Review Article

Pak J Sci Ind Res 2000 43 (1) 65 -72

ANALYSIS OF PROHIBITED AMINE IN AZO DYES USED IN TEXTILE AND LEATHER GARMENTS

*Shahina Waheed and C M Ashraf**

Applied Chemistry Research Centre, PCSIR Laboratories Complex, Lahore-54600, Pakistan

(Received 12 May 1998; accepted 7 July 1999)

The dyes based on specific 20 arylamines have been used on industrial scale due to their desirable colouring properties. These dyes release these amines under different environmental and physiological conditions and have been established to be potentially carcinogenic in nature. Therefore, trace level determination of these prohibited amines is of great practical importance. The present review embodies details of various methods used for their determination. These methods spell out procedures and techniques for the quantitative determination of these amines under chromatogenic spot test, spectrophotometric method, chromatographic method, potentiometric titration and polarographic estimation. Various reagents and colour reactions are described for spot tests and spectrophotometric determinations. The techniques such as column chromatography, thin layer chromatography, gas chromatography, gas liquid chromatography, high performance liquid chromatography and optical densitometry have also been reported. Various columns and solvent systems are described for the separation of a mixture of amines. The potential and limitations of various methods have also been discussed in the light of our practical experience

Key words: Prohibited arylamine, Diazotization, Coupling and chromatography.

Introduction

The colourants which contain one or more azo groups in their chemical structures are known as azo dyes. As is commonly known almost 65 to 70% of all dyes being used by the textile industry in Pakistan are azo dyes, mainly because of their relative cheapness (as compared to other dyes), general brilliance and fastness in colour. They are used to colour a large number of different substrates, such as synthetic and natural textile fibres, plastic leather, paper, mineral oils, waxes and even foodstuffs and cosmetics

The intermediate chemicals used in the production of azo dyes consist mainly of unsubstituted and substituted aromatic arylamines. These amines have been in use internationally for years together without any restriction on their use for the dye industries. Before 1970 symptoms diagnosed as bladder cancer frequently occurred among workers who handled benzidine in the production of benzidine dyes. It was observed that under good working conditions no benzidine or its primary metabolites were detectable in the urine of the exposed workers. In contrast, such metabolites were detected in the urine of workers in plants where good industrial hygiene was not maintained. Thus, the major dye producers voluntarily decided to cease the manufacture of benzidine and benzidine-based dyes in the early 1970's (Anliker 1977; Boeniger 1980; Meal *et al* 1981; Anliker 1986).

In general, it can be concluded that azo compounds capable of forming a carcinogenic amine on reductive cleavage of the azo bonds are more likely to be carcinogenic. According to Matsui (1981), 1-arylazo-2-naphthol (i) is considered to undergo photochemical transformation to finally afford a peroxy product (v). The latter decomposes to 1, 2-naphtho-quinone (vi) with simultaneous release of peroxyanion (viii) and the diazonium ion (vii) which ultimately gets reduced to an amine (1). This type of photochemical splitting in a different azo dye (2) has also been mentioned by another group of workers (Nobuhiro and Teijiro 1980) in Scheme I (a,b). Thus, after thorough investigation, the German senate commission for testing harmful substances known as MAK (maximum workplace concentration) banned the azo dyes based on the 20 arylamines also listed in Scheme I (a,b).

The commission also recommended that azo dyes should be treated in the same way as the amines on which they are based. The recommendation resulted from the observation that azo dyes can be split under certain physiological conditions to form one of these carcinogenic amine. This aspect was finally considered, on July 1994, in a second amendment to the ordinance on materials and articles prohibiting the use of certain azo dyes in the manufacture of material and articles that are designed for more than temporary contact with the human body. Presently the ban covers those azo colourants that, through the splitting of one or more azo groups, can form one of the 20 carcinogenic amines Scheme I (a,b) (Geisberger 1995).

No one in Europe and America would like to import textile and other goods from any country in the developing world including Pakistan, without certification that the material is

