Dictionary of Analytical Reagents

CHAPMAN & HALL
CHEMICAL DATABASE

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Principal Contributors

R. Łobiński, Z. Marczenko, P. Rhodes

Project Editors

F.M. Macdonald, V.M. Lingard

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Periodic Table of the Elements

IUPAC Notation

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

Previous IUPAC Notation

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0

1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71 See Lantha-nides	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209.98)	85 At (209.99)	86 Rn (222.02)
87 Fr (223.02)	88 Ra (226.03)	89–103 See Acti-nides	104 Unq (261.11)	105 Unp (262.11)	106 Unh (263.12)	107 Uns (262.12)	108 Uno	109 Une	110 Uun								

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (144.91)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (239.05)	95 Am (241.06)	96 Cm (244.06)	97 Bk (249.08)	98 Cf (252.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (256.09)	102 No (259.10)	103 Lr (262.11)

Lanthanides

Actinides

Periodic Table of the Elements

IUPAC Notation

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Previous IUPAC Notation

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19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98.91)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57–71 See Lantha-nides	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209.98)	85 At (209.99)	86 Rn (222.02)
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89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (239.05)	95 Am (241.06)	96 Cm (244.06)	97 Bk (249.08)	98 Cf (252.08)	99 Es (252.08)	100 Fm (257.10)	101 Md (256.09)	102 No (259.10)	103 Lr (262.11)

Lanthanides

Actinides

Dictionary of Analytical Reagents

Caution

Treat all chemical substances as if they have dangerous properties.

The publisher makes no representation, express or implied, with regard to the accuracy of the information contained in this Dictionary, and cannot accept any legal responsibility or liability for any errors or omissions that may be made.

The specific information in this publication on the hazardous and toxic properties of certain substances is included to alert the reader to possible dangers associated with the use of those compounds. The absence of such information should not however be taken as an indication of safety in use or misuse.

Introduction

1. Using the Dictionary

The Dictionary is arranged alphabetically by entry name. Every entry is numbered to assist ready location. Many reagents are included as derivatives of main entry compounds; the extensive indexing of the Dictionary means that these can be readily located through the Name, Molecular Formula or Type of Compound indexes.

Indexes

There are four printed indexes:

Name Index. This lists every name given throughout the Dictionary, whether it refers to an entry, stereoisomer or derivative, and including some names embedded in the text of entries.

Molecular Formula Index. This lists all molecular formulae given in the Dictionary in Hill convention order. Molecular formulae are reported for all reagents but not normally for derivatives such as hydrates or salts of neutral compounds. Cationic compounds are given a molecular formula which is that of the cation and the various salts are listed as derivatives, together with their molecular formulae.

CAS Registry Number Index. Lists all CAS (Chemical Abstracts Service) Registry numbers given throughout the Dictionary in serial order.

Type of Compound Index. This valuable index classifies all reagents included in the Dictionary under three or more of approximately 200 headings according to analyte (e.g. copper), compound group (e.g. phenothiazine) and analytical application (e.g. chromatographic derivatisation reagent). A full list of the headings used is given at the beginning of the Index.

2. Compound selection policy

In compiling this Dictionary the aim of the International Editorial Board has been to select all those reagents thought to be of interest to the majority of analytical chemists. This has been done by consulting laboratory chemical suppliers' catalogues, IUPAC analytical reagent recommendations and by searching the primary literature. It does not include macromolecular materials, such as enzymes, ion-exchange resins and antibodies which, although widely used in analytical procedures, cannot readily be defined by a molecular formula.

3. Chemical names and synonyms

The Dictionary contains a wide range of synonyms which may be (*a*) those found in the primary literature, (*b*) *Chemical Abstracts* names, (*c*) a small proportion of names added editorially to achieve as much consistency as possible, or (*d*) tradenames and *Colour Index* names.

Most entries are headed by a systematic name but in the case of very well known reagents the trivial name is preferred. Care has been taken to incorporate as many helpful synonyms as possible, including trivial and semitrivial names, generic names and tradenames (including *Colour Index* names).

Frequently a trivial name of a reagent strictly applies to a derivative of the parent compound (e.g. a sodium salt or a hydrochloride) but for ease of use the trivial name is used as the entry name and an appropriate note to this effect is added to the entry.

