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PRESENT AND FUTURE STATUS OF ORGANIC ANALYTICAL REAGENTS— PART I: GENERAL REMARKS

Prepared for publication by

L. SOMMER[1], G. ACKERMANN[2], D. THORBURN BURNS[3] and S. B. SAVVIN[4]

[1]Dept. of Analytical Chemistry, Masaryk University, 611 37 Brno, Czechoslovakia
[2]Sektion Chemie, Bergakademie Freiberg, 9200 Freiberg, German Democratic Republic
[3]Chemistry Dept., Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland, UK
[4]Vernadskii Inst. of Geochemistry & Analytical Chemistry, Academy of Sciences, Moscow, USSR

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Present and future status of organic analytical reagents—Part I: General remarks

Abstract

The earlier emphasis of organic analytical reagents (OAR) for UV-visible spectrophotometric analysis has now broadened to encompass most modern instrumental methods of analysis. The main factors to be considered in the *a posteriori* examination, investigation by computational methods, nature of coordination selectivity and the *a priori* prognosis of OAR are surveyed. The literature, 1970-1985, has been surveyed to prepare a list of compounds, classified by functional group, regarded as important by usage. Further papers will consider specific aspects and compounds important for individual instrumental techniques such as nuclear magnetic resonance spectroscopy*, atomic absorption spectroscopy and electroanalysis.

INTRODUCTION

Prior to the 1980's, research in the field of organic analytical reagents (OAR) was one of the most active research areas in inorganic analytical chemistry (1-28). The development of OAR was stimulated by research and progress in coordination chemistry and by studies of complex equilibria in solution (27-33). At present the significance of OAR is considered by many as having decreased in favour of instrumental methods, especially for routine, trace and automated analysis. However, OAR remain essential for many current, frequently used, methods such as molecular spectrophotometry in the UV-visible region, luminescence analysis and the liquid-liquid extraction of neutral, anionic and cationic species. In addition, OAR are essential in the application of highly efficient separation procedures such as high performance liquid chromatography, preconcentration of trace elements, a variety of continuous and automated analytical procedures, methods such as AAS, ESR, NMR, NAA and some electroanalytical methods.

A review of this field is considered useful since conflicting or insufficient information about the behaviour and reactivity of particular OAR is frequently reported. Much of the present research with OAR deals with known or modified analogue reagents which are useful or promising for analytical practice. There remains a need to select and optimise conditions for the most sensitive, selective and reliable reagents for particular applications.

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* B.D. Flockhart and D. Thorburn Burns, "Organic Analytical Reagents in Nuclear Magnetic Resonance Spectroscopy", Pure and Applied Chem., Vol 59, 915 (1987).

Earlier studies of OAR's were aimed at long term preparative work and modifications of reagent structures, experimental evaluation of their reactivity, selectivity and properties of the complex species formed with the analyte. More recently modern structural methods together with theoretical and empirical numerical approaches have become important, especially for radiation absorbing reagents and their reaction products. The expected properties can then be interpreted using models of atomic and electronic structure. Such work contributes to a better knowledge and understanding of OAR's so that the selectivity and reactivity of each new OAR may be predicted. The formation of binary, ternary or quaternary complex species may also lead to the establishment of complex equilibria which must be elucidated. In general, the main aim in preparing a new OAR, or in optimising the reactivity of a known reagent, is to increase sensitivity, selectivity or method reliability for an analyte.

EXPERIMENTAL CHARACTERISATION OF OAR: *a posteriori* EXAMINATION

The reactivity of an OAR ligand depends on the nature and steric arrangement of the donor atoms, usually O, N, S, in the ligand (35-43) the number of donor atoms bound to the analyte, the type of outer electronic shell of the analyte ion (41, 42, 44) and the overall structure of the reagent (45). In particular, the nature of chelate ring stabilisation (46, 47) and the basic strength of the ligand (15-17, 35, 36) are important. Much valuable information can be obtained from mixed or non-aqueous solution studies over a broad range of experimental conditions (48-50). The detailed reaction schemes, the stoichiometry, stability and properties of the complexes formed are usually determined by spectrophotometry (48, 51-55) *potentiometry* (49, 50, 56-61) or solvent extraction (62-67) in some cases with computer treatment (48, 53, 68-70), of tabulated or graphical data. Optimum conditions for the use of an OAR in a particular method may be deduced from investigations of distribution diagrams or response surfaces with respect to the various components (48, 68). Analytically useful interactions are usually based on the formation of chelates, ion association complexes, ternary or quaternary complexes with various organic or inorganic ligands (72-90). Complex formation in the presence of surfactants (cationic anionic or non-ionic) has been frequently investigated and is now widely exploited (82-88).