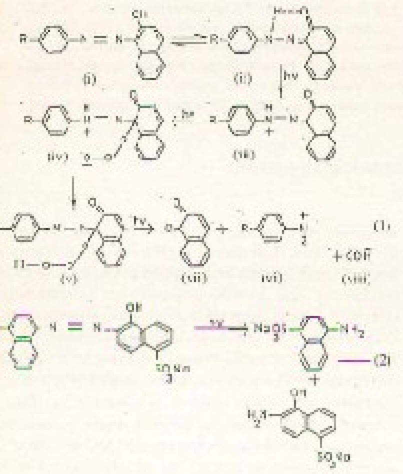
---

*Author for correspondence

a. List of Banned Azo Arylamines

1. p-Aminodiphenyl
2. Benzidine
3. p-Chloro-o-toluidine
4. β-Naphthylamine
5. o-Aminoazotoluene
6. o- Amino-p-nitrotoluene
7. p-Chloroaniline
8. p-Cresidine
9. o, p Diaminoanisole
10. p, p'-Diamino diphenyl methane
11. o-Toluidine
12. 3, 3'-Dichloro Benzidine
13. 3, 3-Dimethyl Benzidine
14. p, p'-Oxydianiline
15. 3,3'-Dimethoxy Benzidine
16. p, p'-Diamino-3,3'-Dimethyl diphenyl methane
17. 2, 4, 5-Trimethyl Aniline
18. p, p'-Thiodianiline
19. o, p-Diaminotoluene
20. p, p'-Methylene-bis-(2-chloroaniline)

b. Demonstration of splitting of azo dyes to free amine



Scheme 1

question does not contain any of these azo dyes. Our textile sector is one of the major foreign exchange earner, and the ban on the export of undesired textile and other products started adversely affecting our export. The manufacturers of these goods, could ill afford the cost of this type of certification from abroad. They started storming PCSIR Laboratories, Lahore for necessary assistance. Under these compelling circumstances the methods for the qualitative and quantitative determination of benzidine and other forbidden amines have been assessed and reviewed.

Materials and Methods

Chromogenic spot test method. The formation of chromatogenic and fluorogenic derivatives of certain aromatic amines as cancer suspect agents has allowed these compounds to be detected at very low levels through chemical spot tests. The investigations of (Weeks Jr 1976) proceeded along two pathways, namely: (a) Chromogenic spot tests readily recognised by the unaided eye, (b) Formation of fluorescent derivatives made visible by irradiation with an ultraviolet light source. In both the cases, simplicity and sensitivity were prerequisite for the sampling and detection methods. To meet these requirements, various chemical reactions were tested with primary amines using: Ehrlich's reagent (Feigl 1966; Yasuda 1975), dimethylaminocinnamaldehyde (Morrison and Boyd 1973), chloranil (Feigl 1966), ethchlorvynol (Frank *et al* 1973), fluorescamine (Udenfriend *et al* 1972, Bohlen *et al* 1973, Tindal *et al* 1974, Sherma and Marzoni 1974), o-phthalaldehyde (Roth 1971, Troll and Rince 1975), and ceric ammonium nitrate (Kamtikar and Joglekar 1979). Among these reactions several sensitive detection methods for the carcinogens of interest have been found and the conditions to achieve detection limits previously not accomplished with these compounds, i.e., nanogram quantities have been reported.

Jones (1973) described the behaviour of each compound with more useful reagents for detection of amines and the reagents/reactions used were:

i) *Diazotization and coupling.* To elaborate this technique, the amino compound was diazotised with pentyl nitrite in acidic medium. The diazotized amine was then coupled with β-naphthol in alkaline medium. Most of the diazotizing mixture worked affectively, but the dye formation was not satisfactory for the amines diazotized with high concentrations of acids. The problem was overcome by increasing the pH of the coupling agent. The colours of the dyes formed are given for mono and diamines (Damschroder and Peterson 1940; Sturgeon *et al* 1975).

ii) *Vanillin.* Chromatograms run on TLC plates were dried and sprayed with freshly prepared 2% solution of Vanillin in n-propanol and heated at 110 °C for 10 min. The condensation product of amine and vanillin (at the aldehyde group) gave green yellow fluorescence under ultraviolet light. The colours produced by this technique were stable, but somewhat difficult to see when only trace amounts were present (Hais and Macek 1963).

iii) *Carbonate and folin-ciocalteu.* Chromatograms were sprayed with 20% aqueous sodium carbonate, air-dried, and sprayed with the folin-ciocalteu reagent diluted to one quarter strength with water. The blue coloured product was obtained due to the reduction of folin-ciocalteu reagent. The phosphotungstic/phosphomolybdic acid in the reagent was very unstable and decomposed quickly reacted with amine to bring about the rapid destruction of the reagent (Folin and Ciocalteu 1927).

iv) *Ferric ferricyanide.* Equal volumes of 0.1m aqueous ferric chloride and 0.1m aqueous potassium ferricyanide were mixed just before use and sprayed directly. Ferric ion gave blue coloured complex. The use of the reaction for the determination of amines was described (Gillio-Tos *et al* 1964).

v) *Dichromate sulphuric acid.* Compounds on the plates were sprayed with a solution of 5% potassium dichromate in 40% sulphuric acid. The oxidized products in the presence of amines gave different coloured products (Beretti 1954).

