the bands of these two components. Subsequent adsorption on magnesium carbonate from ethanol solution of a number of aminoanthraquinone compounds showed that almost all exhibited this immobile band at the top of the column. The fact that on some occasions this immobile band could not be obtained with a particular sample while on other occasions the same sample did reveal the impurity, illustrated that only when a sufficiently large sample was chromatographed could the impurity be detected. In the case of simple aminoanthraquinone compounds the concentration of this impurity was usually quite high, but since it was much lower in the substituted derivatives detection was more difficult.

The compounds chromatographed are grouped in Table III according to the colour of their most strongly adsorbed band, and also as to the effect of water as eluent on this band. Four compounds exhibit no immobile bands and might therefore on this evidence be assumed to be pure. However, this seems to be due to limited solubility of

these compounds in ethanol, since reverse conclusions are drawn when the solvent is changed to carbon tetrachloride in which these compounds are much more soluble. The only derivatives which show blue immobile bands are those having 1,4-substituents, and are themselves blue; and the red derivatives (those having substituents in the 1-, 1,5- and 1,8-positions) are the only ones to give red immobile bands. Purple immobile bands are given by various derivatives, but of these, those which are not eluted by water are all from hydroxy derivatives of anthraquinone.

It seems that the substituents in the molecule of the impurity are in the same positions as they are in the main component. That the immobile bands from the aminoanthraquinone compounds are eluted by water, means that water is more strongly adsorbed by the adsorbent than the impurities. Conversely, the impurities from the hydroxy derivatives are more strongly adsorbed than water. This indicates that the nature of the substituents is probably different in the former impurities to that in the latter. In the alumina/carbon tetrachloride system, hydroxyanthraquinone compounds behave like the impurities in staying at the top of the column, but since their behaviour is different in the magnesium carbonate/ethanol system where the hydroxyanthraquinone compounds move down the column, the impurities cannot be simple hydroxy derivatives.

The impurities present in the substituted aminoanthraquinone compounds do not seem to arise from reaction of the amine with the impurities in the intermediates from which they are prepared. Thus, when 1,8-dianilinoanthraquinone was prepared from a sample of 1,8-dichloroanthraquinone, previously purified by chromatography from carbon tetrachloride on alkaline alumina, and the product was passed down alkaline alumina in carbon tetrachloride and eluted with acetone it showed identical bands to those obtained with a sample prepared from commercial 1,8-dichloroanthraquinone. This indicates that the impurity is being formed during the condensation of the amine with the chloroanthraquinone.

It is known[10] that 1-chloroanthraquinone and 2-methylaminoanthraquinone will condense to form 1,2-dianthraquinoylamine, the methyl group being eliminated as formaldehyde. This reaction is favoured by the use of a high-boiling solvent and the presence of cupric acetate and potassium carbonate. The latter two agents are present in the preparation of substituted aminoanthraquinone compounds, and high temperatures obtain just above the surface of the reaction mixture where overheating occurs at the walls of the vessel. It is therefore possible that the impurity is a di- (or tri-) anthrimide, depending on the particular main component. While it is difficult to see how the piperidino derivatives fit into such a scheme, it is notable that they contain extremely low concentrations of immobile band impurity. Hydroxy derivatives might be thought of as giving a similar molecule with the imino bridge replaced by an oxygen bridge. This may possibly account for the differences in behaviour of the impurities contained in the amino- and hydroxyanthraquinone derivatives. Whatever the nature of these impurities they are not, as CROPPER[5] suggests, other aminoanthraquinone compounds. If he had chromatographed these other amino derivatives on his adsorbent/solvent system he would have found that they travel down the column. Also they are not artifacts produced by decomposition on the column.

BANSHO *et al.*[6] have described in detail the procedure they used to chromatograph a sample of 1-amino-4-hydroxyanthraquinone. The solvent used was a 4:1 (v/v) mixture of benzene and carbon tetrachloride; acetone eluted 1,4-diaminoanthra-

TABLE III

CHROMATOGRAPHY OF ANTHRAQUINONE COMPOUNDS ON THE MAGNESIUM CARBONATE/ETHANOL/ETHANOL SYSTEM

Colour of immobile band	*Anthraquinone derivative*
None	1,4,5-Triamino- 1,8-Dianilino- 1-Methylamino- 1,5-Bis-(methylamino)-
Blue (can be eluted with water)	1,4,5,8-Tetramino- 1,4-Dianilino- 1-Methyl-4-anilino- 1,4-Bis-(methylamino)-
Red (can be eluted with water)	1,5-Diamino- 1,8-Diamino- 1-Anilino- 1,5-Dianilino- 1,8-Dianilino-
Purple (can be eluted with water)	1-Amino- 2-Amino- 1,4-Diamino- 2-Piperidino-
Purple (cannot be eluted with water)	1-Hydroxy- 2-Hydroxy- 1,8-Dihydroxy-

quinone, ethanol the main component, and glacial acetic acid eluted quinizarin. By following his directions exactly, his results for this compound could not be repeated. It was found that only small amounts of a red solution could be eluted by ethanol, and the whole upper part of the column was left a deep violet. All hydroxy derivatives chromatographed from non-polar solvents on alkaline alumina have shown this behaviour, but it may be that the Japanese workers used a different type of alumina.