Ternary species of interest may be 'inner sphere complexes' such as $ML_nX_pH_x(OH)_y$ or $M_mL_lH_x(OH)_y$ involving different kinds of bonding between the components or 'outer sphere' ion association complexes such as $[ML_nX_x]^{2-}$ or$[ML_nH_x]^{2-}$. $[qB]^{2+}$. Inner sphere complexes are if particular significance for zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, platinum metals, lanthanides and actinides (78). Complexes with anionic dyes or basic cationic dyes with charged colourless metal or non-metal species are often characterised by ease of extraction as well as considerable spectrophotometric or fluorimetric sensitivity (75-81). The additional ligand in ternary species may also provide masking of interferents or may hinder metal ion or complex

hydrolysis, however the sensitivity of a particular reaction may decrease in comparison with the parent binary species (79).

In addition to the traditional methods of investigation of OAR the significance of NMR and kinetic studies of fast reactions with chromogenic reagents has recently grown in importance. The use of ^{13}C-NMR and ^{1}H-NMR enables distinctions to be made between alternative structures of reagent species and reaction products. It is also possible to obtain information about the rate of exchange and position of tautomeric equilibria of reagents and their dependence on solvent. ^{13}C-NMR spectra show, for example, the quinone/hydrazone structures of some N-heterocyclic azo dyes in solution but that the regular structure occurs in the corresponding metal chelates (89-92). Rapid scanning of absorption spectra of reagents and their reaction products provides information about the forms of the reagent during stepwise complexation or successive coordination of various reagent donor atoms during reaction (90). Relatively little solid state information is available concerning analyte-OAR bonding. The structure, properties and nature of the bonding in the reaction product may be evaluated by diffuse reflectance IR, UV, NMR or ESR spectroscopy or by X-ray diffraction (93).

INVESTIGATION OF OAR BY COMPUTATIONAL METHODS

Quantum chemical calculations and the method of atom-to-atom potential with conformation studies are useful tools to obtain information concerning:-

(a) the structure, conformation and electron distribution in the assumed or modelled reagent molecules and their analyte complexes,

(b) the spectral properties of the reagent and its complexes,

(c) the expected nature of chemical bonding in the reaction products (94, 95).

Semi-empirical quantum chemical procedures (94-106) are normally concerned with π-electron density distribution around the atom of selected donor atom groups or chromophores of the reagent molecule's ground and excited states. The derived data are then considered with respect to various structural features in the main frame of the reagent and the effect of any substituents. Substituents in an OAR molecule influence the behaviour by changing the electron density around the donor atoms of the coordination centre or the analytical functional group. The values of coulombic integrals at selected donor atoms of the reagent may be varied in calculations to simulate the effects of π-donor and π-receptor substituents in various positions relative to the reagent chromophore or the key donor atom group. The maxima of the absorption spectra of the reagent and of its complexes can be predicted from the differences between the ground and the excited state electronic levels of the reagent and of complexes with the analyte. Thus the probable structure of the reagent and the nature of the bonding between the reagent and analyte ion may be elucidated by comparison of experimental and calculated absorption wavelength maxima. Optimal structures for proposed or modelled OARs also result from such comparisons. Electrostatic and covalent

bonding may be distinguished using the electron density maps since the electron density shift in the analyte-OAR complex is proportional to the increased degree of covalent bonding. In addition, various tautomeric forms of the OAR and their acid-base character may be deduced (92-94).

If the optimal OAR in a series of assumed or modelled OAR and analogues could be selected with the aid of quantum chemical calculations it could limit the number of OAR to be synthesised and tested. Such procedures are not yet in common use because of the magnitude of the computations involved, the poor agreement between calculated and experimental data and low correlation between properties of the systems and parameters studied. The calculations are sensitive to the values of input parameters such as molecular geometry, bond lengths, and values of coulombic, resonance and overlap integrals. In addition the calculated absorption maxima for the reagent and its metal complexes must often be compared with experimental spectra obtained under conditions where the true equilibria or stoichiometrics are unknown. These reasons have been advanced for the partial disagreement with the experimental results for 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)resorcinol and their metal chelates (96, 98, 107, 108). In spite of the problems the method has been effective in predicting some suitable reagents (97, 100, 101).