vi) *Phenol hypochlorite.* The compounds on the plates were sprayed with 2% ethanolic phenol, followed by 0.2% sodium hypochlorite in aqueous sodium hydroxide to produce compounds in mauve to purple colours (Hais and Macek 1958).

vii) *Folin reagent.* The chromatograms were sprayed with freshly prepared solution of 0.02% sodium 1,2-naphthoquinone-4-sulphonate in 5% aqueous sodium carbonate and the chromatograms were heated at 115°C for 5 min. 1,2-naphthoquinone -4- sulphonate reacted in alkaline solution with amine by the removal of hydrogen and a deeply coloured paraquinoid condensation product resulted (Muting 1952; Stahl 1965).

viii) *2,3,5,6-Tetrachlorobenzoquinone.* The spray reagent consisted of 0.2% quinone in monochlorobenzene. The monosubstituted amino quinone was a blue or purple coloured product (Pires and Roseir 1971).

ix) *Phthalaldehyde.* Plates were sprayed with 1% phthalaldehyde in xylene and heated at 110°C for 10 min. The amines reacted with o-phthalaldehyde as fluorogenic reagent to yield fluorescent products which were made visible by irradiation with an ultraviolet light (Turner and Wightman 1968).

Spectrometric determination. Qualitative and quantitative determinations by spectrophotometer are also included so as to detect and make allowance for the presence of other amines such as homologues or analogues of these amines. Everson *et al* (1937) also reported the formation of a yellow colour when sodium hypochlorite reacts with amine in acid solution. On the other hand Pope *et al* (1966) used sodium perchlorate and the stable violet colour developed was measured photometrically at 533nm.

Diazotization and coupling method depends on the diazotization of amines and subsequent formation of a chloroform soluble azo dyestuff by coupling with different coupling agents such as N-(1-naphthyl) N-N-diethylethylenediamine. 2HCl (Tsuji and Kotaki 1964; Chetti *et al* 1968), H-acid (George and Keliher 1984), J-acid (Ramachandra and Gupta 1993) and alpha-naphthol (Maslowska and Swat 1990). The absorption is measured between 570 575nm after 20 45 min for maximum colour development. It was noted that intensity of colour measured was proportional to the amine content in the sample. Ciuhandu *et al* (1977) described a similar method for the determination of aromatic amines down to the μg range by coupling amine with 4-nitrophenyl diazonium ion. The azo dye obtained exhibited characteristic absorption maxima. Beer's law was found to obey up to 100μg level. Similar method was reported by Bupt and Strafford (1956).

Levin *et al* (1967) described a new method for determining small quantities of some primary amines in which highly coloured intermediates form during the reaction with thiotrithiazyl chloride. Rapid colour development was achieved at room temperature over a bed of thiotrithiazyl chloride mixed with dry sand. Similar studies were made by Cohen *et al* (1960) who determined undiluted organic amines with thiotrithiazyl chloride to give highly coloured products.

Rawal and Singh (1975) devised a sensitive method for the determination of aromatic amines by reacting with acetyl chloride and ferric ion to produce a greenish violet coloured complex which was determined colorimetrically, where as Siegfried *et al* (1990) reacted amines with 1,10 -phenanthroline and Fe(III) and the colour developed was measured spectrophotometrically at 515 nm.

Smith and Davis (1984) developed a colour reaction by reacting aromatic amine with chloranil or 2,3,5,6, -tetrachlorobenzoquinone in dioxane/propyl alcohol (1:4) to produce a blue to purple colour. The colour reaction product was identified as a monoaminequinone in which the amine displace one of the chlorine atoms of the chloranil.

Sawicki and Johnson (1966) reported a photometric detection of amines. To the test solution was added 2,5 dimethoxytetrahydrofuran (0.5% in acetic acid) and the colour was developed with dimethylaminobenzaldehyde solution and the absorbance was measured at λ_{max} against the reagent blank. Instead of benzaldehyde, derivative could also be used.

Chromatographic techniques. The mixtures of amines are more difficult to analyse by colour reactions but a semiquantitative estimate can be made following separation with column chromatography (CC), paper chromatography (PC) and thinlayer chromatography (TLC) by comparing the intensities of individual spots with standards.

Dasenko and Pakhomov (1978) reported a method to determine diphenyl amine in the presence of primary aromatic amines by extraction followed by spectrophotometric analysis. The aqueous sample was placed on a column packed with finely dispersed Ph_2O which acted as a solid adsorbent for Ph_2NH. The column was washed with water and the diphenylamine was eluted with decane. The decane eluate was treated with 0.01M $K_2Cr_2O_7$-25% H_2SO_4 reagent and the diphenyl amine was determined in the aqueous phase by measuring the absorbance at 570nm.

