Notes

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Some problems in the purification of monoazo disperse dyes by column chromatography on alumina

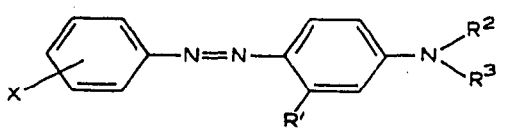
During the course of a series of investigations concerned with the relationships between structure and properties of disperse dyes of all chromophoric types, the necessity of utilising dyestuffs of unquestionable purity arose. The value of correct microanalytical data was found in some cases to be a tenuous property when utilised as the sole criterion of dye purity.

In ranges of dyestuffs of the nitrodiphenylamine[1,2], anilinonitropyridine[3], nitroanilinopyridine[4] and benzothiazolylazo[5] type, the value of mass spectrometry as a control in ascertaining the presence and possible level of impurities of higher molecular weight than the parent dye was found to be particularly useful; in all these cases, the dyes were satisfactorily purified by conventional column chromatography on activated alumina (Type H, 100–200 mesh, Laporte Chemicals) using benzene or benzene–acetone mixtures as solvent and eluent, with, in some cases, small additions of ethanol. The basic principles behind this method of dyestuff purification have been reported recently[6], and some of the problems arising with certain anthraquinone dyestuffs discussed.

We report now some of the difficulties which we observed in the purification of some monoazo disperse dyes and the extent to which chromatographic techniques can be applicable in the context of both purifying and ascertaining the final purity of these dyes.

3-Methyl-4-N-β-cyanoethyl-N-β-hydroxyethylaminoazobenzenes

Diazotisation of a series of mono-substituted anilines and coupling to a range of N-substituted anilines afforded a range of monoazo disperse dyes of general formula I



(I)

The coupling components utilised were of a technical grade nature and contained minor amounts of impurities. Purification of the crude dyes was readily effected in most cases by column chromatography on activated alumina (Laporte Chemicals, Type H, 100–200 mesh). For dyes in which neither of R^2 or R^3 was β-hydroxyethyl, benzene was used as solvent and eluent; with dyes in which one of R^1 or R^2 was β-hydroxyethyl, addition of acetone was found necessary to obtain satisfactory elution

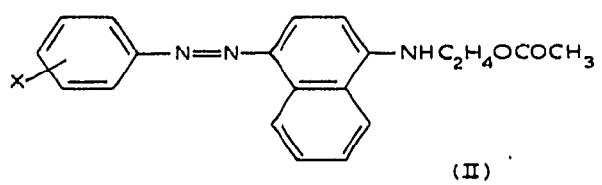
(benzene–acetone (9:1) being particularly useful); with dyes of very high absorptive power, *e.g.* where R^1 and R^2 both were β-hydroxyethyl, some impurities eluted readily with the above solvent mixtures, but the parent dyes required the use of acetone–ethanol (98:2) for satisfactory elution and separation.

In most cases, extraction of the principal zone with ethanol afforded dyestuffs of a high degree of purity, showing one spot only on TLC on Eastman chromagram sheets (Type K 301 R2, silica gel), giving excellent microanalytical data and showing no impurities above P^+ on the mass spectrum. The range of dyes in which R^1 = Me, $R^2 = C_2H_4OH$ and $R^3 = C_2H_4CN$, however, as extracted from an apparently homogeneous zone on alumina, whilst giving satisfactory microanalytical data, showed an impurity at $P \pm 44$ in the mass spectrum. TLC, as above, using ethyl acetate–toluene (1:1) as eluent, confirmed the presence of two components at R_F 0.23 and 0.39. Repeated column chromatography on these dyes on activated alumina as above resulted in no noticeable separation, irrespective of several variations in eluents used.

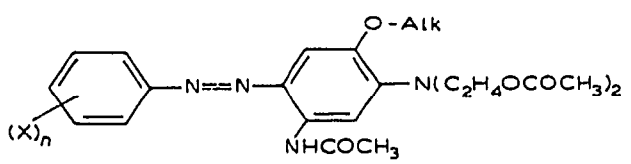
Use of a silica gel column packed with Kieselgel $PF_{254+366}$ (Merck), using ethyl acetate–toluene (1:1) as eluent, resulted in effective separation, permitting isolation in 5–8% amount, and eventual identification of the impurity as I ($R^1 = CH_3$, $R^2 = C_2H_4CN$, $R^3 = C_2H_4OC_2H_4OH$), presumably arising during the preparation of the coupling component in the ethylene oxide condensation stage.

O-Acyl-N-β-hydroxyethylaminoazobenzenes

A range of monoazo dyes of general formula II and III were prepared by acetylation of the corresponding hydroxyethyl derivatives.



(II)



(III)

The course and extent of the acetylation can be readily followed by TLC (Eastman Chromatogram sheets, as above) using ethyl acetate–toluene (1:3) as eluent, the acyl derivatives having considerably higher R_F values. Acetylation was carried out so that only minor traces of unacetylated dyes remained. Attempted purification of the dyes and isolation of the pure acetyl derivatives was, however, found to be impractical using column chromatography on alumina.

In all cases, benzene was used as solvent and eluent; in the early stages of the chromatograph, the acyl derivative appeared to elute down the column as anticipated, for periods of 20–40 min, after which time separation and band movement ceased completely. No further development of the column occurred even on adding initially small, and then increasing, amounts of acetone to the benzene and only on use of an

eluent comprising acetone–ethanol (98:2) was any further band movement noted. The product, isolated by elution or extraction, was found in all cases to be the hydroxyalkyl derivative.

It is apparent that a fairly rapid de-acetylation occurs; it was found possible, using a very short column height, to elute some acetylated dye prior to deacetylation being complete.

Successful purification of the acetyl derivatives was, however, found to be satisfactory on a silica gel packed column (*loc. cit.*).

Conclusions

Whilst the use of activated alumina column chromatography for the purification of many azo disperse dyes is quite satisfactory, care must be taken in regarding the products from apparently homogeneous bands as being pure, even in conjunction with appropriate microanalytical data.

The use of additional TLC control tests, possibly in conjunction with mass spectrometry, is essential if problems such as these described above are to be overlooked. The conclusions reached[6] on the advantages of activated alumina columns for the purification of, *e.g.* anthraquinone dyes, must therefore not be taken to be generally applicable to all classes of dyes. Consideration should equally be given to preparative methods for the dyes involved and possible decomposition patterns to which it might be susceptible.

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