The overall conformation of the OAR molecule is important since this determines the configuration of the analytical reactive centre of the OAR. The method of atom-to-atom potentials permits calculation of energy of interchange between the various conformations, evaluation of freedom of rotations and reagent rigidity and hence the probable geometry of the coordination centre of the reagent for particular analytes (109-112). Results of such calculations are available for the Arsenazo III group and other 2,2'-disubstituted azo dyes (113).

THE PROGNOSIS OF A SUITABLE OAR: *a priori* EXAMINATION

The reliable prediction of an optimal structure for the most suitable reagent for a particular analyte is a challenge, as yet unfulfilled (114). However the following factors are important for prognosis:-

(a) the concept of analytically useful functional groups of donor atoms (7, 36-40),

(b) the hard/soft acid-base concept of Pearson (115-118),

(c) the quantum chemical calculations of the electron density around the atoms of the OAR coordination centre (97, 100-105),

(d) conformational analysis and calculations of atom-to-atom potentials in the region of the OAR coordination centre (109-112, 119).

The most suitable procedure for prognostic purposes would be to deduce mathematically, using suitable algorithms, all possible structures of selected types of reagents which might be analytically useful. This would precede chemical synthesis. At present the theoretical approaches must be followed by experimental verification of the analytical reactivity of the selected or recommended reagents.

THE NATURE OF COORDINATION SELECTIVITY

Careful consideration of the coordination selectivity of an OAR towards metallic or non-metallic ions is the usual precursor to studies aimed at improving analytical selectivity (120-122). Important factors are the particular donor atoms in the reagents' coordination centre, the nature of the donor-receptor interation between the analyte and the OAR and the various geometrical and steric factors influencing the centre of analytical reactivity. In addition, the size and electron configuration of the analyte ion control the ability of the ion for covalent metal ion - reagent bonding involving back coordination or electron transfer between reagent and analyte orbitals (35, 36, 123-126).

Thus the well-known chromogenic reaction of Fe^{II} with 1,10-phenanthroline and its derivatives does not take place if substituents are introduced into positions adjacent to the functional group of the reagent or these positions are blocked by further benzene nuclei. However the reaction with Cu^{I} is not blocked and is thus selective (93, 127).

The introduction of substituents may introduce changes in the basicity and the hydrophobicity of ligands which may affect reactivity and course of reaction. Thus, in contrast to 8-hydroxyquinoline, the lack of reaction of aluminium with 2-methyl-8-hydroxyquinoline in aqueous solution unlike the reactions with Cr^{III}, Fe^{III} or Ga^{III} (90, 128-130) is not, as was thought earlier, due to the small size of Al^{III} being unable to accommodate three ligand molecules but rather to the lowering of the formation constant, the pH must be raised to such a level that the competing reaction, the precipitation of aluminium hydroxide predominates, (130).

A special form of selectivity, known as internal masking, results from the competition between two different reagent donor atom groupings in a single reagent molecule which can bind separately the selected analyte and the interfering species. For example in 1,8,dihydroxy-2-[N,N bis(carboxymethyl)-aminomethyl]naphthalene-3,6-disulphonic acid (131, 132) the 1 and 8-dihydroxy groups are responsible for the chromogenic reaction of Ti^{IV} but several other ions such as Fe^{III}, Al^{III} Zr^{IV} and Th^{IV} are simultaneously bound with the iminodiacetic acid group of the excess reagent forming almost colourless chelates and are thus masked (131). The formation of ternary or quaternary complex species may result in larger differences in stabilities between complexes of different analytes and hence selectivities in comparison to binary species (101).

Complete structural characterisation of reagents is important as lack of such knowledge has, in the past, caused confusion over the mode of action of what were, it now appears, likely to be the same compound. For example the product of the self coupling of diazotised 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (133-135), which forms a selective reagent for the calcium ion, has been named Calcion (133, 135) and Calcichrome (134) with bis azo and cyclic tris azo structures given, respectively. Polarographic studies support the bis-azo structure (136). Detailed nmr and synthetic studies now confirm

the product as mono azo, 2,8,8'-trihydroxy-1,1'-azonaphthalene-3,5,6,6'-tetrasulphonic acid (137).

The cause and nature of analytical reactivity and selectivity has been well established for various OAR groups such as 2,2'-bipyridine, 1,10-phenanthroline and related reagents (127, 138-143), dioximes of aliphatic 1,2-diketones (144-147), reagents containing phenolic hydroxyls (148-151) derivations of 8-hydroxyquinoline (152, 153), 2,2'-disubstituted bis-azo dyes (Arsenazo III) and analogues (154) 2-hydroxy substituted N-heterocyclic azo dyes (155-159), functionalised crown ethers (160) and others (161-164).