Edward and Katarzyna (1979) investigated a stepwise gradient development in tanks for quasicolumn TLC. The isocratic and stepwise elution development were performed with 5% and 50% solutions of methyl ethyl ketone in cyclohexane. The mixture could not be separated by isocratic development but in stepwise elution the components formed separate spots on the chromatogram.

Nakanishi (1968) reported a method in which the fluorescence of dimethylaminobenzaldehyde and its application to separation and determination of some amines by PC were described, whereas Dixon and Groffman (1975) described the chromatographic properties of this aldehyde and cinnamaldehyde derivatives of some amines by TLC. Comparison of the positions and colours of spots in the sample with standards were tabulated. Confirmation of identity by spectrophotometric analysis was made in the range of 350-600nm. Tadeusz and Teresa (1979) also detected the amines on the chromatoplates by colour reaction with dimethylaminobenzaldehyde. The amines were separated by TLC and high pressure column chromatography (HPCC) by using Al_2O_3 as adsorbent and the solutions of polar solvents in a non polar diluent, as the mobile phase.

Logradi (1966) presented a selective detection of aromatic amines by PC by forming red or orange coloured derivatives of these amines with 2,4-dinitrofluorobenzene. The amines were detectable in lower concentration on filter paper impregnated with the reagent. Similarly Obtemperanskaya and Nguyen (1979) used 2,4-dinitrobenzenesulfenyl chloride as the reagent for the determination of amines. The sulfenamides formed were determined photometrically at 640-50 nm after separation from other components by chromatography on Silufol plates. The optimum elution mixture consisted of benzene, ethyl alcohol, dimethyl ketone (1.3.7 respectively).

Thieleman (1978) reported a sensitive detection of substances capable of coupling aromatic amines on Silufol UV 254 films impregnated with 0.02% methanolic solution of 1,1'-diazo-4,4'-disulphostilbene. By UV irradiation the stilbene compound was converted into the azo compound which reacted with the sample to give various brown spots. R_f values of amines obtained by using mixture of benzene and dimethyl ketone (80.20) and benzene and acetone (90.10) were reported. The separation of aromatic amines on TLC plates was improved by impregnating silica gel with picric acid (Ajmal *et al* 1990), Triton-X100 (Bhatia 1990), copper sulphate (Ali *et al* 1991), ammonium cerium (IV) nitrate (Sing and Mishra 1992) and soap (Lepri *et al* 1979). The developing solvents used are cyclohexane-benzene mixtures as eluents (1:5). The method is rapid and useful for separating amines at micrograms as well as milligram levels.

New analytical techniques were reported which were based on the differential migration of coloured derivatives formed by the formed by the reaction of the diazotized amines with different passive components such as J-acid (Kralick and Reifler 1996), diazotized sulfanilic acid (Thielemann 1978) on silica gel G. Several analytical procedures are detailed where the use of TLC and the AMD (automated multipledevelopment) unit developed by EMPA, St Gallen, Switzerland etc. is detailed which employs TLC followed by diazotization of the amines produced and subsequent coupling with N-(1-naphthyl)-ethylene-diammonium chloride and the dyes produced are examined by colour tests and colorimetric analysis (Mefford *et al* 1977).

Gas and high performance liquid chromatography. Different gas chromatographic (GC), Gas liquid chromatographic (GLC) and High performance liquid chromatographic (HPLC) and Gas solid chromatography (GSC) techniques have been used to separate and identify carcinogenic amines.

Methods for the identification of carcinogenic amines by GC were reported by Andersons *et al* (1981), where the identification was made by determining the relative partition coefficients in binary systems of immiscible solvents and by Schulz and Palauschek (1988) who determined the substituted aromatic amines by capillary column GC with flame ionization (FI) or mass spectrometry (MS) detection. On the other hand Eiseman reported the ion exchange packing with high temperature stability for GSC which was prepared with a high temperature stable polymer and characterized in Cu^{++} form using aromatic amine. Silica gel glass beads were coated at 2.2 wt % with poly-2,6-diphenyl-p-phenylene oxide which was then sulfonated and exchanged by using Cu^{+2} (Eiseman 1982) whereas Jenkins *et al* (1981) separated and identified these amines by GLC respectively.

Pashkevich *et al* (1977) studied the sensitivity of an electron capture detector for the separation of aromatic amides of polyfluorocarboxylic acids by GC at 200°C on a glass column packed with 5% XE-50/chromaton-N-AW whereas Sopkova and Singliar (1984) studied the sorptive abilities of tetracyano complexes for the determination of aromatic amines. The thermal stability and sorption properties of transition metal complexes are reported in the latter work.