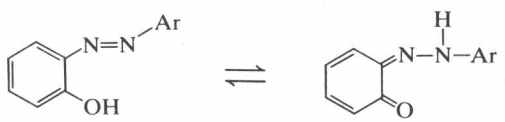
Names corresponding to those used by CAS during the 8th and 9th Collective Index Periods (1967–1971 and 1972–1976 respectively) are labelled with the suffixes 8CI, 9CI. Names first introduced since 1976 are referred to as 9CI as there have been no substantial changes of CA nomenclature affecting organic compounds since that date.

If a compound cannot be located immediately in the main body of the entries, **it is important to use the indexes.**

Tautomerism

Some of the analytical reagents with more than one functional group are capable of tautomerism, the nature of which may be influenced by solvation and, especially, complexation.

The following example shows the type of tautomerism frequently encountered amongst azo compounds in particular, and which may lead to difficulties in registering the compound in *Chemical Abstracts* and in this Dictionary.



Arylazophenol ⇌ Cyclohexadienedione monoarylhydrazone

The tautomeric equilibrium even in neutral solution will be shifted according to the precise structure of the reagent, and for a particular compound may or may

not have been investigated in detail. The CAS policy for registering such compounds is generally to index them under the azo tautomer whether this is the predominant tautomer or not. There are some exceptions to this, for example acetoacetanilide azo derivatives are indexed under the ketohydrazone tautomer. The Dictionary policy is to list the compound under the CAS name but to present the structure of the more favourable tautomer. A comment to indicate the likelihood of tautomer formation is usually added (see for example entry no. H-00391). Where CAS numbers have been assigned to individual tautomers these are listed at the end of the entry in brackets.

4. Bibliographic references and literature coverage

The selection of references is made with the aim of facilitating entry into the literature for the user who wishes to locate more detailed information about a particular compound. Reference contents are indicated using suffixes e.g. (*detn*, *Au*).

Journal abbreviations generally follow the practice of the Chemical Abstracts Service Source Index (CASSI). In patent references, no distinction is made between patent applications and granted patents. Wherever possible, English-language patent equivalents are quoted.

In compiling this Dictionary the primary literature has been surveyed to early 1992 and extensive reference has been made to reviews available at that time.

5. Hazard Information

Many reagents are toxic. Information on their toxicity is highlighted by the use of the symbol ▷, which also appears in the indexes. Whilst every effort has been made to alert the user to potential hazards associated with particular reagents, **the absence of such information cannot be taken as a guarantee of safety in use or misuse**. The information provided is given in good faith but the Editors cannot be held responsible for any inaccuracies therein.

6. Principal Abbreviations

[α]	specific rotation
abs. config.	absolute configuration
Ac	Acetyl
AcOH	Acetic acid
Ac_2O	Acetic anhydride
alk.	alkaline
amorph.	amorphous
anal.	analytical applications, analysis or detection
aq.	aqueous
B	base
bibl.	bibliography
biosynth.	biosynthesis
Bp	boiling point
BAN	British Approved Name
c.	concentration
ca.	(*circa*) about
cd	circular dichroism
chromatog.	chromatography
C.I.	Colour Index
cmr	^{13}C nuclear magnetic resonance
col.	colour, coloration
conc.	concentrated
config.	configuration
constit.	constituent
compd.	compound
cryst. struct.	X-ray crystal structure determination
d	density
dec.	decomposes, decomposition
degradn.	degradation
deriv(s)	derivatives
descr.	described
detn.	detection
dil.	dilute, dilution
dimorph.	dimorphic
esr	electron spin resonance
Et	Ethyl
EtOAc	Ethyl acetate
fluor.	fluoresces, fluorescence
glc	gas liquid chromatography
Glc	β-D-glucopyranosyl
haz.	hazard
hplc	high performance liquid chromatography
hydrol.	hydrolyses, hydrolysed, hydrolysis
i.m.	intramuscular
INN	International Nonproprietary Name
i.p.	intraperitoneal
ir	infra-red spectrum
isol.	isolation
isom.	isomerises, isomers
i.v.	intravenous
JAN	Japanese Accepted Name
LD	lethal dose: LD_{50}, a dose which is lethal to 50% of the animals tested
M	molecular weight (formula weight)
max.	maximum
Me	Methyl
metab.	metabolism, metabolite
misc.	miscible
mixt.	mixture