ANALYTICALLY IMPORTANT OAR

Because of the large and growing number of available OAR it is important for the practising analyst to have compilations of the most important reagents for specific applications. Some monographs (4-14, 8-23, 165, 166) and special publications (167-169) provide comprehensive collections, most classifying the reagents according to the analyte. From the reagent/reaction chemistry viewpoint it is more logical to classify based on the characteristic functional group of donor atoms in the various reagents since this primarily determines the reactivity of the reagents (11, 14).

The list of important OAR's in Appendix I was drawn up after the evaluation of more than 11,000 publications between 1970 and 1985. The table contains only those compounds which were mentioned 10 or more times in application studies. Coordinating solvents and commonly used extracting agents tri-n-butyl phosphate, tri-n-octylphosphine oxide, bis(2-ethyl-hexyl)hydrogen phosphate etc and certain ion-pair forming reagents were excluded since they are dealt with in detail in specific monographs (167-169).

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APPENDIX I. IMPORTANT ORGANIC ANALYTICAL REAGENT

1. Coordinating Reagents
1.1. Chelating Reagents
1.1.1. O-O-Donating Reagents
1.1.1.1. Enolisable 1,3-Diketones

1. Acetylacetone
2. Thenoyltrifluoracetone; 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione
3. Dibenzoylmethane
4. 4-benzoyl-1,4-dihydro-3-methyl-1-phenylpyrazol-5-one
5. Curcumin (C.I. 75300)

1.1.1.2. o- and peri-Diphenols
1. Pyrocatechol
2. 4-Nitropyrocatechol
3. 3,5-Dinitropyrocatechol
4. Pyrogallol
5. Gallic acid
6. 4,5-Dihydroxybenzene-1,3-disulphonic acid; Pyrocatechol-3,5-disulphonic acid; Tiron
7. 1,8-Dihydroxynaphthalene-3,6-disulphonic acid; Chromotropic acid
8. Haematoxylin (C.I. 75290)

1.1.1.3. Enediols
1. Ascorbic acid
2. Rhodizonic acid; 5,6-Dihydroxycyclohex-5-ene-1,2,3,4-tetrone

1.1.1.4. Phenol Carboxylic Acids
1. Salicylic acid
2. 5-Sulphosalicylic acid

1.1.1.5. 3-Hydroxy-4-pyrones
1. 3-Hydroxy-2-methyl-4-pyrone; Maltol

1.1.1.6 Hydroxyflavones
1. 3-Hydroxyflavone; Flavonol
2. 3,4',5,7-Tetrahydroxyflavone; Kaempferol (C.I. 75600)
3. 2',3,4',5,7-Pentahydroxyflavone; Morin (C.I.75660)
4. 3,3',4',5,7-Pentahydroxyflavone; Quercetin (C.I. 75670)

1.1.1.7. Hydroxyanthraquinones
1. Alizarin Red S (C.I. 58005)
2. Quinizarin -2-sulphonic acid;
   9,10-Dihydro-1,4-dihydroxy-9,10-dioxoanthracene-2-sulphonic acid
3. 1,2,4-Trihydroxyanthraquinone, Purpurin (C.I. 58205)
4. 1,2,5,8-Tetrahydroxyanthraquinone, Quinalizarin (C.I. 58500)
5. 1,5-Diamino-9,10-dihydro-4,8-dihydroxy-9,10-dioxoanthracene-3,7-disulphonic acid (C.I. 75470)
6. Carminic acid (C.I. 75470)
7. 1,1'-Iminodianthraquinone; 1,1'-Dianthrimide

1.1.1.8 Hydroxyxanthenes
1. 3',4',5'.6'-Tetrahydroxyfluorone; 3',4',5',6'-tetrahydroxyspiro [isobensofuran-1(3H),9'-[9H]xanthen]-3-one; Gallein
2. Pyrogallol Red
3. Bromopyrogallol Red
4. 2,6,7-trihydroxy-9-phenylxanthen-3-one; Phenylfluorone
5. 2,4-Dibromophenyl-2,6,7-trihydroxy-9-phenylxanthen-3-one
6. 2-Nitrophenyl-2,6,7-hydroxyxanthen-3-one
7. 2,6,7-trihydroxy-9-(2-hydroxyphenyl)xanthen-3-one; Salicylfluorone
8. 9-(5-Carboxyphenyl)2,6,7,-hydroxyxanthen-3-one
9. 2,4-Disulphophenyl2,6,7,-hydroxyxanthen-3-one