Svetlova *et al* (1984) investigated the permissible errors for retention indexes in the GC identification of banned amines. The reproducibility of retention indexes obtained on columns (with Apiezon L, Triton-X-305 and PEG-1000 as stationary phases) was investigated within a retention index range 500-1600. Similar investigations were reported by Rosiak and Pereira (1986) for standard organic compounds of environmental interest which were determined by GC/mass spectrometry (MS) using a DB-5 fusedsilica capillary column.

Keller *et al* (1973) reported a procedure utilizing HPLC for the separation and determination of picomole quantities of carcinogenic aromatic amines, whereas Narang *et al* (1982) described a rapid screening of aromatic amines by this technique accomplished on a cyanopropylbonded phase column with UV (254 nm) detection. Similar procedure was followed by Chung and Shang (1995) for trace determination of aromatic amines in dyestuff with online preconcentration with a precolumn followed by HPLC with UV absorption detection. Many others investigators reported complementary TLC, GC and HPLC methods for the qualitative and quantitative deter minations of carcinogenic amines in dyestuffs and dye intermediates. The developing solvent system for the separation of mixture of amine are described. The column and conditions to separate the aromatic amine by GC and HPLC have also been given (Thielemann 1972, Jakovljevic *et al* 1975 Schulze *et al* 1975; Tomaselli *et al* 1995).

Kometiani and Tbilisi (1974) presented a modification of the ultramicro determination of aromatic amines as dansyl derivatives. Two dimentional chromatography in TLC of silica gel was used for microdetermination of dansyl derivatives of amines. The optical density of the spots was measured quantitatively on densitometer.

Potentiometric titrations. Kreshkov *et al* (1964) described potentiometric titration for the determination of banned amines in methyl cyanide with 0.1N $HClO_4$ in an organic solvent e.g. methyl ethyl ketone or mixture of chloroform and benzene, whereas Kalidas (1966) followed a similar procedure with hydrochloric acid in 1, 3 propylene glycol chloroform mixture. Benzidine can also be determined in 1:3 glacial acetic acid chloroform mixture by titration with $HClO_4$ with methyl violet as indicator.

Alerin (1975) described potentiometric titrations where amines were determined by the automatic coupling of their solutions with 0.05 N diazobenzene-4-sulphonic acid followed by measurement of the redox potential at a pH electrode vs glass electrode.

Polarographic estimation. Junar (1994) carried out studies on aromatic amines by polarography. Diazonium salt which was formed by diazotization of primary aromatic amines showed a sensitive polarographic wave at peak potential of 0.53 in NH_3 H_2O-NH_4Cl solution and the aromatic amines was thus determined. The influence of various substituting groups and substituting position on the sensitivity of the polarographic waves were discussed.

Selection of procedure in our laboratories. Different methods described in the preceding pages for determining banned azo amines in various industrial samples have their own merits and demerits depending upon the nature of samples being analysed, type of dyestuffs used and the extent of laboratory facilities available. We have been analysing the prohibited dyes used in textile and leather industries in our laboratories for the last many years to certify the export oriented products. We used most of the methods described which gave satisfactory results. For qualitative analysis we initially use Chromogenic Spot Test for the evaluation of various amines followed by spectrophotometric/chromatographic analysis for their quantitative estimation. For spectrophotometric studies we make use of different reagents which provide coloured products and from them we select those reagents which give sharp and reproducible colours. The coloured products are visually assessed before their quantitative determination is made colorimetrically. Depending upon the nature of the sample, we also resort to different chromatographic techniques for the qualitative as well as quantitative determination of amines.

References

Ajmal M, Ali M, Shahena A 1990 Separation of aromatic amines on thinlayer plates impregnated with picric acid. *J Planar Chromatogr-Mod TLC* **3** (11-12) 511-514.

Alerin E B 1975 Potentiometric end point determination using coupling titrations. Determination of phenols and aromatic amines. *Fresenius' Z Anal Chem* **274** (5) 363-365.

Ali M, Ajmal M, Shahana A 1991 The separation of aromatic amines on copper sulphate impregnated silica gel. *J Planar Chromatogr-Mod TLC* **4** (7-8) 315-322.

Andersons A, Titarenko S V, Shimanskaya S V 1981 Gas liquid chromatography of some amines. XXI Partition-chromatographic method in the analysis of amino compounds. *Latv PSR Zinat Akad Vestis Kim Ser* **6** 672-678.