CHROMATOGRAPHY IN DIFFERENT ADSORBENT/SOLVENT SYSTEMS

The progress of the purification of various aminoanthraquinone derivatives has been followed by chromatography on several adsorbents and in various solvents. Apart from the differences in behaviour of the immobile bands as the adsorbent/solvent system is changed, differences are also shown by the mobile bands. The most noticeable of these is the change in colour which often occurs when either the adsorbent or solvent is changed. In addition the adsorption sequence is sometimes reversed. This was the case with the mixture produced in the preparation of 1,8-dianilinoanthraquinone. The major product, 1,8-dianilinoanthraquinone, gave a purple band on alkaline alumina, while the other product (1-anilino-8-hydroxyanthraquinone) gave a red band, so the two components could be easily distinguished on the column. Only partial separation of these two compounds was achieved on cellulose powder as adsorbent. When using ethanol as solvent the purple band travelled ahead of the red band, but on using petroleum ether as solvent this order was reversed, being the same as for the alkaline alumina/petroleum ether system. Four immobile bands were

obtained on this last column, yet when the eluent was changed to ethanol three of these bands were carried down the column.

Careful selection of the eluent is important, since if it is too powerful incomplete resolution of the different zones is obtained. The same consideration applies to the solvent. The presence of π-electrons in benzene gives it a very slight eluting power, and so it is not such a satisfactory chromatographic solvent as the non-polar petroleum ether and carbon tetrachloride. When 1-anilinoanthraquinone was chromatographed on alkaline alumina from benzene, green and blue immobile bands were obtained. However, carbon tetrachloride separated these completely into yellow and blue bands, the green presumably being a mixture of the yellow and blue.

USE OF CHROMATOGRAPHY AS A TEST FOR HOMOGENEITY

Chromatography is often used for testing the homogeneity of a substance; a substance being homogeneous in the chromatographic sense if it cannot be resolved on any adsorption column. In some cases mixtures possess practically the same adsorption coefficient on a particular column. In this case, the adsorbent/solvent system should be changed, since it is unlikely that the adsorption isotherms of the two substances will change in a strictly similar manner when either the adsorbent or solvent is changed. Many workers have not appreciated this and have tested their dyes on only one adsorbent/solvent system. Several examples of anomalous purity have been found in the present work. Thus many compounds appear to be pure on weak adsorbents, such as cellulose powder, especially from polar solvents. Even alumina may be deceptive if the impurity is insufficiently soluble in the particular solvent chosen. A change of solvent is usually all that is necessary to rectify the situation.

The question of impurity concentration is even more important when paper chromatography is used. The drop of dye solution used on paper chromatograms will only contain about 10^{-7} g of compound, whereas the 25 ml of dye solution used in the present work on test columns contains about 10^{-3} g. Certain samples, *e.g.* 1,5-dipiperidinoanthraquinone, would only reveal the presence of an immobile band when chromatographed on a large column using some 10 g of dye, and even then its presence was only just perceptible. This corresponds to an impurity concentration of about 5 parts per million of the main component. It is estimated that the limit of impurity detection on these large columns is of the order of 1 part per million. Owing to the fact that the impurity on a column is spread over a large surface (the cross-sectional area of the column) before it becomes noticeable as a band of any depth, about $4 \cdot 10^3$ times as much impurity is required on these 4 cm diameter columns as is required on paper chromatograms for detection. This gives a figure of $2.5 \cdot 10^4$ parts per million, or 2.5 %, for the minimum impurity detected by paper chromatography. This is why a sample of 1,8-dianilinoanthraquinone revealed no impurities on paper chromatography, even though it contained at least 2 % of a dark purple impurity as revealed by chromatography on alkaline alumina from benzene.

CONCLUSIONS

A study of the literature reveals a scarcity of chromatographic data in papers concerned with research into dye behaviour; either the dyes used have not been

subjected to chromatographic analysis, or little reference is made to the chromatographic system used. It has been found in the present work that many chromatographic systems will indicate homogeneity in a dye which is impure, and so it is essential that the adsorbent, solvent and eluent be stated. As a method for establishing the identity of a compound, by means of its characteristic R_F value, paper chromatography is excellent. However, the resolution of the method is such that components present in concentrations less than a few per cent, will not be revealed. Paper chromatography cannot therefore be relied upon for proving the homogeneity of a substance.

Column adsorption chromatography has the advantage that very large quantities of material can be chromatographed and hence very minute concentrations of impurity of the order of one part per million can be detected. Care should be exercised in interpreting results from adsorption columns since in certain cases decomposition of the solute may occur. Many workers who have not used chromatography, have relied solely on optical and melting point measurements for their criteria of purity. The present work suggests that removal of the final small quantities of impurities by chromatography has little effect on the melting point, while the resolution of modern spectrophotometers is only of the same order as that of paper chromatography and so does not confer any advantages over the latter in this direction.

SUMMARY

Some of the difficulties involved in the purification of organic dyes are discussed. It is shown that preliminary purification by recrystallisation from a suitable solvent, followed by chromatographic purification on an adsorption column of alkaline alumina, and finally by recrystallisation from ethanol is the most satisfactory method for purifying many anthraquinone dyes. In the final stages of purification there is little significant change in the melting point of the solid dye, or in its absorption spectrum in a suitable solvent. Paper chromatography is not a satisfactory method for detecting dye impurities which are present only in small quantities.

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