mod.	moderately
Mp	melting point
ms	mass spectrum
n	index of refraction (e.g. n_D^{20} for 20° and sodium light)
obt.	obtained
occur.	occurrence
ord	optical rotatory dispersion
pet. ether	Petroleum ether (light petroleum)
Ph	Phenyl (C_6H_5)
pharmacol.	pharmacology
pmr	proton (^1H) nuclear magnetic resonance
props.	properties
purifn.	purification
Py	Pyridine
ref.	reference
resoln.	resolution
rev.	review
r.t.	room temperature
s.c.	subcutaneous
sl.	slightly
sol.	soluble
soln.	solution
solv.	solvent
subl.	sublimation, sublimes
synth.	synthesis
tautom.	tautomerism
tlc	thin layer chromatography
tox.	toxicity, toxicology
unsatd.	unsaturated
USAN	United States Adopted Name
uv	ultraviolet spectrum
v.	very
vol.	volume

7. Further information

For further information about the presentation of data in this and other Dictionaries, see the introduction to the *Dictionary of Organic Compounds*, Fifth Edition and Supplements.

Analytical Reagents

Despite the major advances that have been made in analytical instrumentation in the past decade, it is still rare for an analytical measurement to be made on a sample without the use of chemical reagents. Pretreatment of the sample may simply be the adjustment of pH or precipitation of unwanted compounds, or it can involve conversion of the analyte into a form suitable for quantitation by a particular instrumental technique. Examples of the latter are the use of chromogenic reagents for the spectrophotometric determination of metal ions and the derivatisation of organic compounds prior to gas chromatographic separation and detection. Most reagents used for such purposes are organic compounds, and it is such compounds that are described in this Dictionary. Uniquely in the Dictionary, the reagents are also indexed according to their analytical application, inorganic analyte and type of reagent. More detailed discussions of the applications of analytical reagents are available in numerous textbooks and review articles.

Additional references to general sources of information

Welcher, F.J., *Organic Analytical Reagents*, Van Nostrand, New York, 1947–8.

Flagg, J.F., *Organic Reagents used in Gravimetric and Volumetric Analysis*, Interscience, New York, 1948.

Feigl, F., *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949.

Busev, A.I. and Polianskii, N.G., *The Use of Organic Reagents in Inorganic Analysis*, Pergamon, Oxford, 1960.

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Cheng, K.L., Ueno, K. and Imamura, T., (Eds), *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, 1982

Jungreis, E., *Spot Test Analysis. Clinical, Environmental, Forensic and Geochemical Applications*, Wiley-Interscience, New York, 1985.

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Hulanicki, A., *Reactions of Acids and Bases in Analytical Chemistry*, Horwood, Chichester, 1987.

Sommer, L., Ackermann, G., Burns, D.T. and Savvin, S.B., Present and Future Status of Organic Analytical Reagents – Part I: General Remarks, *Pure. Appl. Chem.*, 1990, **62**, 2147.

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Sommer, L., Komarek, J. and Burns, D.T., Present and Future Status of Organic Analytical Reagents

– Part IV: Organic Analytical Reagents in Atomic Absorption Spectrophotometry of Metals, *Pure Appl. Chem.*, 1992, **64**, 213.
Ackermann, G., Sommer, L., and Burns, D.T., *Organic Analytical Reagents for the Determination of Inorganic Substances*, in *Handbook of Chemistry and Physics*, 74th Edn., CRC Press, Boca Raton, 1993.

1. Description of main applications of analytical reagents

In this Dictionary, the following analytical application areas are identified. Reagents having entries in the Dictionary are indicated in boldface type.

1.1. Amperometric reagent

Amperometry is the determination of a species by titration with a reagent whilst monitoring the change in the voltammetric current. The current may be that produced by oxidation or reduction of the analyte or the titrant, or both. The end-point of the titration is indicated by a sharp break in the titration graph.

The titrant may react with the analyte to form a complex which is not electroactive at the potential used, or a precipitate.

Additional references

Stock, J.T., *Amperometric Titrations,* Wiley-Interscience, New York, 1965.
Scholz, E., *Karl-Fischer Titration*, Springer Verlag, Berlin, 1984.
Crow, D.R., *Principles and Applications of Electrochemistry*, 3rd Edn., Chapman & Hall, London, 1988.
Hulanicki, A. and Glab, S., Present and Future Status of Organic Analytical Reagents – Part III: Organic Analytical Reagents in Electroanalysis, *Pure Appl. Chem.*, 1991, **63**, 1805.