Anliker R 1977 Colour chemistry and the environment. *Ecotox Environ. Safety* **1** (2) 211-237.

Anliker R 1986 In *Toxic Hazard Assessment of Chemicals*, ed Richard M L (London, Royal Society of Chemistry) **166.**

Bertetti J 1954 Chromatography on paper of aromatic amine. *Ann Chim* (Rome) **44**, 495-499.

Bhatia A 1990 Rapid TLC separation of aromatic amines on surfactant impregnated silica gel plates. *J Indian Chem Soc* **67**, 355-356.

Boeniger M 1980 Carcinogenicity and metabolism of azo dyes especially those derived from benzidine. DHHS (NIOSH) Publication 80-119.

Bohlen P, Stein S, Dairman W, Udenfriend S 1973 Fluorometric assay of proteins in the nanogram range. *Arch Biochem Biophys* **155** (1) 213-220.

Butt R L T. Strafford 1956 Papilloma of the bladder in the chemical industry. Analytical methods for the determination of benzidine and 2-naphthylamine. *J Appl Chem* **6** (12) 525-539.

Ciuhandu G, Beczy O, Oancea G 1977 Photometric determination of several aromatic amines by coupling with the p-nitrophenyl diazonium ion. *Rev Roum Chim* **22** (4) 583-586.

Cohen M E, Kent R A, Mac Diarmid A G, Marcantonio N H 1960 *A new class of inorganic molecules consisting basically of sulphur and nitrogen.* U.S.Dept., Comm., Office Tech Serv PB Rept **161** 883-899.

Damschroder R E, Peterson W D 1940 1,2,3, Benzotriazole. *Org Syntheses* **20** 16-18.

Datsenko E I, Pashomov L G 1973 Determination of diphenylamine in the presence of primary aromatic amines. *Zh Anal Khim* **33** (3) 502-604.

Dixon E J, Croffan D M 1975 The determination of unsulphonated primary aromatic amine in water-soluble food dyes and other food additives. *Analyst* **100** 476-481.

Edward S, Katarzyna C 1979 Stepwise gradient development in sandwich tanks for quasi-column thinlayer chromatography. *J Chromatography* **168** (1) 230-235.

Eiceman G A 1982 Ion-Exchange packing with high temperature stability for gassolid chromatographs. *J Chromatography* **242** (2) 267-274.

Everson O L, Kline J A, Forrest S S 1957 Determination of small quantities of 2-naphthylamine, aniline and o-toluidine in certain food dyes. *J Ind Engg Chem (Anal)* **9** (2) 74-75.

Feig F 1966 Spot Tests in Organic Analysis In: *Detection of Characteristic Functional Groups in Organic Compounds.* 7th ed Elsevier Publishing Company. New York N.Y. p245 and p249.

Folin O, Ciocalteu V 1927 On Tyrosine and Tryptophane determinations in proteins. *J Biol Chem* **73** 627-650.

Frank F, Joerg P N, Paul M R, Carella A 1973 Ethylchlorovinyl reagent for functional groups detection *Anal Chem* **45** (2) 338-390.

Geisberger A 1997 Azo dyes and the law-an open debate. *JSDC* **113** 197-200.

George N, Kelliher P N 1984 Further application of diazotized coupling spectrophotometric technique to the determination of aromatic amines with H-acid and N-(1-naphthyl) ethylene diamines as coupling reagents. *Talanta* **31**(4) 295-297.

Ghetti G, Bartalini E, Armeli G, Pozzoli L 1968 Separation and determination of aromatic amines, benzidine, o-tolidine, dianisidine, dichlorobenzidine, 1-naphthyl amine and 2-naphthylamine. *Lav Um* **20** (6-7) 349-352.

Gillio-Tos M, Previtera S A, Vimercati A 1964 Separation of some aromatic amines by thinlayer chromatography. *J Chromatography* **13** (1-2) 571-572.

Hais I M, Macek K 1958 *Hand Book der Papier Chromatographie Bank I.* Fischer, Jena

Hais I M, Macek K 1963 *Paper Chromatography: A Comprehensive Treatise.* Academic Press New York and London.

Imai K, Bohlen P, Stein S, Udenfriend S 1974 Detection of fluorescamine-labelled amino acids, peptides and other primary amines on thin layer chromatograms. *Arch Biochem biophys* **161** (1) 161-163.

Jakovljevic I M, Zynger J, Bishara R H 1975 Thin layer chromatographic separation and fluorometric determination of 4-aminobiphenyl in 2-aminophenyl. *Anal Chem* **47** (12) 2045-2046.