1.1.1.9 Hydroxytriphenylmethane Dyes

1. Triammonium salt of 5-[(3-carboxy-4-hydroxyphenyl)(3-carboxy-4 oxocyclohexa-2,5-dien-1-ylidene)methyl]-2-hydroxybenzoic acid; Aluminon (C.I. 43810)
2. Eriochrome Azurol B (C.I. 43830)
3. Pyrocatechol Violet
4. Bromophenol Blue
5. Bromocresol Green
6. Eriochrome Cyanine R (C.I. 43820)
7. Chrome Azurol S (C.I. 43825)

1.1.1.10 Hydroxylamines

1. N-Nitroso-N-phenylhydroxylamine; Cupferron
2. N-Benzoylhydroxylamine
3. 2-hydroxybenzylhydroxylamine; Salicylhydroxylamine
4. N-Benzoyl-N-phenylhydroxylamine
5. N-2-Nitrobenzoyl-N-2-tolylhydroxylamine
6. N-3-Methoxybenzoyl-N-2-tolylhydroxylamine
7. N-Cinnamoyl-N-phenylhydroxylamine

1.1.1.11 Diantipyrylmethanes

Antipyryl = 2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl

1. Diantipyrylmethane
2. Diantipyrylmethylmethane
3. Diantipyrylpropylmethane
4. Diantipyrylhexylmethane
5. Diantipyrylphenylmethane

1.1.1.12 Crown Ethers

1.1.2. O-N-Donating Reagents

1.1.2.1 o-Substituted Monoazo Dyes

1. 3-Hydroxy-4-(4-sulpho-1-naphthylazo)naphthalene -2,7-disulphonic acid; Azorubin S (C.I. 16185)
2. Methyl Red (C.I. 13020)

1.1.2.2. o-Disubstituted Monoazo Dyes

1. 3-Hydroxy-4-(2-arsonophenylazo)naphthalene-2,7 -disulphonic acid; Thorin; Thoron
2. 2-(1-Arsonophenylazo)-7-(3-sulphophenylazo)- chromotropic acid; Arsenazo I
3. Chlorophosphonazo I

1.1.2.3. o,o'-Dihydroxymonoazo Dyes

1. Lumogallion
2. Magneson IREA; Eriochrome Blue 2 RL
3. 4-(4-Sulpho-1-naphthylazo)resorcinol; SNAR
4. 2-(2-Hydroxy-3-carboxy-5-sulphophenylazo)- chromotropic acid; Chromazol KS
5. 2-(2-Hydroxy-5-chlorophenylazo chromotropic acid; Eriochrome Blue SE (C.I. 16680)
6. 5-Amino-3-(3-chloro-2-hydroxy-5-nitrophenylazo) -4-hydroxynaphthalene-2,7-disulphonic acid; Gallion
7. 8-Hydroxy-7-(2-hydroxy-3,5-dinitrophenylazo) naphthalene-1,6-disulphonic acid; Picramine E
8. 3-Hydroxy-4-(2-hydroxy-1-naphthylazo)naphthalene -1-sulphonic acid; Calcon; Solochrome Dark Blue B (C.I. 15705)
9. 3-Hydroxy-4-(2-hydroxy-1-sulpho-1-naphthylazo) naphthalene-2,7-disulphonic acid; Hydroxynaphthol Blue
10. Eriochrome Black T (C.I. 14645)
11. 4,5-Dihydroxy-3-(8-hydroxy-3,6-disulpho-1-naphthylazo) naphthalene-2,7-disulphonic acid; Beryllon II.
12. 2,8,8'-Trihydroxy-1,1'-azonaphthalene- 3,3',6,6', tetrasulphonic acid; Calcichrome; Calcion

1.1.2.4. o,o'-Substituted Bisazo Dyes

1. 2,7-Bis-(2-hydroxy-5-chloro-3-sulphophenylazo)-chromotropic acid; Sulphochlorophenol S
2. 2,7-Bis-(2-sulphophenylazo)chromotropic acid; Sulphonazo III, Orthanilic S
3. 2,7-Bis-(2-sulpho-4-nitrophenylazo)chromotropic acid; Nitrosulphonazo III; Nitro-orthanilic S
4. 2,7-Bis-(2-sulpho-4-methylphenylazo)chromotropicacid; Dimethylsulphonazo III
5. 2-(2-Arsonophenylazo)-7-(2-carboxyphenylazo)-chromotropic acid; Carboxyarsenazo; Arsenazo K
6. 2,7-Bis-(4-arsonophenylazo)chromotropic acid; Arsenazo III; Palladiazo III
7. Chlorophosphonazo III