1.2. Buffer (pH)

pH buffers are substances that resist a change in the pH of a solution when acid or base is added. Simple buffers are mixtures of, e.g. a weak acid and its anion (acetic acid/sodium acetate), and are widely used. However, in some instances, the buffer components interact in undesirable ways with the analytical system, especially when biochemical studies are being undertaken, e.g. by forming complexes or by inhibiting enzymes. To minimize such interactions, a series of zwitterionic *N*-substituted aminosulfonic acids (the so-called "Good" buffers) have been introduced, which include compounds such as **4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid** (HEPES). The pH of particular buffer solutions may be calculated from the pK_a values for the buffering compound, or found in one of numerous compilations.

Additional references

Good, N.E., Winget, G.D., Winter, W., Connolly, T.W., Izawa, S. and Singh, R.M.M., *Biochemistry,* 1966, **5**, 467.
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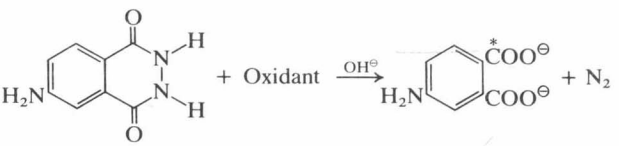
Hulanicki, A., *Reactions of Acids and Bases in Analytical Chemistry*, Horwood, Chichester, 1987.
Handbook of Chemistry and Physics, 74th Edn., CRC Press, Boca Raton, 1993.

1.3. Chemiluminescence generation agent

Chemiluminescence (CL) is the light generated by a chemical reaction. The product of the reaction is formed in an excited state, which can then emit light, or transfer its energy to another species (sensitizer, fluorophore) which then emits. The most common CL reaction is the oxidation of **Luminol** (5-amino-2,3-dihydrophthalazine-1,4-dione, catalysed by various metal ions) in alkaline solution, to form the emitter 3-aminophthalate:



Analytical applications of CL measurements based on luminol involve determination of the oxidant, or trace metal catalyst, or monitoring various enzyme-catalysed reactions which produce hydrogen peroxide, which is then determined by CL. Glucose determination using glucose oxidase:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{oxidase}]{\text{glucose}} C_6H_{10}O_6 + H_2O_2$$

is a typical example.

A useful way of generating sensitized CL is by the use of aryl oxalates such as **Bis(2,4,6-trichlorophenyl) oxalate**. On oxidation they only emit very weak CL, but they are capable of stimulating intense

luminescence from a wide range of fluorophores, including polyaromatic hydrocarbons and rhodamine-type compounds. The reactions are usually used for determination of fluorophores, often on-line after liquid chromatographic separation.

Additional references

Burr, J.G., (Ed.) *Chemi- and Bioluminescence*, Dekker, New York, 1985.

Campbell, A.K., *Chemiluminescence: Principles and Applications in Biology and Medicine*, Horwood, Chichester, 1988.

Townshend, A., *Analyst*, 1990, **115**, 495.

Robards, K. and Worsfold, P.J., Analytical Applications of Liquid-phase Chemiluminescence, *Anal. Chim. Acta*, 1992, **266**, 147.

1.4. Chromatographic derivatisation agent

Gas and liquid chromatography are extremely popular analytical techniques for analysis of multi-component mixtures. Supercritical fluid chromatography, capillary electrophoresis and ion-exchange chromatography have also become popular in the last decade. Derivatisation in chromatography is often required either to improve the amenability of the analytes to chromatographic separation or to improve their detectability. For example, methylation or silylation is often used to make compounds more volatile, so that they can be separated and determined by gas chromatography. Analytes can be converted to fluorescent derivatives (before or after liquid chromatographic separation) so that they can be detected with great sensitivity by their derivative's fluorescence. A typical example is the reaction of amines with **1,2-Benzenedicarboxaldehyde** in the presence of 2-mercaptoethanol to produce a fluorescent derivative:

Additional references

Knapp, D.R., *Handbook of Analytical Derivatisation Reactions*, Wiley-Interscience, New York, 1979.

Frei, R.W. and Lawrence, J.F., *Chemical Derivatization in Analytical Chemistry*, Vol. 1: *Chromatography*, 1981; Vol 2: *Separation and Continuous Flow Techniques*, 1982, Plenum, New York.

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Blau, K. and King, G.S., *Handbook of Derivatives for Chromatography*, 2nd Edn., Wiley, New York, 1992.