Jenkins R L, Baird R B, Cappona L C 1981 Determination of benzidine and other aromatic amines in aqueous solutions by gas liquid chromatography. *IARC Sci Publ* **40** 153-157.

Jones G R N 1973 Detection of primary arylamine on thinlayer chromatograms by diazotization and coupling. Comparison of a new reagent with existing methods. *J Chromatography* **77** (2) 357-367.

Janan Li, Changjiang Zhu, Zaofan Zhao 1994 Study on aromatic amines by polarography and its application in food analysis. *Fenxi Ceshi Xuebao* **13** (6) 60-63.

Kalidas Ch 1966 Estimation of benzidine by non-aqueous titration. *Fresenius' Z Anal Chem* 223 261-26

Kametiani A O, Tbilisi P A 1974 Modification of the ultramicrodetermination of amino acids and biogenic amines as dansyl derivatives. *VOP Med Khim* **20** (1) 31-37.

Kamtikar S A, Joglekar V D 1979 Use of ceric ammonium nitrate for detection of aromatic amines and phenolic compounds. *J Anal Toxicol* **3** (6) 265-266.

Keller R, Oke A, Mafford I, Adams R N 1973 Separation of aromatic amine by Chromatographic Technique. *Anal Lett* **6** 465-466.

Kralick P, Reifler F 1996 New method for the testing of textiles for azo dyes. *Melliand Textilber* **77** 140-143.

Kreshkov A P, Bykova L N, Pevzner I D 1964 Quantitative analysis of diamines and their mixtures. USSR **151** 170.

Legradi L 1966 Selective detection of aromatic amines. *Magy Kem Foly* **72** 480-482.

Lepri L, Desideri P G, Heimler D 1979 Soap thinlayer chromatography of sulfonamides and aromatic amines. *J Chromatography* **169** (1) 271-278.

Levin V, Nippoldt B W, Rebertus R L 1967 Spectrophotometric determination of primary aromatic amines with thiotrithiazyl chloride. *Anal Chem* **39** (6) 581-584.

Lu Chung-Shin, Shang-Da H 1995 Trace determination of aromatic amines or phenolic compounds in dyestuffs by HPLC with online preconcentration. *J Chromatography* **696** (6) 201-208.

Maslowska J, Swat B 1990 A method for determination of trace amounts of aromatic amines in dyed cotton textiles. ROCZN. *PZH* **41** (5-6) 285-289.

Matsui M, Kobayashi K, Shibata K, Takase Y 1981 Ozonation of dyes. *JSDC* **97** 210-212.

Meal P F, Cocker J, Wilson H K, Gilmour J M 1981 Search for benzidine and its metabolites in urine of workers weighing benzidine-derived dyes. *Brit J Ind Med* **38** (2) 191-193.

Mefford L, Keller R W, Adams R N, Sternson L A S, Yllo M S 1977 Liquid chromatographic determination of picomole quantities of aromatic amine carcinogens. *Anal Chem* **49** (4) 683-685.

Morrison R T, Boyd R N 1973 *Organic Chemistry*. Allyn and Bacon Boston, Mass p859.

Muting D 1952 Detection of arylamines with reagents. *Naturwissenschaften* **39** 303-306.

Nakanishi Ai 1958 Fluorescence of p-dimethylaminobenzal aromatic amines and its application to the separation and determination of some amines by paper chromatography. *Eisei Kagaku* **14** 198-201.

Narang A S, Choudhury D R, Richard A 1982 Separation of aromatic amines by TLC and HPLC. *J Chromatographic Sci* **20** (5) 235-237.

Nakahira K, Teijiro K 1980 The photofading of 1-arylazo-2-naphthol in solution. *JSDC* **96** 529-534.

Obtemperanskaya S I, Naguen K K 1979 Photometric determination of amines and analysis of their mixtures. *Zh Anal Khim* **34** 2421-2423.

Pashkevich K I, Kravchenko V E, Postovskii I Ya, Kulikova G S, Bil'dinov K N, Dees L E 1977 Study of the sensitivity of an electron-capture detector for aromatic amides of polyfluorocarbonylic acids. *Zh Vses Khim* **22** (7) 225-227.

Pires L M, Roseir A N 1971 Solvent effect in the use of chloranil as a reagent in the identification of aromatic amines on silica gel thin layers. *J Chromatography* **56** (1) 59-67.

Popa G, Jerzan El R, Albert F M 1966 Photometric determination of some aromatic amines. *Rev Roum Chim* **11** (12) 1449-1452.

Ramachandra K N, Gupta V K 1993 New analytical technique for the simultaneous determination of aromatic amines. *Fresenius J Anal Chem* **348** (4) 457-458.