1.1.2.5. o-Substituted Heterocyclic Azo Dyes

1. 2-(2-Pyridylazo)-4-methylphenol; PAC
2. 2-(2-Pyridylazo)-5-diethylaminophenol; PAAP
3. 5-(2-Pyridylazo)-2-ethylamino-4-methyl phenol; PAAK
4. 4-(2-Pyridylazo)resorcinol; PAR
5. 4-(5-Chloro-2-pyridylazo)-1,3-diaminobenzene; 5-Cl-PADAB
6. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol; 5-Br-PADAP
7. 2-(3,5-Dibromo-2-pyridylazo)-5-diethylaminophenol; 3,5-DiBr-PADAP
8. 4-Hydroxy-3-(2-pyridylazo)naphthalene-1-sulphonic acid; α-PAN-4S
9. 1-(2-Pyridylazo)-2-naphthol; PAN
10. 7-(4-Sulpho-1-naphthylazo)-8-quinolinole-5-sulphonic acid; SNAZOX
11. 4-(2-Thiazolylazo)resorcinol; TAR
12. 2-(2-Thiazolylazo)-4-methylphenol; TAC
13. 2-(2-Thiazolylazo)-4-methoxyphenol; TAMP
14. 2-(2-Thiazolylazo)-5-dimethylaminophenol; TAM
15. 2-(2-Thiazolylazo)-5-diethylaminophenol; TAAP
16. 1-(2-Thiazolylazo)-2-naphthol; TAN
17. 5-(5-chloro-2-hydroxy-3-sulphophenylazo)rhodanine
18. Eriochrome Red B (C.I. 18760)

1.1.2.6. Miscellaneous Azo Derivatives

1. 2-Phenylazo chromotropic acid; Chromotrope 2R (C.I. 16570)
2. 2-(4-Sulphophenylazo)chromotropic acid; SPADNS
3. 3-(4-Diethylaminophenylazo)-1,4-dimethyl-1,2,4-triazole
4. 4,4'-Bis-(3,4-dihydroxyphenylazo)stilbene-2,2'-disulphonic acid; Stilbazo R.

1.1.2.7. Azo-Azoxy Dyes

1. 2-Hydroxy-2'-(2-hydroxy-1-naphthylazo)-5-methyl azoxybenzene; Azo-azoxy BN

1.1.2.8. Diazoamino Dyes

1. 4-{4-[3-(2-arsono-4-nitrophenyl)triazen-1-yl] phenylazo}benzenesulphonic acid; Sulfarsazene; Plumbon IREA
2. 1-(4-nitro-1-naphthyl)-3-(4-phenylazophenyl)triazene; Cadion 2B
3. Titan Yellow (C.I. 19540)

1.1.2.9. Nitroso and Isonitroso Compounds

1. 1-Nitroso-2-naphthol
2. 3-Hydroxy-4-nitrosonaphthalene-2,7-disulphonic acid; Nitroso R Salt
3. 2-Nitroso-5-dimethylaminophenol; Nitroso-DMAP
4. 4-Heptanone oxime
5. Salicylaldehyde oxime.
6. 2-Hydroxy-1-naphthaldehyde oxime
7. Acetynaphthene-1,2-quinone monoxime
8. Phenanthrene-9,10-quinone monoxime
9. 3',5'-Dichloro-2'-hydroxyacetophenone oxime
10. α-Benzoin oxime; Cupron
11. 2'-Hydroxy-4-methoxy-5'-methylchalcone oxime
12. 2-Pyridyl 2-thienyl ketone oxime
13. Dihydro-2-thioxopyrimidine-4,5,6(1H)-trione 5-oxime; Thiovioluric acid
14. 1-Hydroxy-2-nitroso-naphtho[2,1-b]pyran-3-one

1.1.2.10.1. Colourless Complexans

1. Nitrilotriacetic acid; NTA
2. N-(2-Hydroxeythyl)ethylenediamine-N,N,N-triacetic acid; HEDTA
3. Ethylenediaminetetraacetic acid; EDTA
4. Cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid; DCTA
5. Diethylenetriaminepentaacetic acid; DTPA

1.1.2.10.2. Complexan Dyes

1. Alizarin fluorine Blue
2. Metalphthalein; Phthalein Purpur
3. Thymolphthalexon; Thymolphthaleincomplexon
4. Glycine Cresol Red
5. Glycine Thymol Blue
6. Xylenol Orange
7. Methylxylenol Blue
8. Methylthymol Blue