1.5. Enzyme substrate or co-factor

Enzyme-catalysed reactions are widely used for analytical purposes, for the determination of substrates (e.g. glucose oxidase for determination of glucose) and of inhibitors (such as pesticides, by their inhibition of cholinesterase) and activators. Although enzymes are very useful as analytical reagents, they are not classified individually in this Dictionary. However, enzymes themselves are extensively assayed by clinical chemists, biochemists, forensic scientists and food chemists, and the substrates used for such assays are carefully chosen to achieve optimum sensitivity, selectivity and reliability. Such substrates are listed in this Dictionary, as are the co-enzymes (co-factors) required by many redox enzymes, for example nicotinamide adenine dinucleotide (NAD^+/NADH) which is a co-enzyme for many dehydrogenases, e.g.

$$CH_3CH_2OH + NAD^+ \xrightarrow[\text{dehydrogenase}]{\text{alcohol}} CH_3CHO + NADH + H^+$$

Additional reference

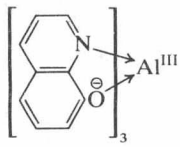
Bergmeyer, H.U. (Ed.), *Methods of Enzymatic Analysis*, 3rd Edn. 12 vols, VCH, Weinheim, 1986.

1.6. Extractant

Analytes can be separated from the sample matrix (or vice versa) or from other analytes by extraction into a water-immiscible liquid phase. Such extractions are carried out for a number of reasons (removal of, or from interfering species, increasing the analyte concentration, improving the detectability of the analyte). For most organic analytes, extraction takes place without the aid of another reagent, although recently the improved extraction achieved with the aid of micelles or cyclodextrins has been extensively investigated. The main exceptions are the extraction

of charged species, such as quaternary ammonium ions, or long chain sulfonate ions, which is achieved after ion-pair formation with a bulky anion (e.g. **Methyl orange**) or cation (e.g. **Methylene blue**), respectively. In such instances, the highly coloured extracted species are readily detected by spectrophotometry.

Inorganic ions can also be extracted with the aid of organic reagents. Oxoanions such as $Cr_2O_7^{2\ominus}$ can be extracted as ion pairs with bulky cations e.g. benzyltributylammonium ions. Metal ions can be converted into chelates. If the chelate is uncharged, as, for example, in tris(8-quinolinolato)aluminium:



it is likely to be readily extractable (and to precipitate from aqueous solution). If it is charged, as in **Tris-(1,10-phenanthroline-N^1,N^{10})iron(*II*)(2+)** (ferroin), a polarizable counterion e.g. iodide or thiocyanate can be added to facilitate extraction.

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1.7. Fluorescent label

Fluorimetry provides a very sensitive means of detection in organic and inorganic analysis. Most analyte species, however, are not fluorescent, or are only weakly so. Thus, if they are to be detected fluorimetrically, they have to be 'tagged' or 'labelled' with a fluorophore by reaction with derivatives of molecules such as **Fluorescein**, **Anthracene** or **Rhodamine B**. Such derivatives are valuable for liquid chromatographic detection. They are also useful for labelling of antibodies or antigens in immunoassay procedures, and for labelling of DNA fragments.

1.8. Gravimetric reagent

Most inorganic ions can be determined by precipitation, collection of the precipitate, and either weighing the dry precipitate as such or after conversion to another (more stable) compound, usually by heating. Certain organic reagents have been particularly effective as gravimetric precipitants because the compounds formed are readily filtered off, have a reproducible, stoichiometric composition, and can readily be dried and weighed. The analyte element proportion of the precipitate is often quite small, so that a small amount of analyte gives rise to a large weight of precipitate, which can be weighed relatively precisely. For example, reaction of aluminium with 8-quinolinol produces a precipitate that contains 5.9% by weight of aluminium.

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1.9. Indicator

An indicator is a compound that is added to a solution being titrated to indicate the equivalence point of the titration. During the titration, there is an abrupt change in a visual property of the compound, denoted the 'end-point' which, if the indicator has been properly chosen, will be coincident with the equivalence point. The visual property involved is usually colour, i.e. there is a distinct colour change at the end point, but there are many examples of fluorescent indicators and chemiluminescent indicators, where the end-point is usually indicated by the appearance or disappearance of luminescence.