Rawal I P, Singh I P 1975 Sensitive method for spectrophotometric determination of amines. *Anal Chem* **47** (4) 738-741.

Rostac C E, Pereira W E 1986 Kovat and Lee retention indexes determined by gas chromatography-mass spectrometry for organic compounds of environmental interest. *Chromatogr Commun* **9** (6) 328-334.

Roth M 1971 Fluorescence reaction for amino acids. *Anal Chem* **43** (7) 880-882.

Sawicki E, Johnson H 1966 Photometric detection of primary amines. *Chemist-Analyst* **55** 101-103.

Scholz B, Palauschek N 1988 The determination of substituted aromatic amines in water and sediment samples. *Fresenius' Z Anal Chem* **331** (3-4) 282-289.

Schulze J, Charles G, Parkes D 1978 Determination of trace quantities of aromatic amines in dyestuff. *Anal Chem* **50** (1) 171-174.

Sherma J, Marzoni G 1974 Detection and quantitative of aniline by TLC (thinlayer chromatography) using fluorescamine reagent. *Am Lab* **6** (10) 21-28, 30-31.

Siegfried K, Gerhard A, Peter L 1990 Spectrophotometric determination of aromat amines with iron (III)/1, 10-phenanthroline. *Z Chem* **30** (2) 74-75.

Sing D K, Mishra A 1992 Thinlayer chromatography of aromatic amines on silica gel G impregnated with ammonium cerium (IV) nitrate. *J Planar Chromatography TLC* **5** (4) 284-285.

Smith R E, Davis W R 1984 Spectrophotometric determination of amines with p-chloranil. *Anal Chem* **56** (13) 2345-2349.

Sopkova A, Singliar M 1984 The sorptive abilities of tetracyano complexes. *Inclusion Compd* **3** 245-256.

Stahl E 1965 *Thinlayer chromatography*: B. Organic Bases. III Amines. A Laboratory Handbook. Academic press INC, publishers III Fifth Avenue, New York 10003 p301-303.

Sturgeon R, Schulman S, Stephen G 1975 Fluorometric determination of arylamine by coupling with N-(1-naphthyl) ethylenediamine. *Anal Chim Acta* **75** (1) 225-226.

Svetlova N I, Grigor'eva D N, Zhuravleva I L, Golovnya R V 1984 Permissible errors for retention indexes in gas chromatographic identification of amines. *Zh Anal Khim* **39** 1292-1296.

Tadeusz D, Teresa W 1979 Detection of amines by colour reaction. *Chem Anal* **24** 923-933.

Thielemann H 1972 Sensitive detection of substances capable of coupling aromatic amines, phenolic compounds on ready-made UV 254 TLC impregnated with 1, 1'-diazido-4,4'-disulphostilbene. *Fresenius' Z Anal Chem* **252** 286-288.

Thielemann H 1978 Detection limits as well as determination of aromatic amines, amino phenols, amino acids in diazido (4,4')-disulfo (2,2') stilbene impregnated. *Sci Pharm* **46** (4) 318-320.

Thielemann H 1979 Detection limits and semiquantitative determination of some aromatic amines, amino acids and amino phenols in commercial sheets and silica gel layers with the application of different spray reagents. *Sci Pharm* **47** (4) 327-329.

Tomaselli M, Cozzolino A, Calemme L, Stasio A 1993 Determination of benzidine and other aromatic amines in dyes and dyed leather. *Cuoio Pelli Mater Concianti* **69** (6) 253-263.

Troll W, Rinde E 1975 Metabolism of benzidine and benzidine azo dyes. *National Cancer institute Carcinogenesis Programme Third annual collaborative conference.* Orlando, Fla February 2-5

Tsuji A, Kotaki K 1964 Microdetection of primary aromatic by ion exchange resins. *Nippon Kagaku Zasshi* **85** 146-148.

Turner T D, Wightman S L 1968 Detection of arylamines on Thinlayer chromatograms. *J Chromatography* **22** 315.

Udenfriend S, Stein S, Bohlen P, Dairman W 1972 *New Fluorometric Procedure for Assay of Amino Acids, Peptides and Proteins in the Picomole Range in Chemistry and Biology of Peptides.* Ann Arbor Science Publishers, Ann Arbor, Mich, p655.

Weeks Jr R W, Dean B J, Yasuda S K 1976 Detection limits of chemical spot tests toward certain carcinogens on metal, painted and concrete surface. *Anal Chem* **48** 2227-33.

Yasuda S K 1975 Determination of 3,3'-dichloro-4,4'-diaminodiphenylmethane in air *J Chromatography* **104** (1-2) 233-235.