1.1.2.11. Schiff's Bases

1. 2,2'-Ethanediylidenedinitrilobisphenol; Glyoxal bis-(2-hydroxyanil)

1.1.2.12. Formazans and Derivatives

1. 1,5-Diphenylcarbonohydrazide; sym-Diphenylcarbazide
2. 1,5-Diphenylcarbazone; sym-Diphenylcarbazone
3. 2-[1-(2-Hydrozy-5-sulphophenyl)-3-phenyl-formazan-5-yl] benzoic acid; Zincon

1.1.2.13. 8-Quinolinol and Derivatives

1. 8-Quinolinol; 8-Hydroxyquinoline; Oxine
2. 5,7-Dichloro-8-quinolinol
3. 5,7-Dibromo-8-quinolinol
4. 8-Hydroxyquinoline-5-sulphonic acid
5. 8-Hydroxy-7-iodoquinoline-5-sulphonic acid; Ferron

1.1.2.14. Miscellaneous Reagents

1. Ammonium salt of 5-(hexahydro-2,4,6-trioxo pyrimidin-5-ylimino)pyrimidine-2,4,6(1H,3H,5H)-trione; Murexide

1.1.3. N-N-Donating Reagents

1.1.3.1. Dioximes

1. Biacetyl dioxime; Dimethylglyoxime
2. 1,2-Cyclohexanedione dioxime; Nioxime
3. α-Benzil dioxime; Diphenylglyoxime; Nikelone
4. 2,2'-Furil dioxime; Neonikelone

1.1.3.2. Bipyridines
1. 2,2'-Bipyridyl
2. 1,10-Phenanthroline
3. 4,7-Diphenyl-1,10-phenanthroline; Bathophenanthroline

1.1.3.3. Disubstituted Bipyridines
1. 2,9-Dimethyl-1,10-phenanthroline; Neocuproine
2. 2,2'-Biquinoline; Cuproine
3. Bathocuproine disulphonic acid

1.1.3.4. Triazines
1. 3-(2-Pyridyl)-5,6-bis-(4-sulphophenyl)-1,2,4-triazine; Ferrozine

1.1.3.5. Aryl-1,2-diamines
1. 3,3'-Diaminobenzidine
2. o-Phenylenediamine
3. 2,3-Diaminonaphthalene

1.1.3.6. Hydrazones
1. Pyridine-2-carbaldehyde 2-quinolylhydrazone
2. Oxalic acid bis-(cyclohexalidenehydrazide); Cuprizon

1.1.3.7. Heterocyclic Aldazines
No reagent of analytical importance was reported

1.1.3.8. Porphyrins
1. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphintrisulphonate

1.1.4. S-Donating Reagents

1.1.4.1. Thioureas
1. Thiourea

1.1.4.2. Thiones
1. Thiobenzoylacetone
2. Thiobenzoylmethane
3. Bis-(4-dimethylaminophenyl)methanethione; Thio-Michler's ketone
4. m-(Mercaptoacetamido)phenol

1.1.4.3. Xanthates
1. Ethyl xanthate

1.1.4.4. Thiocarbazones
1. 1,5-Diphenylthiocarbazone; Dithizone
2. 1-Salicylidene-3-thiocarbazone
3. 1,3-Cyclohexanedione dithiosemicarbazone

1.1.4.5. Dithiooxamides
1. Dithiooxamide; Rubeanic acid

1.1.4.6. Monothiols
1. Thioglycolic acid
2. Thiosalicylamide

1.1.4.7. Dithiols
1. Toluene-3,4-dithiol; Dithiol

1.1.4.8. Dithiocarbamates
1. Diethyl dithiocarbamate; Cupral
2. Dibenzyl dithiocarbamate
3. 1-Pyrrolidinecarbodithioic acid, Pyrrolidine dithiocarbamate
4. Morpholine dithiocarbamate
5. Tetraethylthiuram disulphide; Dicupral

1.1.4.9. Heterocyclic Thiols
1. 8-Mercaptoquinoline; Thiooxine
2. 2-Mercaptobenzoxazole
3. 2-Mercaptobenzothiazole
4. 5-Mercapto-3-phenyl-1,3,4-thiadiazole-2(3H)-thione; Bismuthiol II

1.1.4.10. Heterocyclic Thiones
1. 1-Phenyl-2,3-dimethylthiopyrazol-5-one; Thiopyrine
2. 4,4'-methylene bis-(1,5-dimethyl-2-phenyl)pyrazoline-3-thione; Dithiopyrylmethane