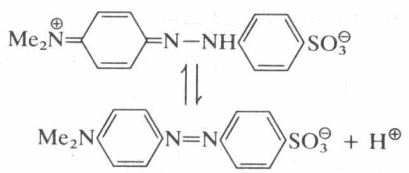
The mode of action of the indicator depends on the type of titration:

(a) Acid-base

An acid-base indicator is a weak acid or weak base, whose conjugate forms have distinctly different colours, e.g. for an indicator A which is a weak acid,

$$A \rightleftharpoons A^{\ominus} + H^{\oplus}$$

A and $A^{\ominus}$ have different colours. The colour of the solution during the titration depends on their relative concentrations, which in turn depends on the pH of the solution and the acid dissociation constant of the indicator (k_A). A colour change is visible approximately from $[A] = 10[A^{\ominus}]$ to $[A] = 0.1\,[A^{\ominus}]$, so the pH range for the colour change is given by $(0.1 - 10)\,k_A$. A typical example is **Methyl orange**.



(b) Argentimetric (adsorption)

The end-point of a precipitation titration of substances (usually halides and pseudohalides) with silver ions can be detected by the change in colour of certain compounds adsorbed on the precipitate. The colour change results from a change of the charge on the precipitate surface at the equivalence point, which leads to a change in the light absorption properties of the adsorbed indicator. The best-known example is **Fluorescein**, which changes from colourless to pink when silver ions become in excess in the solution.

(c) Complexímetric

Almost all complexímetric titrations of metal ions are carried out with EDTA or related compounds as titrant. The equivalence point, when all the metal ion has just been complexed by titrant, can be located by using chromogenic complexing agents which form significantly weaker complexes with the metal ion than does EDTA. The final drops of titrant remove the metal ion from its coloured complex, thus causing an abrupt colour change. A large range of spectrophotometric reagents for metals can be used as complexímetric indictors. Typical examples are **Xylenol orange** (an iminodiacetic acid derivative) and **Chrome black special** (Eriochrome black T, an azo dye). A limited number of fluorescent indicators is also available. These become fluorescent when their metal chelates are dissociated at the end-point.

(d) Redox

The equivalence point of a given redox titration occurs at a particular electrochemical potential, governed by the standard redox potentials of the reactants and the reaction conditions. A redox indicator is a compound that reversibly changes its colour (or, rarely, luminesces) at a particular potential. Thus the indicator is chosen so that its transition potential overlaps the equivalence potential of the titration system.

There are two main types of indicator. One involves a complex of a metal ion, which changes colour when the oxidation state of the metal ion changes. The iron-1,10-phenanthroline system is a typical example, the iron(*II*) chelate (ferroin) being red, the iron(*III*) chelate (ferrion) being essentially colourless (actually very pale blue). The transition potential is about 1.1 *V*, so the indicator is very suitable for use in titrations with cerium(*IV*) in sulphuric acid. The second type of indicator comprises various types of organic compound (aromatic amines, triphenylmethane dyestuffs, for example) which can be oxidised and reduced reversibly, and change colour on doing so. ***N,N'*-Diphenylbenzidine** is a typical example.

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1.10. Masking agent

A masking agent is a molecule that binds with another species to form a soluble product, thus preventing it from reacting with a particular analytical reagent and interfering with an analytical measurement. In most instances, such masking agents are complexing agents, and act by complexing with the potential interferent so that it does not participate in the

analytical reaction. The analytical reaction may itself be a complexing reaction, but also could be, for example, precipitation, a redox reaction (including an electrochemical process), or extraction. Some typical examples are given below. Small amounts of Cu(*II*) can be separated from Hg(*II*) by extraction with **Dithizone**, if a 1*M* bromide solution is used to mask (i.e. complex with) the Hg. Oxalate, tartrate or citrate can prevent precipitation of the hydrated oxides of Fe(*III*) or Al. Triethanolamine masks Al and Fe(*III*), thus allowing the titration of Ca with EDTA in the presence of these other ions using murexide as indicator. In this last example, the masking agent also prevents reaction of Fe(*III*) and Al with the indicator. These ions block the indicator action in that the Fe(*III*) and Al complexes of murexide are not broken down by EDTA.

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1.11. NMR shift reagent

Such reagents are used to disperse the NMR peaks obtained for certain types of compound over a larger frequency range, thus often allowing overlapping peaks to be separated. These reagents are usually complexes of the paramagnetic ions $Eu^{3\oplus}$ or $Pr^{3\oplus}$, e.g. the dipivalomethanato complex of Pr(*III*) **[Tris(2,2,6,6-tetramethyl-3,5-heptanedionato-*O*,*O*′)-praseodymium(*III*)**, $Pr(thd)_3$], generally dissolved in non-polar solvents such as CCl_4, $CDCl_3$ or C_6D_6, to avoid competition of the solvent with the analyte for sites on the metal ion. The shift is caused by the interaction with the analyte of the magnetic field generated by the large magnetic moment of the paramagnetic ions in the reagent complex.

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1.12. Scintillator

A scintillator is a compound which, when dissolved in an appropriate solvent, is raised to an excited state by collision with β-particles. The β-particles mainly excite the solvent molecules, and the excitation energy is then transferred to the scintillator. The subsequent de-excitation results in the emission of a photon. Excitation is caused even by low energy β-particles, such as those emitted by ^{3}H, ^{14}C, ^{35}S and ^{125}I, so that the scintillation process is widely used to monitor such emitters, the detector being a photomultiplier tube. Scintillation counting is used in a wide range of analytical procedures, especially in radioimmunoassay and radiotracer studies.

The solvent used is usually an aromatic hydrocarbon (toluene or xylene are most common), or sometimes dioxan. The scintillator is a polyaromatic fluorophore, such as **2,5-Diphenyloxazole** (PPO). In the past it has sometimes been necessary to add a secondary scintillator to which the energy is transferred from the primary scintillator. Secondary scintillators, of which **2,2′-(1,4-Phenylene)bis-[5-phenyloxazole]** (POPOP) is the most well known, are somewhat larger molecules, with more delocalisation than the primary scintillators: they emit at longer wavelengths at which photomultiplier tube sensitivity is greater.

1.13. Spectrofluorimetric reagent

Relatively few organic compounds, and only a handful of inorganic species are sufficiently fluorescent to be detectable at trace levels by direct monitoring of their native fluorescence. In order to provide sensitive spectrofluorometric procedures for most analytes, therefore, reagents have to be used which convert the analyte into fluorescent derivatives. For metal ions, such reagents are generally chelating agents (and which can often also be used as extractants). A typical example is **8-Hydroxy quinoline**, which forms fluorescent chelates with a number of metal ions. For organic compounds, a wide variety of reagents is available, which themselves are generally highly fluorescent, and produce intensely fluorescent products. Typical reagents are **1,2-Benzenedicarboxaldehyde** or **Dansyl chloride**, which form fluorescent derivatives with amines. Some of these reagents are used as chromatographic

derivatizing agents in conjunction with fluorimetric detection.

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1.14. Spectrophotometric reagent

Absorption spectrophotometry in the UV-visible region is arguably the most common analytical technique in current use, being employed in batch analysis, flow systems (including chromatography and electrophoresis), and in optical sensors (opt(r)odes). Many inorganic and organic species are sufficiently absorbing at particular wavelengths within the UV-visible range that they can be determined without further treatment. However, for poorly absorbing species, or for increasing the sensitivity or changing the wavelength at which absorbance measurements are made, reaction with appropriate reagents is commonplace. For metal ions, reaction with chromogenic chelating agents is the usual procedure. For example, iron(*II*) gives an intense red, water soluble complex with 1,10-phenanthroline $[Fe(1,10\text{-phen})_3]^{2\oplus}$ which has a molar absorptivity of 1.1×10^4 $1\,mol^{-1}\,cm^{-1}$. The most highly absorbing chelates have molar absorptivities of the order of 10^5 $1\ mol^{-1}\ cm^{-1}$, and consequently provide a means of high sensitivity detection.

There is a great variety of chromogenic reactions for inorganic compounds; sulphur dioxide, for example, is frequently determined spectrophotometrically after reaction with **Tris(4-aminophenyl)-methanol** (pararosaniline). There is also an extremely large selection of reagents available for organic compounds, either for classes of compounds (for example, amines, carbonyl compounds) or for individual species.

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1.15. Surfactant

Surfactants find a variety uses in analytical processes. One is the formation of micelles (or microemulsions) which can provide protective environments for analytes or reagents which may enhance stability, or luminescence intensity, for example, or allow reagents to act in conditions not normally accessible to them. They also find application in sample pretreatment including flotation procedures, electroanalytical measurements (e.g. suppression of polarographic maxima) and flow systems.