1.2 Non-chelating Reagents
1. Pyridine
2. Picoline (1-, 2-, 3-)
3. Diphenylguanidine
4. 1,2-Dihydro-1,5-dimethyl-2-phenylpyrazol-3-one; Antipyrine
5. Tributyl phosphate

2. Non-coordinating Reagents
2.1. Ion-pair Forming Reagents
2.1.1. Aminotriarylmethanes
1. Fuchsin (C.I. 42510
2. Malachite Green (C.I. 42000)
3. Methyl Violet (C.I. 42636)
4. Crystal Violet (C.I. 42555)
5. Brilliant Green (C.I. 42040)
6. Ethyl Violet (C.I. 42600)
7. Victoria Blue 4R (C.I. 42563
8. Victoria Blue B (C.I. 44045)
9. Bis-(4-dimethylaminophenyl)antipyrylmethanol; Chromepyrazole
10. 4-Dimethylaminophenyl-4'-(N-methylbenzylamino)-phenylantipyrylmethanol; Chromepyrazole I
11. Bis-(4-methylbenzylaminophenyl)antipyrylmethanol; Chromepyrazole II

['Antipyryl = 2,3-dihydro-1,5-dimethyl-3-oxo-2-phenyl-1H-pyrazol-4-yl']

2.1.2. Xanthenes
1. Pyronine G (C.I. 45005)
2. Rhodamine B (C.I. 45170)
3. Rhodamine 6G (C.I. 45160)
4. Butylrhodamine B
5. Eosin (C.I. 45380)
6. Erythrosin, Iodoeosin (C.I. 45430)
7. Rose Bengal (C.I. 45440)

2.1.3. Oxazines
1. Capri Blue (C.I. 51015)
2. Gallamine Blue, Modern Violet (C.I. 51045)
3. Solochrom Prune AS, Gallo Blue (C.I. 51040)
4. Meldola Blue (C.I. 51175)
5. Nile Blue A (C.I. 51180)

2.1.4. Acridines
1. Acridine Orange (C.I. 46005)

2.1.5. Thiazines

1. Dimethylthionine, Azure I (C.I. 52005)
2. Trimethylthionine; Azure II (C.I. 52010)
3. Methylene Blue (C.I. 52015)
4. Methylene Green (C.I. 52020)
5. 10-Diethylaminoethyl phenothiazinium chloride; Diethazine hydrochloride
6. 10-(3-Dimethylaminopropyl)phenothiazinium chloride; Promazine
7. 10-(2-Dimethylaminoisopropyl)phenothiazinium chloride; Promethazine
8. 10-(3-Dimethylaminopropyl)-3-chlorophenothiazinium chloride; Chloropromazine, Propaphenine; Megaphen

2.1.6. Diazines

1. Neutral Red (C.I. 50040)
2. Phenosafranine (C.I. 50200)
3. Safranine O or T (C.I. 50240)

2.1.7. Miscellaneous Ion-Pair Forming Reagents

1. Sodium Tetraphenylborate
2. 3,5,6-Triphenyl-2,3,5,6-tetrazabicyclo-[2.1.1.]-hex-1-ene; Nitron
3. Tetraphenylphosphonium bromide
4. Tetraphenylarsonium chloride
5. Triphenyltetrazolium chloride

2.2. Cationic Surfactants

1. Methyltrioctylammonium chloride; Aliquat 336; Capriquat
2. Tri-n-octylammonium chloride; Alamin 336-S
3. Hexadecyltrimethylammonium bromide; Cetrimide
4. Tetradecyldimethylbenzylammonium chloride; Zephiramine
5. Hexadecylpyridinium Bromide
6. 1-Ethoxycarboxylpentadecyltrimethylammonium bromide; Septonex

2.3. Nonionic Surfactants

1. α-[4-(1,1,3,3-tetramethylbutyl)phenyl](ω-hydroxypoly (oxy-1,2-ethanediyl); OP; Triton X-100
2. Tween 80

2.4. Anionic Surfactants

1. Lauryl sulphate

2.5 Redox Reagents

1. Diphenylamine
2. Benzidine
3. 3,3'-Dimethyl-1,1'-binaphthalene-4,4'-diamine; 3,3'-Dimethylnaphthidine
4. Variamine Blue (C.I. 37240)
5. Luminol
6. Cacotheline; Nitrobrucine
7. Ferrocene

2.6. Miscellaneous Reagents

1. 1-Napththylamine
2. Sulphanilic acid
3. Barbituric acid